

SCIENTIFIC AND PRACTICAL ASPECTS OF DEVELOPMENT OF ULTRAFINE DISPERSIONS OF MODIFIED PETROLEUM OILS

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The possibility of dispersing depressing additives in diesel oil using a static radiator for production of ultrafine emulsions having disperse-phase particles sized between 2.5 and 4 μm is shown. Depressing additives such as olefinic hydrocarbon-based linear high-molecular compounds, which possess exceptional physico-chemical resistance to oxidation, thermoelasticity, and high mechanical properties, but do not exhibit a coagulating effect, are produced by nanophase catalysis technology. Compound (mixed) solvents are used as additive diluents. Laboratory tests of the additives in hydrofined diesel, furnace, and marine oils, and various crude-oil fractions showed a high depressing effect.

Key words: *compound depressing additives, marine oil, furnace oil, ultrasonic action, low-temperature properties, dispersity, pour point.*

Rational utilization of combustible petroleum materials (CPM), improvement of their quality, and expansion of reserves are critical problems of the oil-refining and petrochemical industry. The problem of improving the low-temperature properties of CPM is an urgent problem for Russia and other northern countries, since the cold climatic zone occupies 80% of the Russian landmass. This problem is exacerbated by the fact that all the more paraffinic crudes are being extracted in Russia. High-molecular paraffins are responsible for degraded low-temperature properties of the crudes themselves, and also the products of their refinement. For this reason, the diesel fractions with a boiling point no higher than 290°C must be separated to ensure an acceptable pour point. This gives rise to a significant reduction in refinement of diesel oil (DF), and, accordingly, the depth to which the crude is refined [1-5].

Use of depressing additives is the most effective and economically expedient means of improving the low-temperature properties of the crudes. High-molecular compounds (HMC) with a capacity to mix rapidly with petroleum oils at an elevated temperature are employed in the production of depressing additives. The degree of dispersity of the additive will depend on its ability to mix with the oil. The process of combining DF with HMC takes place in two stages: emulsification and subsequent swelling, or complete solution

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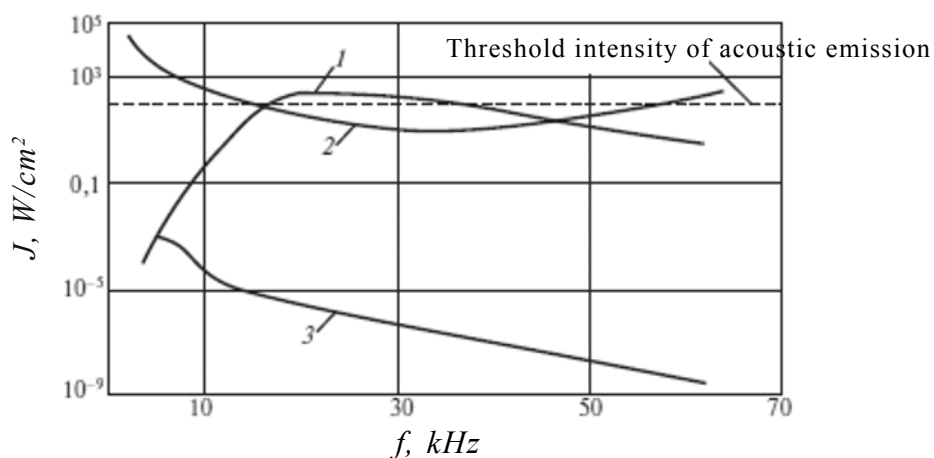


Fig. 1. Dependence of intensity of acoustic emission on its frequency for dispersers: 1) RPAE; 2) static ultrasound dispenser USD; 3) RPE.

of the additive [6]. The procedure employed for the combination should completely eliminate fractionation of the oil and destruction of the HMC.

Diesel oils modified with HMC, including block-copolymers are disperse nonuniform systems, and, consequently, are thermodynamically unstable, giving rise to their stratification (pentization), especially at elevated temperatures under static conditions in the absence of agitation). The higher the physico-chemical affinity of BMC for DF, the higher the degree of dispersity of the additive in the oil and stratification stability of the composition petroleum product.

Use of acoustic equipment to disperse additives in oils. Best results are achieved when the HMC and oils are combined using highly productive equipment – colloidal mills, rotary-pulsation equipment (RPE), rotary-pulsation acoustic equipment (RPAE), and ultrasonic dispersers (USD), which ensure highly disperse systems with optimal physico-chemical properties. Figure 1 shows a comparison between experimental data on the variation in the intensity J of emission of the acoustic field as a function of the frequency f of the acoustic emission for the various dispersers.

As has been noted in [7, 8], production of ultrafine emulsions is possible when a static USD emitter is used. As is apparent from Fig. 1, the intensity of the acoustic emission of the USD in the frequency region to 74 kHz is close that of the RPAE in this same range. The intensity of the acoustic emission of the RPE, however, is substantially lower than that for the RPAE and USD. In the RPE, therefore, ultrafine dispersions (particle diameter $d < 0.1 \mu\text{m}$ of the disperse phase) cannot be obtained. This fact ambiguously illustrates the contribution of high-intensity acoustic emission to ultrafine dispersal in the RPAE and USDA, and the fact that high-intensity acoustic emission is absent in the RPE owing to which production of ultrafine dispersions in the latter is impossible.

It can be assumed that vaporous-gaseous cavitation with an intensity sufficient for formation of vapor-gas bubbles always accompanies acoustic vibrations in a liquid. A negative effect of cavitation is also observed – a portion of the acoustic energy is spent not on emulsification, but on pulsation of the vapor-gas bubbles, and their size reduction and coalescence. Since the density of the gas and liquid differ by several orders, and the absorptance of sound is inversely proportional to the density of the medium, the gas bubbles rapidly absorb the acoustic vibration energy. Moreover, reflection of acoustic waves will also occur on the gas-liquid interface; this will also increase the losses of acoustic energy.

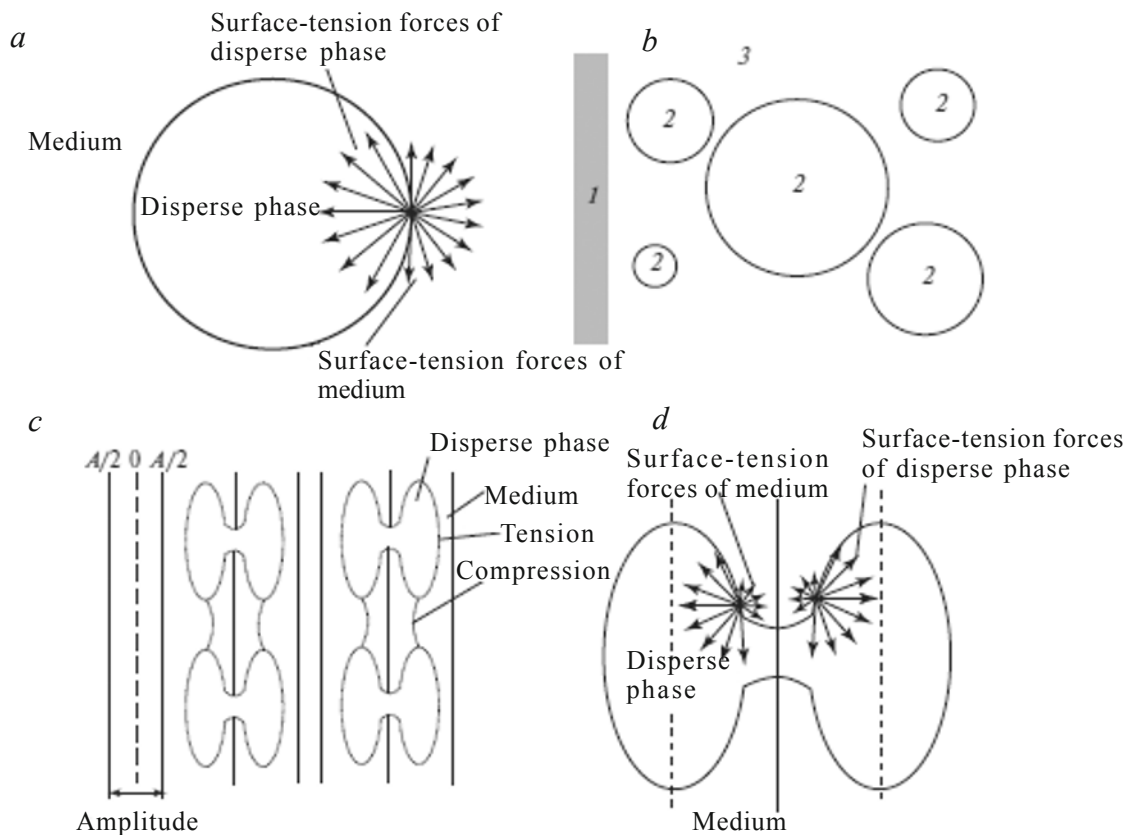


Fig. 2. States of molecular dispersion of composition systems in USD: a) dispersion of surface-tension forces; b) dispersed medium with inclusions of disperse-phase particles (1 – wall of vessel; 2 – drops of liquid disperse phase; 3 – liquid medium); c) effect of “compression-tension” waves on disperse medium; deformation of disperse-phase particles; d) breakdown of disperse-phase drops.

At the present time, there is no reliable model of the cavitation domain that adequately describes its behavior and the behavior of an individual cavitation bubble existing in the domain. The behavior of the cavitation domain (Fig. 2) will depend on many phenomena and factors: increase in the number and coagulation (coalescence) of bubbles, their interaction, variation in the pattern of bubble pulsations due to shock waves and the sonic emission of neighboring bubbles, variation in the average acoustic properties of the medium, microflows within the cavitation domain and on the boundary of a bubble, distribution of cavitation-nucleation centers, gas content, etc. This physical model of the mechanisms responsible for the effect of acoustic vibrations on the emulsification and dispersion processes is in accord with on-going research involving the rheologic and physico-chemical properties of modified DF.

The depth of occurrence of HMC dispersion in the oil is determined by the chemical nature and molecular mass of the HMC, the composition of the oil, and the HMC:oil ratio. By varying the type and concentration of the HMC, it is possible to obtain a modified oil with a given set of physico-chemical properties. Dispersing in the DF, the HMC forms a new, comparatively coarsely disperse phase (see Fig. 2), which is readily distinguished under a $\times 9000$ microscope. After acoustic treatment of the modified DF, the coarsely disperse structure with particles sizes of up to $15\mu\text{m}$ in the disperse phase is transformed into a finely disperse structure with particle

Table 1

Duration of treatment, min	Pour point, °C
Initial oil	-10
1	-13
2	-13
3	-13
4	-13.5
5	-14

sizes ranging from 2.5 to 4 μm in the disperse phase. Let us assume that for this reason that the oil has acquired the low-temperature and thixotropic properties required.

To ascertain the effect of ultrasound on the low-temperature properties, we investigated a low-viscosity marine oil from the Lower Kama Refinery operated by the JSC Taif-NK (Technical Specification 38.101567–2005). The dependence of the pour point of the low-viscosity marine oil without depressing additives on the duration of the ultrasonic treatment is indicated in Table 1. As is apparent, ultrasonic treatment alone will only have a negligible effect on the pour point.

Proceeding from composition and property characteristics of the, a linear type of LSO Grade HMC that we had synthesized, and which exhibit exceptional physico-chemical resistance to oxidation, thermoelasticity, high mechanical properties, but no coagulating action, can be referred to as most promising for modification of oils. The characteristics of the LSO are: up to 8 wt. % of unsaturated compounds, conditional tensile strength of 299 kgf/cm², relative elongation of up to 600% at rupture, and glass-transition temperature of -50°C .

The basic problem encountered in modifying oils is the search for rational means of combining the oil and HMC. When the HMC is introduced directly into the oil, it is impossible to attain optimal operating properties and sufficient uniformity of the polymeric dispersions in oils in the form of a HMC of high structuring capacity, despite the fact that the mixing process was carried out at temperatures in excess of 50°C . In this study, the following composition solvents-plasticizers were used to dilute the HMC: a polyolefin (PO) type of solvent containing up to 12 wt. % of monocyclical aromatic hydrocarbons, a steric polyolefin (SPO) compound, and a distillate petroleum absorbent (DPA). Some of the physico-chemical characteristics of the composition solvents are presented below.

PO

Molecular mass	500
Density at 20°C , kg/m ³	800
Flash point, °C	120
Pour point, °C	-30

SPO

IBP, °C	170
EP, °C	300
Flash point (open cup), °C	70
Pour point, °C	-60
Kinematic viscosity at 20°C , mm ² /sec	6.0

DPA

Density at 20°C, kg/m ³	800
IBP, °C	30
EP, °C	250
Content of aromatic hydrocarbons, wt. %	60
Saturated-vapor pressure, kPa, no greater than	66.6

Effectiveness of additives to diesel oil (GOST 305 – 82, Grade L). Under the combined action of a depressor and diluent, and simultaneous ultrasound, it is possible to develop a synergistic effect caused by the influence of the diluent on the chemical structure of the depressor owing to the intermolecular interactions that develop between them [7] as a result of which the depressor effect is intensified. Low-temperature characteristics of the modified DF are presented in Table 2.

The composition additives developed exhibit a depressor-dispersing effect, i.e., a reduction is achieved in the pour point and limiting filterability temperature simultaneously. A characteristic feature of the LSO compositions is the combination of a flexible basic chain and lateral branches that interact more vigorously one with the other. An increase in the depressor activity of the additives is ensured in a non-polar hydrocarbon medium when, for example, high-molecular ethylene or propylene oligomers are added to the diluent. A particular synergistic effect is observed when the SSO diluent is used.

Comparison of the solubility of the copolymers with their depressing activity in the diesel and marine oils made it possible to formulate a oil-acceptability criterion for the additive. Thus, a co-polymer with a molecular mass of 16 000 is more effective in marine oil with a pour point of –24°C than a co-polymer with a molecular mass of 8 000 μ n the oil with a pour point of –9°C. The effect of ultrasound on the pour point of the marine oil suggests reverse relaxation, i.e., the structure of the newly formed system is thixotropic.

Effectiveness of additives in marine oil. In the marine oil, which was refined in conformity with GOST 10585–75, the same additives were introduced as in the DF to ascertain the depressing effect of

Table 2

Content of LSO solution in DF, wt. %	Pour point of modified DF, °C, containing LSO solution with concentration of, wt. %					
	5	10	15	20	30	35
0	-4	-6	-8	-10	-12	-26
<i>LSO/(PO + DPA)</i>						
0.1	-4	-9	-11	-17	-14	-31
0.2	-4	-12	-13	-17	-18	-34
0.3	-4	-14	-17	-18	-21	-35
0.4	-6	-15	-18	-18	-22	-42
0.5	-7	-16	-18	-18	-22	-47
<i>LSO/(SPO + DPA)</i>						
0.1	-4	-10	-12	-18	-15	-33
0.2	-4	-13	-14	-18	-18	-36
0.3	-5	-15	-17	-18	-22	-37
0.4	-7	-17	-18	-19	-24	-43
0.5	-8	-18	-18	-19	-24	-47

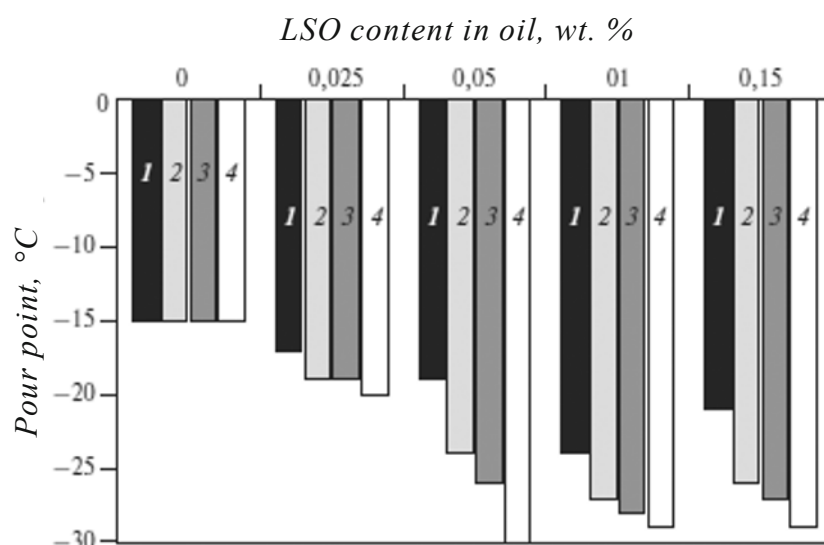


Fig. 3. Effect of concentration of LSO solution and LSO content in marine oil at its pour point: 1) 10%; 2) 20%; 3) 30%; 4) 35% solution of LSO (solvent – PO + SPO; all solutions received 5-min ultrasound treatment).

Table 3

Content of LSO solution in oil, wt. %	Pour point, °C
0	-7.5
0.025	-19
0.05	-30
0.1	-34
0.15	-30

the LSO with respect to the 280-240°C fraction. The LSO content in the oil was 0.025, 0.05, and 0.1 wt. %. As follows from Fig. 3, the greatest depressing effect is achieved for an LSO content of 0.05 wt. % in the oil, a 35% LSO solution is used in the PO + SPO mixture, and the ultrasound treatment is applied for 5 min. In that case, maximum acceptance acceptability of the oil to the additive is observed. The effectiveness of the additive will depend on the co-polymer content in the diluent. When a 10% solution of LSO is introduced to the oil, the maximum depressing effect is achieved when the content of the additive solution in the oil is 0.1 wt. %; this corresponds to a co-polymer content of 0.01 wt. % in the oil. When a 35% solution of the additive is introduced, however, the maximum depressing effect is attained when the content of the additive solution in the oil is 0.05 wt. %, i.e., a co-polymer content of 0.0175 wt. % in the oil.

Effectiveness of additives in furnace oil. The additives developed were also tested in the composition of a furnace oil produced by the Lower Kama Refinery in accordance with Technical Specification 38.101656–2005. Characteristics of this furnace oil were: cloud point of –5°C, pour point of –7.5°C, IBP of 146°C, and boil-off of 10% at 170, 50% at 295, and 96% at 360°C, and density of 839 kg/m³ at 20°C. In terms of pour point, the oil corresponds to the technical specification for a oil drawn-off in the period from 1 April through 1 September (pour point no higher than –5°C). The pour point of the oils tapped in the period from 1 September through 1 April should be no higher than –15°C.

The sample that had demonstrated the best results in the composition of the marine oil was selected as the additive to the furnace oil: 35% solution of LSO in a mixture of SO + SSO. The solution additive was introduced to the oil in concentrations ranging from 0.025 to 0.15 wt. %. Results of the tests are presented in Table 3.

It is necessary to mention the high effectiveness of the additive in the furnace oil: the depression of the pour point ranges from 11.5°C to 26.5°C, depending on the content of the additive solution in the oil. The optimum content of the additive solution in the oil is 0.1 wt. % (depression of 26.5°C); this corresponds to an LSO content of 0.035 wt. % in the oil. In contrast to the marine oil tested, the optimal content of additive in the furnace oil is higher by a factor of two, i.e., responsiveness of the oil to the additive is two times lower.

The results obtained suggest the possibility of the production of commercial furnace oil for the winter period without significant outlays for low-pouring kerosene and diesel fractions on the one hand, and expansion of reserves of furnace oil by implication of high-boiling and high-pour fractions in its composition on the other, i.e., creation of heavy furnace oils.

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