

## CHEMMOTOLOGY

### INFLUENCE OF DISPERSE PHASE ON THERMOOXIDATIVE STABILITY OF METAL-DISTILLATE FUELS

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One of the most important properties of middle-distillate engine fuels in terms of their performance is the degree to which they tend to form deposits on heated surfaces. Until quite recently, in studies of the mechanism of deposit and sludge formation under service conditions [1, 2], no consideration was given to the presence of a disperse phase in the fuel and the influence of this phase on the process of sludge formation.

It was shown in [3, 4] that all light petroleum fractions (motor fuels) are polydisperse colloidal systems in which the disperse phase consists of native heteroatomic compounds and additives. Consequently, the basic concepts of the theory of controllable phase transitions in petroleum systems [5] should be taken into account in investigating fuels. Hence the determination of the extremal state of a petroleum disperse system and the identification of its active states in application to fuels are lines of investigation that are of enormous practical importance.

In the work reported here, we used electron microscopy to investigate the state of the disperse phase and its influence on the thermooxidative stability (TOS) of various fuels. The data obtained in these studies demonstrate the existence of a direct relationship between TOS indexes and the state of the disperse phase in the fuel. From the temperature dependences of deposit thickness on a preheater tube in tests on various fuels (Fig. 1), it can be seen that RT fuel [thermally stable jet fuel], which does not contain any disperse phase, has the highest TOS, i.e., the minimum thickness of deposits (curve 4). Quite similar is RT fuel in which a disperse phase is formed by the introduction of additives (curve 3).

For the TS-1 fuel, in which 0.2-1.2  $\mu\text{m}$  particles are present (see Fig. 1 and Table 1), the TOS indexes are much poorer:  $t_{\text{id}}$  is no higher than 110°C, the thermal stability index (TSI) varies from 1.8 to 2.8 units, and the rate of pressure drop increase (PDI) increases to 150 Pa/min. These indexes are still poorer for the diesel fuels, in which the disperse phase exists in the form of a dense network structure; under the microscope, they show up as a wavy surface (Fig. 2).

It is known that the oxidation of straight-run fuels is not a chain-type reaction [2]; this indicates that the disperse phase is the first to be subjected to oxidative conversion under the influence of dissolved atmospheric oxygen. At high temperatures, as a result of oxidative condensation, the native associates of polyheteroatomic compounds making up the base of the disperse phase coagulate to form a coarsely dispersed system.

This phenomenon explains the variation of the temperature interval for maximum deposit formation when comparing fuels with identical distillation range and group composition but with different sizes of the disperse-phase particles: 0.8-1.2  $\mu\text{m}$  for the TS-1, in comparison with 10-50 nm for the RT (see Fig. 1, curves 2 and 3). The slight advantage of diesel fuels in terms of level of thermooxidative stability in comparison with straight-run jet fuels (Table 1) is explained satisfactorily by the presence of a structured disperse phase in the diesel fuels and their higher viscosity.

In petroleum disperse systems, the resins and asphaltenes may be present in a dissolved state, colloiddally dispersed, or in the form of a macrophase. Transitions from one state to another will occur as a result of changing the temperature or changing the properties of the dispersion medium (solvent).

The changes in properties of diesel fuel (dispersion medium) upon introduction of a compound containing polar groups, such as Cellosolve (Table 1), or dilution of the diesel fuel with hydrocarbon mixtures of lower molecular weight, such as

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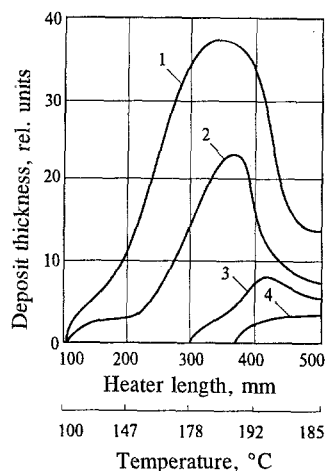


Fig. 1. Thickness of deposits on preheater tube as a function of temperature, for following fuels: 1) TS-1 with additive; 2) TS-1, severely treated; 3) RT with additive; 4) RT, severely treated.

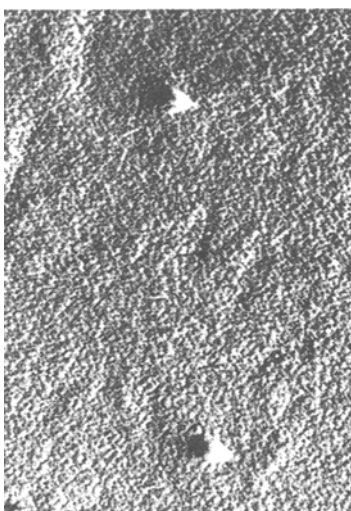


Fig. 2. Diesel fuel L-0.5 in initial state.  
× 45,000.

reformer naphtha (Table 2), results in a very marked increase of deposit formation. In the case of addition of Cellosolve,  $t_{d}$  decreases from 118° to 89°C, and PDI increases from 550 to 1340 Pa/min, i.e., a 2.5-fold increase (see Table 1).

Analysis of the results of electron microscope examination (Table 2) shows that when the diesel fuel is greatly diluted, or when compounds with polar groups are introduced, the fuel structure is broken up into individual fragments. Because of the much lower viscosity of the medium, these fragments coagulate, thus increasing the severity of deposit formation in the system. In addition to the large associates in these blends, we observe fine spherical particles with a diameter of 20-50 nm (Fig. 3); i.e., the native disperse phase is partially dispersed.

We investigated the possibility of dispersing the native disperse phase in straight-run jet fuels by the introduction of compounds with polar groups. The results of these experiments are presented in Table 3. The most effective dispersants are 2,6-di-tert-butyl-4-methylphenol (Ionol) and 3,5-di-tert-butyl-4-hydroxybenzene-N,N-dimethylamine (IKhP-712). In Table 4 we show the relationship between the size of the disperse-phase particles in TS-1 fuel and the concentration of the additive Ionol.

TABLE 1

Fuel	Characteristics of disperse phase		TOS indexes		
	size, $\mu\text{m}$ (or nm)	appearance and quantity	$t_{id}$ , $^{\circ}\text{C}$	TSI, rel. units	PDI, Pa/min
Jet fuel, severely treated (hydrotreating, adsorbent finishing)	None	–	190	0,11	0
Hydrogenated product, freshly produced	(20–50)	Fine, spherical, $10^3$ particles per $\text{mm}^3$	182	0,27	0
TS-1					
Sample 1	0,2–0,8	Irregular shape, loose	108	1,8	78
Sample 2	0,2–0,8	Same	106	2,8	150
Sample 3	0,2–1,2	Irregular shape, loose; dense core in center (foreign contaminant)	103	2,1	86
180–280 $^{\circ}\text{C}$ cut	0,8–1,2	Same	103	1,47	0
RT					
Sample 1	(10–50)	Fine, spherical; some crystalline formations	173	0,24	11
Sample 2	(10–50)	Same	182	0,38	0
Hydrogenated product after 20-year storage	(35–70)	Fine, spherical, $10^{10}$ particles per $\text{mm}^3$	104	0,6	60
RT after 8-year storage	(10–50)	Same	110	3,4	25
Diesel fuel					
L-1	–	Dense network	115	5,1	710
L-0.5	–	Same	118	2,92	550
Without additive	–	Same	89	5,86	1340
With 5% Cellosolve	1,5–5	Individual large conglomerates; small particles (20–50 nm) throughout entire fuel			

**Notation:**  $t_{id}$  is the temperature of initial deposit formation; TSI is the thermal stability index (thickness of deposit); PDI is the rate of increase of the pressure drop across the filter.

TABLE 2

Fuel	Appearance and quantity of disperse-phase particles	Initial crystallization temperature, $^{\circ}\text{C}$	TOS indexes		
			$t_{id}$ , $^{\circ}\text{C}$	TSI, rel. units	PDI, Pa/min
A-76 gasoline*	None	Ниже $-65$	115	0,2	79
L-0.5 diesel fuel	Barchan network, individual particles 20–50 nm	$-30$	116	5,6	950
TS-1 jet fuel	0,2–0,8 $\mu\text{m}$ , $10^6$ particles per $\text{mm}^3$	$-50$	100	0,75	0
Blends					
25% L-0.5 + 75% A-76	Large conglomerates (3–5 $\mu\text{m}$ ); regularly shaped particles with a dimension of 20–50 nm throughout the entire sample	$-32$	115	4,3	1150
5% TS-1 + 5% L-0.5 + 90% A-76	No barchans; 20–50 nm spherical particles through entire sample, $10^{10}$ particles per $\text{mm}^3$	$-25$	112	8,0	1250
10% TS-1 + 10% L-0.5 + 80% A-76	Spherical particles with dense and loose structures, respective diameters 20–50 and 50–100 nm, $10^{10}$ particles per $\text{mm}^3$	$-28$	108	3,3	1400

\*Pressure in DTS-2 system 1 MPa.

TABLE 3

TS-1 fuel	Additive concentration, wt. %	TOS indexes			Sludge content (GOST 11802-88, TSRT-2), mg/100 cm <sup>3</sup>
		t <sub>id</sub> , °C	TSI, rel. units	PDI, Pa/min	
Sample 1					
Without additive	-	105	0,7	25	11,8
With additive					
2-tert-butyl-4-methoxyphenol	0,05	174	0,41	35	-
2-tert-octyl-4-methoxyphenol	0,03	168	0,33	0	-
	0,05	170	0,28	0	-
3,5-di-tert-butyl-4-hydroxybenzyl-N-piperidine	0,05	176	1,09	0	-
N-3,5-di-tert-butyl-4-hydroxybenzylacetamide	0,05	171	0,63	0	-
N,N-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-N-methylamine	0,05	165	1,27	0	2
N,N-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-N-benzylamine	0,03	168	1,07	0	5,7
3,5-di-tert-butyl-4-hydroxybenzyl-N,N-dimethylamine (IKhP-712)	0,03	179	0,38	120	-
Sample 2					
Without additive	-	102	1,23	26,5	17,9
With additive					
2,6-di-tert-butyl-4-methylphenol (Ionol)	0,05	168	0,38	9	None
2,6-di-tert-butyl-4-dimethylaminomethylphenol (OMI)	0,05	180	0,60	306	None
Isopropyloctadecylamine (IPODA)	0,05	103	2,2	175	12,6
3,5-di-tert-butyl-4-hydroxybenzyl-N,N-dimethylamine (IKhP-712)	0,05	175	0,38	35	2,2

TABLE 4

Ionol concentration in TS-1 fuel, wt. %	Disperse-phase particle size, m	TOS indexes		
		t <sub>id</sub> , °C	TSI, rel. units	PDI, Pa/min
0	$6 \cdot 10^{-7}$	103	2,10	0
0,003	$6 \cdot 10^{-7}$	102	2,12	0
0,02	$1,5 \cdot 10^{-6}$	103	4,30	55
0,04	$5 \cdot 10^{-7}$	106	0,6	55
0,06	$2,5 \cdot 10^{-7}$	118	0,44	52
0,08	$5 \cdot 10^{-8}$	160	0,3	55
0,10	$3,5 \cdot 10^{-8}$	168	0,3	53
0,20	$3,5 \cdot 10^{-8}$	170	0,27	55

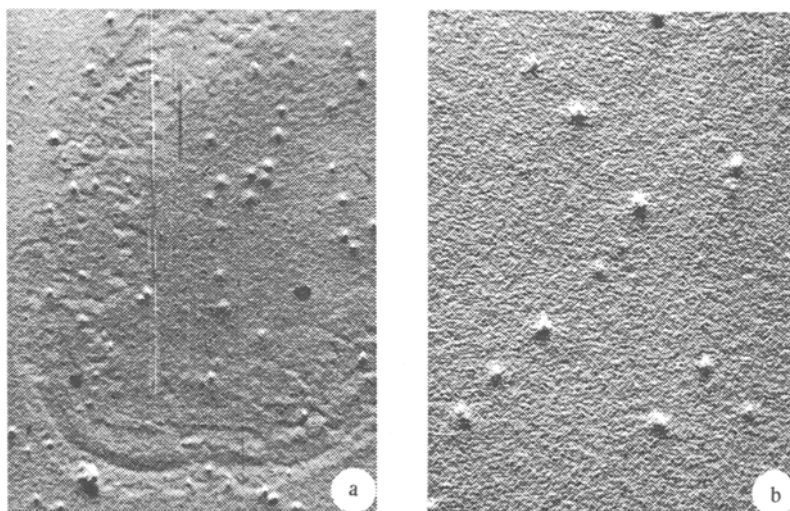


Fig. 3. L-0.5 diesel fuel with 5% Cellosolve by volume,  $\times 45,000$  (a) and  $\times 75,000$  (b).

With increasing concentration of Ionol from 0.003% to 0.02% by weight, the disperse-phase particle size increases appreciably. The quantity of deposits (TSI) on the preheater tube increases from 2.1 to 4.3 units;  $t_{id}$  and PDI remain at the previous levels. Extrema of TSI and  $t_{id}$  with variation of the disperse-phase particle size are observed at Ionol concentrations up to 0.1% by weight. The quantity of deposits decreases by 75%, and  $t_{id}$  increases to 168°C. The disperse-phase particle size in the straight-run fuel decreases from 0.8  $\mu\text{m}$  to 20-50 nm (dispersant effect).

A further increase of the Ionol concentration has very little effect on the disperse-phase particle size or on the TOS indexes of the fuel. This sort of behavior is possible only in case of adsorption of Ionol molecules on the surface of the disperse-phase particles (shielding effect). The dispersant and shielding effects created by Ionol were investigated on 12 samples of commercial TS-1 fuel. The results obtained in these experiments confirmed that an Ionol concentration of 0.1% by weight is optimal.

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