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ENVIRONMENTALLY SAFE ADDITIVES FOR DIESEL FUELS

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The environmental properties of diesel fuels (DF) manufactured in Russia are basically unsatisfactory due to the high content of sulfur compounds and aromatic hydrocarbons (AH). According to the World-Wide Fuel Charter published in December, 1998, DF are divided into three categories [1]: I: medium-sulfur; II: low-sulfur, treated; III: sulfur-free, exhaustively treated. Fuels in these categories should contain a maximum of 0.5, 0.03, and 0.003 wt. % sulfur, respectively.

The content of monocyclic and polycyclic AH in category I fuels has not been standardized. In category II fuels, it must not exceed 25 and 5 wt. %, respectively. In category III fuels, the maximum content of monocyclic AH is 15 wt. % and they should contain no polycyclic AH. With respect to lubricating power, category II and III fuels should be similar to category I fuels: the wear spot diameter should be no greater than 400 mm in testing on a friction machine.

The environmental properties of DF can be improved by including gas condensates with a low content of heteroatomic contaminants in refining and using environmentally safe additives to improve the operating properties.

The studies showed that the antiwear properties of gas condensate diesel fuels, like type DLECh hydrotreated petroleum fuels with a sulfur content below 0.1%, are unsatisfactory [2]. We preferred to use environmentally safe fuel additives that do not form toxic products of combustion to improve them. These additives primarily consist of widely used fuel components – alcohols, esters, etc. [3, 4].

In addition, the following are proposed as antiwear additives to middle-distillate fuels [5-8]: high-molecular-weight monohydric, dihydric, trihydric, and tetrahydric alcohols; carboxylic and polycarboxylic acids; C_{24}-C_{65} mono- or polycarboxylic acid esters with two to three carboxyl groups and C_2-C_9 multihydric alcohols with 2-10 hydroxyl groups; mixtures of synthetic or plant esters of mono-, di-, tri-, and tetrahydric C_2-C_{18} alcohols and carboxylic acids with C_3-C_{45} acyls; the product of the reaction of aromatic triazole (tolyltriazole) and a C_{10}-C_{40} fatty acid, etc.

We investigated the effect of the chemical composition of GDF, including oxygenate additives, on their antiwear properties. Nadym GDF, winter DF according to GOST 305–82 (for comparison), and our two-component reference fuel, similar to GDF in antiwear properties, were tested as the basic fuels. The characteristics of these fuels are reported in Table 1.

The data on the effect of *n*-decyl alcohol on the antiwear properties of the reference fuel are shown in Fig. 1. The wear spot diameter as a function of the concentration of alcohol in the fuel is nonlinear. With an increase in the concentration, the effectiveness of the alcohol decreases, probably due to adsorption saturation of the friction surface. The optimum concentration of *n*-decyl alcohol in the reference fuel is in our opinion within the limits of 0.05-0.1 wt. %.

We tested alcohols with different numbers of carbon atoms in the chain to study the effect of the molecular weight of normal monohydric alcohol on the antiwear properties of the reference fuel. They were added to the reference fuel in concentrations equivalent in oxygen to 0.1 wt. % of *n*-decyl alcohol. The results of the studies are shown in Fig. 2.

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TABLE 1

Individual hydrocarbons, cuts	Diesel fuel		
	winter (GOST 305-82)	gas condensate (TU 51.001-58623-02-93)	reference
Distillation, °C			
IBP	–	86	–
10 %	–	120	100
50 %	260	164	100
96 %	340	339	111
Viscosity at 20°C, mm^2/s	3.9	1.48	0.75
Flash point (open cup), °C	62	17	–
Acidity, mg KOH/100 cm^3	3.7	2.3	None
Content			
sulfur, wt. %	0.2	0.07	None
existent gums, mg/100 cm^3, mg /100 cm^3	32	24	None
Density at 20°C, kg/m^3	860	786	725

The curve obtained is almost linear and indicates the significant effect of the length of the hydrocarbon radical on the antiwear properties of the experimental fuel. These properties improve with an increase in the molecular weight of the alcohol. This dependence is probably due to the formation of molecules of higher molecular weight on the friction surfaces of the thick adsorption layer.

The effect of the length of the hydrocarbon radical in saturated monocarboxylic acids on the antiwear properties of the reference fuel is also shown in Fig. 2. These compounds were also added in a concentration equivalent in oxygen to 0.1 wt. % of *n*-decyl alcohol, and in calculating the concentration, both carboxyl group oxygen atoms were taken into consideration. Carboxyl compounds are superior in surface activity to hydroxyl compounds and probably form a stronger chemisorption film on metal surfaces which protects the metal from wear. The dependence of the antiwear effectiveness of the compounds on the length of the hydrocarbon radical is almost linear.

The studies showed the weak effect of the additive compounds containing carbonyl, ether, and ester groups on the antiwear properties of the fuel. The compounds are in the following order with respect to antiwear effectiveness: acids > alcohols > esters > aldehydes and ketones > ethers.

Some acid-containing compounds, organic acids and alcohols of a certain chemical structure in particular, can thus improve the antiwear properties of fuels.

Based on the results of the studies with consideration of the economic expediency for further research, we selected a technical product with active oxygen-containing groups in the molecules – bottoms from industrial fractionation of a mixture of oxygen-containing compounds. The product tested (arbitrarily called APP) was manufactured in a petrochemical plant; it could hypothetically have other positive properties in diesel fuels and was much less expensive and more readily available than individual acid-containing compounds and existing additives.

Its molecules contain hydroxyl, carbonyl, carboxyl, and other active oxygen-containing groups, and a large amount of hydroxyl groups. The basic properties of APP are reported below:

Density at 20°C, kg/m^3	866
Number, mg KOH/g	
acid	0.4
saponification	78
ester	77.6
hydroxyl	232
Cutpoints, °C	95-248
Total content, wt. %	
ethers	2.4
esters	10.6
alcohol	21.3
aldehydes	11.6
monoglycol ethers	13.3
high-boiling compounds	28.8

As Fig. 3 shows, APP in a concentration of 0.05-0.1 wt. %, similar to the individual compounds, significantly improves the antiwear properties of both Nadym GDF and the reference fuel. However, the effectiveness of APP is

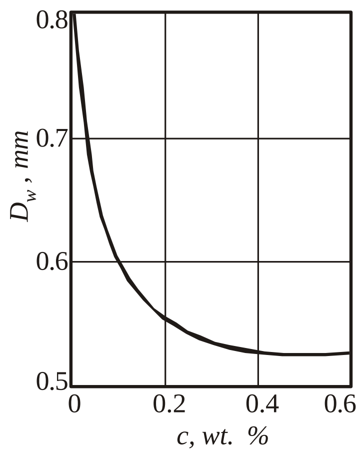

Fig. 1. Wear spot diameter D_w in reference fuel with *n*-decyl alcohol additive vs. concentration *c* of additive.

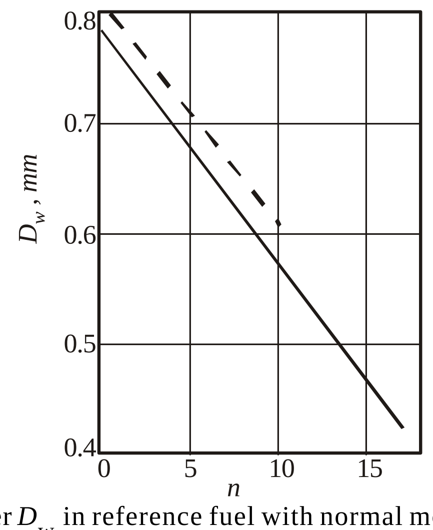

Fig. 2. Wear spot diameter D_w in reference fuel with normal monohydric alcohol (dashed line) and saturated carboxylic acid additive (solid line) vs. number *n* of carbon atoms in the aliphatic radical of the additive molecule.

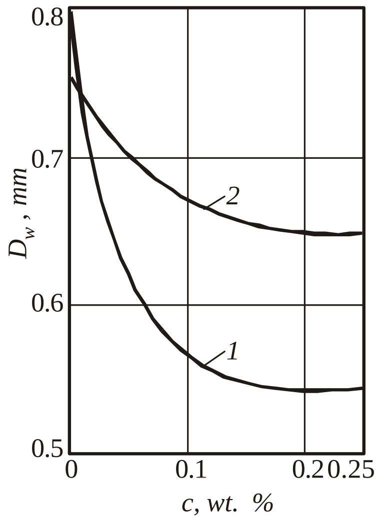

Fig. 3. Wear spot diameter D_w vs. concentration *c* of APP: 1) in reference fuel; 2) in Nadym GDF.

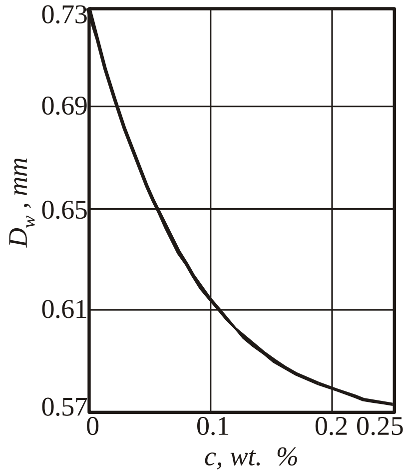

Fig. 4. Wear spot diameter D_w vs. concentration *c* of 150-200°C cut of APP in winter diesel fuel.

lower in GDF than in the reference fuel, which could be due to the intermolecular interaction and effect of antagonism between the compounds added to the GDF and natural heteroatomic compounds in the fuel.

In studying the effect of different APP fractions in the concentration of 0.05 wt. % on the antiwear properties of the reference fuel, it was found that the 150-200°C fraction (D_w = 0.58 mm) exhibited the maximum effect, followed by the >200°C residue (0.62 mm) and finally, the 90-150°C fraction (0.67 mm). This distribution of the activity can be attributed to the decrease in the content of the most active oxygen-containing groups in the residue.

The effect of the 150-200°C APP fraction on the antiwear properties of standard winter diesel fuel is shown in Fig. 4. The character of this dependence is similar to the one in Fig. 3.

Of the oxygen-containing compounds investigated, carboxyl- and hydroxyl-containing compounds with 10-12 carbon atoms in the aliphatic chain of the molecule in the concentration of 0.05-0.3 wt. % are thus the most effective.

The 150-200°C fraction of the residue from distillation of synthetic oxygen-containing intermediate products from production of plasticizers in the concentration of 0.05-0.20 wt. % can effectively decrease metal wear in gas condensate and winter diesel fuels: to a level corresponding to straight-run summer diesel fuel.

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