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RESPONSE OF HYDROCARBON FUELS TO LITHIUM-CONTAINING ANTIKNOCK COMPOUNDS

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Organolithium compounds were investigated as chemical controllers of hydrocarbon combustion. The response of individual hydrocarbons of different classes, reference mixtures, naphtha cuts, and base compositions of commercial gasolines was investigated as a function of the concentration of lithium in them. The mechanism of action of lithium-containing antiknock compounds is proposed.

The use of antiknock additives is usually the simplest and least expensive way to increase the octane number of automotive gasolines [1, 2]. The effect of chemical combustion controllers of motor fuels on the processes that take place in internal combustion engines is a function of the group hydrocarbon composition of the fuel. The response of naphtha cuts (mixtures of hydrocarbons) from different industrial processes and individual hydrocarbons to the entire spectrum of existing antiknock compounds has been investigated in many studies, in [1-6] in particular.

The effect of organoelemental antiknock compounds on the antiknock rating of hydrocarbons of different classes was investigated in detail in [4-6]. It was found that the greatest response was exhibited by paraffins, a smaller response was exhibited by naphthenes, and olefins and aromatics had the smallest response.

A trend was detected for chemical combustion controllers of gasolines based on metals of variable valence: the lower the octane number (ON) of the gasoline or its basic component, the higher the antiknock effect of the additive. The results of the tests on a single-cylinder standard engine with variable compression (Vokesh method) and in full-scale engines in highway conditions show that the greatest increase in the ON is characteristic

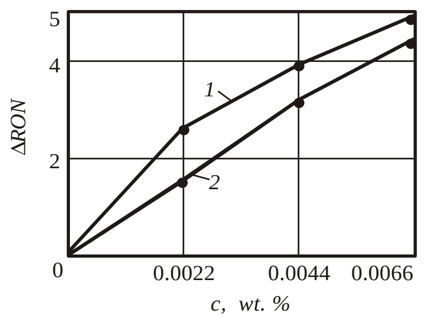

Fig. 1. Effect of the concentration *c* of lithium on the increase in the research octane number ΔRON of base compositions of automotive gasolines: 1) Regular-92 (AI-92); 2) Normal-80 (AI-80).

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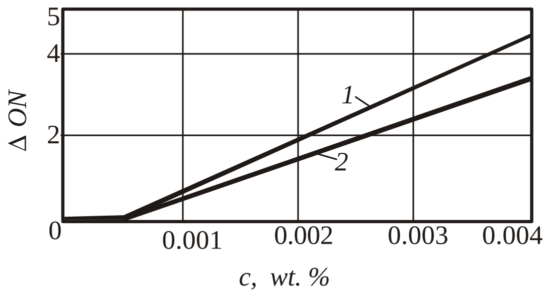

Fig. 2. Effect of the concentration *c* of lithium on the increase in the octane number ΔON of a standard mixture of isooctane (90%) and *n*-heptane (10%): 1) MON; 2) RON.

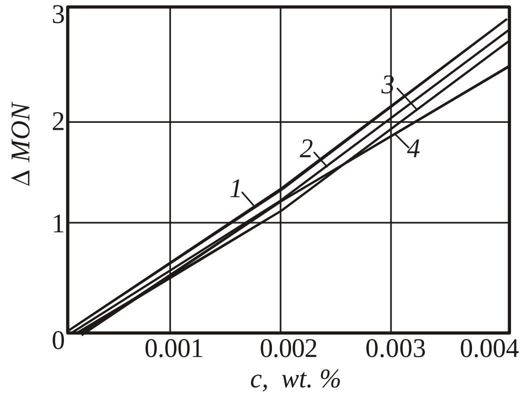

Fig. 3. Effect of the concentration *c* of lithium on the increase in the octane number of individual hydrocarbons: 1) isoparaffins; 2) olefins or normal and isomeric structure; 3) naphthenes; 4) aromatics.

of straight-run naphthene–paraffin-base gasolines, a lower ON is characteristic of catalytic reforming and cracking gasolines, and the lowest ON is characteristic of gasolines with a high aromatic hydrocarbon content.

Organic derivatives of alkali metals are a new class of organoelemental combustion controllers for automotive gasolines [7]. It was found that lithium compounds exhibited the highest activity in testing on an UIT-85 in standard conditions. The response of naphtha cuts of different genesis, individual hydrocarbons, and commercial compositions to lithium-containing antiknock compounds is not known.

We investigated the effect of organic lithium compounds on the antiknock rating of base hydrocarbon compositions of the commercial gasolines Normal-80 (AI-80) and Regular-92 (AI-92) produced according to GOST R 51105 by Surgut Condensate Stabilization Refinery (CSR) on a standard UIT-85 setup according to GOST 511 and GOST 8826. These compositions, which have a RON of 77.1 and 88.2, respectively, contain reforming catalyzate, an isopentane cut, and IBP-70 and IBP-140°C straight-run naphtha cuts.

It was found that on addition of additives containing organolithium compounds to these base compositions, the antiknock rating of the compositions increased (Fig. 1). The required level was attained for an additive concentration of 0.0044 wt. % in terms of lithium.

Further studies were conducted with a concentration of antiknock compounds in the range of 0.002-0.004 wt. % (20-40 ppm), optimum both with respect to the real efficiency and with respect to the requirements of GOST R 51105.

The tests for the antiknock rating of a standard reference mixture of isooctane (90%) with *n*-heptane (10%) with ON = 90 (MON and RON) with different concentrations of lithium in them showed that the motor method is more sensitive to compounds of this metal in fuel than the research method (Fig. 2).

The data on the response of individual hydrocarbons and C_5-C_9 cuts, the most common in commercial gasolines, to lithium combustion controllers are shown in Table 1 and Fig. 3. The antiknock rating of paraffinic hydrocarbons increased most significantly, and the antiknock rating of aromatics increased the least. The

TABLE 1

Individual hydrocarbons, cuts	MON for lithium concentration, wt. %		
	0	0.002	0.004
Paraffins			
Pentane (Nizhnekamskneftekhim OJSC cut)	59.8	60.9	61.2
Isopentane (Surgut CSR cut)	88.9	90.1	91.7
Isohexane (3-methylpentane)	74.2	75.3	76.4
Isooctane (2,2-dimethylhexane)	77.1	78.3	79.8
Naphthenes			
Cyclopentane	89.2	90.1	91.7
Cyclohexane	76.9	78.2	80.1
Methylcyclohexane	72.5	73.1	74.3
Aromatics			
Toluene	100.0	101.3	102.6
Ethylbenzene	96.2	97.1	98.0
Butylbenzene	96.8	97.9	99.1
Isopropylbenzene	98.6	99.8	101.0
KAT-1*	87.6	88.3	89.1
Olefins			
1-Hexene	73.8	75.0	76.4
Iso-C_7-C_8 fraction	84.6	85.6	86.6
KAT-K*	86.8	87.4	89.0

Note. *Component of automotive gasoline.

dependence of the increase in the MON on the concentration of lithium is almost linear when the latter is increased to 0.004 wt %. %.

According to the peroxide theory of the effect of antiknock compounds that prevent the evolution of radical chain reactions and the appearance of a cold flame front in combustion of the fuel-air mixture elaborated in detail in [9], the mechanism of action of lithium-containing combustion controllers can be represented as follows:

$$R' - CH_3 + O_2 \rightarrow R' - CH_2OOH \overset{Li_2O_2}{\rightarrow} R' - CHO + H_2O + Li_2O + 1/2O_2$$

where ROLi is an organolithium compound; $R' - CH_3$ is the hydrocarbon in the fuel.

In contrast to traditional combustion controllers – lead, manganese, iron, i.e., elements of variable valence, organic compounds that form oxides of different composition in combustion in internal combustion engines and can in turn interrupt the evolution of radical reactions, alkali metals, lithium in particular, fall into the flame during combustion of organic compounds containing them and probably are initially oxidized into peroxides. The lithium peroxide then reacts with free radicals and oxidizes them to compounds that are not active in chain reactions and thus prevent autoignition of the fuel and consequently the appearance of “knock” in the engine.

Hydrocarbon-soluble organolithium compounds thus exhibit high activity as fuel combustion controllers by raising their antiknock rating. They increase the MON more than the RON, i.e., they reduce the sensitivity of the fuel.

The response of hydrocarbons of different homologous series to organolithium antiknock compounds is a complex function of the concentration of the antiknock compound, in contrast to their response to other organoelemental antiknock compounds.

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