## Features of the detergent additive behavior in gasolines of different group composition

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To solve the problem of improving the quality of fuels used in internal combustion engines, a comprehensive approach is proposed, which includes the use of additives to gasoline, increasing the detergent properties in parallel with completeness of fuel combustion. The results of laboratory studies of present-day gasolines as well as the results of motor-bench tests of a gasoline injection engine when it operates on gasolines of various group and oxygenate compositions, including those containing detergent additives and a combustion activator are presented. The relation of the group and oxygenate gasoline compositions, concentration of the introduced additive with the technical, economic and environmental characteristics of the gasoline engine is considered. The optimum concentration of multifunctional additive introduction into gasolines of different group composition is determined. It is shown that the efficiency of the additive deteriorates with increasing content of oxygenates.

**Keywords:** gasoline, group composition, oxygenates, detergent additives, combustion activators, motor-bench tests, carbonization, exhaust toxicity

Modern branded motor gasoline almost always contains in composition the detergent additives. The purpose of these additives is to reduce the level of deposits in the fuel system, the intake channels and on the intake valves, in the combustion chamber of the engine [1–6].

Often the detergent is combined with the additive-activator of fuel burning, the objective of which is to increase the speed and completeness of fuel combustion in the engine. The activator of burning enhances the action of detergent additives by activating a "hot" cleaning the combustion chamber — temperature destruction of solid soot deposits on the fire on the surface of the cylinder head and pistons. Thereby improving combustion of the fuel-air mixture departs the threshold of detonation in the engine, reduced the risk of pre-ignition. An important factor in the use of gasoline containing a comprehensive package of additives is the decrease in the rate of contamination of the active zone of the catalyst system to suppress the toxicity of exhaust gases, therefore, extending their service life [5, 6]. In addition, the increase in the speed and completeness of combustion of fuel contribute to the increase of capacity and decrease in fuel consumption of the engine [5, 6].

A comprehensive additive package gasoline performs two interrelated functions. First, improving the quality of fuel combustion contributes to a reduction in the tendency of the fuel to the formation of deposits. Combustion occurs with the formation of lesser amounts of soot deposits, which

adversely affect the working process of the engine. Secondly, the cleaning component of the package contributes to the removal of organic deposits in the "cold" parts in the fuel system (fuel tank, fuel lines, metering components of the fuel), accumulated during the previous operation of the engine and violates the process of mixing. In addition, it should initiate "hot" clean firing surfaces of the combustion chamber of the engine

The experience of numerous experimental studies conducted by the authors of this article [7, 8] showed that there is a significant dependence of the efficiency of the additives from the group composition of the base fuel. However, this issue is almost completely ignored by the manufacturers of additives; recommendations on the dosage of the package are common to all types of base gasolines.

The following are some of the results of experimental studies of the effectiveness of multifunctional additives of domestic production with respect to several different baseline gasoline group compositios, illustrating the foregoing.

Tests were subject to four types of base gasolines of AI-92 with different contents of aromatic hydrocarbons and oxygen-containing component. Physico-chemical characteristics of the base gasoline are summarized in table 1.

Table 1
Physico-chemical characteristics of the base gasoline

The name of the parameter	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4
Research Octane Number, ed.	92.6	92.1	92.7	93.1
Motor Octane Number, ed.	83.1	83.0	83.5	88.4
Fractional composition:				
– % Evaporated @ 70° C, E70	32.2	35.0	42.3	52.4
– % Evaporated @ 100° C, E100	53.3	54.0	61.3	59.1
– % Evaporated @ 150° C, E150	86.3	81.2	87.4	82.3
– Final Boiling Point (FBP), °C	195	209	186	212
– Distillation Residue, % v/v	1.3	1.0	1.0	1.0
Benezene Content, % v/v	0.5	0.4	0.2	0.1
Sulphur Content, mg/kg	3.0	8.7	7.7	61.0
Vapour Pressure (DVPE), kPa	80.0	74.0	63.0	76.0
Oxygen Content, % m/m	0	0	2.14	11.3
Existent Gun Content, mg/100ml	0	1.0	0	5.0
Hydrocarbon Type Content, % v/v:				
- Olefin Content	2.6	0.4	4.2	2.1
- Aromatics Content	34.9	33.0	25.9	16.3
Oxygenates Content, % v/v				
- Methanol	_	_	_	16.9
- Tret-Butyl Alcohol	_	_	_	1.2
- Other Oxygenates (5 or more C atoms)	_	0.7	11.7	_

As follows from the results of determination of physico-chemical characteristics of the base gasoline and samples of No. 1–3 belong to environmental class K5 and fully comply with the requirements of Technical regulations of the Customs Union TR CU 013/2011. Sample No. 4 does not meet these requirements in composition (the presence of methanol), mass fraction of oxygen and sulfur. It is a typical representative of gas condensate of baseline gasoline, frequently used part of the fuel companies with a low turnover of fuel. Despite the illegitimacy of the composition of this sample of gasoline, it was decided to leave it in the study to expand the range of parameters of the group composition of the fuel. The results of the extended analysis of hydrocarbon composition of the samples of the base fuels represented in table 2.

The content of hydrocarbons of certain groups in the studied samples of the base gasoline, % v/v

The group of hydrocarbons	A sample of gasoline					
	No. 1	No. 2	No. 3	No. 4		
N-paraffin	11.43	12.04	12.55	18.47		
Isoparaffin	47.23	48.54	40.54	31.43		
Aromatic	34.87	33.04	25.88	16.34		
Naphthenic	3.92	5.26	5.14	10.14		
Olefin	2.55	0.42	4.18	2.08		
Oxygenates	0	0.70	11.71	21.54		

Tests were successively conducted for each sample of gasoline, then for the same gasoline with multifunctional additives introduced into the

fuel at a concentration recommended by the manufacturer (1000 ppm). For testing we used a motor stand with gasoline 16-valves a fuel injected engine VAZ-2112 (4H 8.2/7.1) capacity 68 kW at rpm n = 5600 rpm. Test procedure each sample of gasoline included the following stages

[9, 10]:

- partial disassembly of the engine, weighing the weight of the control elements (valves, spark plugs, injectors), Assembly, installation stand;
- reference contamination development on a fixed mode, 20 litres special dirt mixture forming on the surfaces of the combustion chamber, the fuel and intake systems of the engine starting of the deposition layer;
- repeated partial disassembly, the determination of the initial mass of sediments Assembly;
- the initial lifting of the performance of the engine for a given program with the measurement of instantaneous fuel consumption and toxicity of exhaust gases on the load characteristics in the operational range of the engine. It is not allowed to work the engine at high loads to exclude the factor self-cleaning temperature of the engine;
- holding a twenty-hour test cycle for variable modes of the subject gasoline;

Table 2

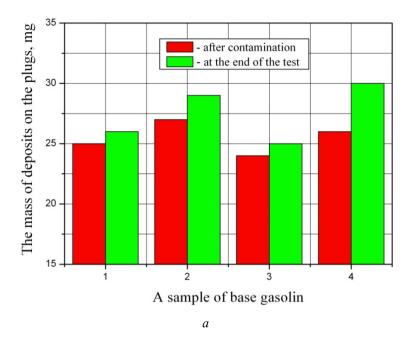
• final removal of the performance of the engine according to a preset program; disassembly of the engine, the determination of the total mass of sediment control details.

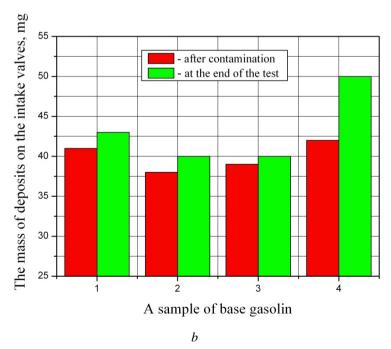
Determination of the mass of sediments was carried out by weighing control parts on the analytical balance with an accuracy of 0.001 g. To remove traces of oil and other contaminants remaining on the surfaces of the parts in the process of dismantling the engine used a specially designed washing procedure of the control parts in the organic solvent with subsequent drying.

The results of the analysis of the data obtained in the first stage of testing, we can draw the following conclusions:

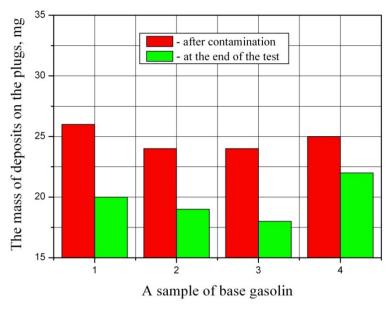
- in the tests the base gasoline is the initial mass of sediments in the reference result of pollution, after a long twenty-hour engine running time increased slightly for all gasoline, however, the growth of deposits was small. This indicates a low tendency to sediment in the base gasoline and the absence in their composition of detergent components. To a greater extent the increase in the weight of deposits was detected in sample No. 4, and is clearly associated with a significant compared to the other samples the content of actual pitches (Fig. 1);
- testing of samples of gasoline containing multifunctional additive, showed a trend to decrease in the weight of deposits on all control weight engine components: spark plugs, intake and exhaust valves, injectors (Fig. 2);
  the greatest efficiency detergent additive component showed on the sample of gasoline № 1 with relatively high content in the base gasoline aromatic hydrocarbons and a complete absence of oxygen-containing component, (Fig. 3). The lowest efficiency of the additives were recorded on the sample of gasoline No. 4 with an abnormally high content of oxygenates, however, when working on a ton of deposits on the surfaces of the control parts began to decrease: the control parts began to decrease;
- best efficiency in the relative decline in the weight of deposits gasoline containing the additive, showed in terms of cleaning the intake valves. Obviously, in this case, cumulative effects are "hot" treatment, in which solid removes soot deposits from firing, the outer surface of plates of valves; and cold cleaning, which removes organic deposits from cores and inner surfaces of plates of valves, lapped by the jet of fuel from the injectors. Minimum relative effect is detected in terms of cleaning injectors of the fuel injection system.

The second phase of the pilot study was to answer the question about the impact of the input concentration of multifunctional additive on the instantaneous effects on reducing fuel consumption and change in toxicity of the fulfilled gases and, depending on the composition of the base gasoline. On the basis of the information received was determined by the value of the optimal concentrations of input multifunctional additive in gasolines of different group compositions.

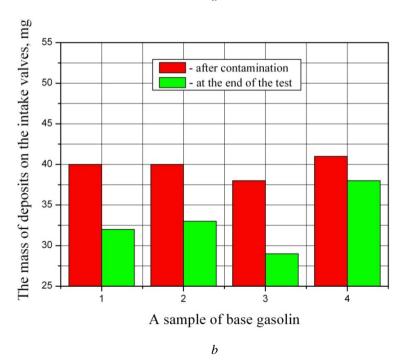




**Fig. 1.** The mass of deposits on the spark plugs (a) and intake valves (b) formed as a result of tests the base gasoline



а



**Fig. 2.** The mass of deposits on the spark plugs (a) and intake valves (b) formed as a result of testing samples of the base gasoline, containing multifunctional additive





a b

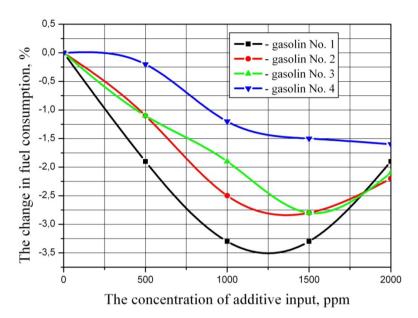
**Fig. 3.** Deposits formed on the surface of the intake valve the tests of petrol No. 1 with detergent additive (a) and without cleaning additives (b)

In the process of implementation of the second phase of work has been carried out engine bench tests of the engine during its operation on the samples of all four types of base gasolines with addition of multifunctional additive in concentrations of 0, 500, 1000, 1500 and 2000 ppm. To exclude the factor of the work of detergent additive component was not allowed long operation of the engine on each fuel sample. The tests were carried out on the engine, subjected to a special cleaning procedure, which was removed sediments and contamination on the surfaces of the combustion chamber, intake and exhaust systems accumulated in previous operation. The test results were obtained information about the influence of the activator of fuel burning, forming part of a multifunctional additive to motor gasoline indicators of different group compositions.

Each test cycle included the following steps:

- start-engine warm up, the time between a fixed mode for 20 minutes;
- removing performance of the engine (engine speed, torque, instantaneous fuel consumption, contents in the exhaust gas component toxic: carbon monoxide, residual hydrocarbons CH, nitrogen oxides  $NO_x$  and carbon dioxide  $CO_2$  mixture, exhaust gas temperature) on the ten modes of the two load characteristics in the operational range of the engine;
- processing of test results with the conversion to standard atmospheric conditions, the calculation of the average efficiency of the engine and exhaust toxicity.

Some results of the performed tests is given below. Fig. 4 shows the dependence of the relative change of averaged fuel specific consumption of the engine when operating on gasoline containing the additive, the concentration of its input in the fuel.



**Fig. 4.** The dependence of the relative change in specific fuel consumption the concentration of the input multifunctional additives

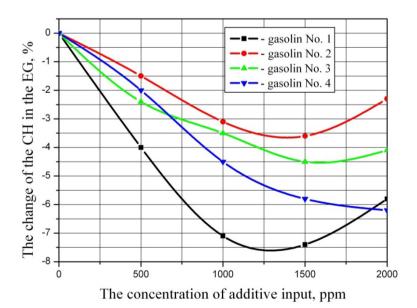
In Fig. 4 the graphs show a pronounced dependence of the optimal additive concentration at which the maximum energy-saving effect, from the group composition of gasoline. Also it is clearly seen the dependence of this parameter from the content in oxygenated gasoline component. So, for gasoline samples No. 1 and No. 2 not containing in the composition of oxygenates, the value of an optimal concentration close (about 1300 ppm), which exceeds the stated manufacturer of the additive (1000 ppm). For gasoline containing bound oxygen, optimum concentration is shifted in a big way. So, for sample No. 3, the best results are obtained when the concentration 1600 ppm of the additive. Moreover, for gasoline No. 4 in the studied range of concentrations the optimum was not determined, that is, it is achieved at the concentration of the additive substantially in excess of 2000 ppm.

Also the curves in Fig. 4 show the effect of fuel composition on the efficiency of the activator burning. The greatest effect (about 3.5 % reduction in fuel consumption relative to operation of the engine on base gasoline) obtained at the fuels, based on which the base gasoline No. 1, con-

taining the maximum amount of aromatic hydrocarbons in the absence of oxygenates. The minimum effect was obtained on the samples of the base fuel at petrol No. 4, with a minimal content of aromatic hydrocarbons too high content of oxygenates. He was about 1.6 % reduction in fuel consumption, however, as mentioned above, when the concentration of the additive input of more than 2000 ppm, perhaps the effect would be higher. However, the increase of concentration of multifunctional additives leads to an unacceptable increase in the cost of fuel.

This result correlates with data on the content of a toxic component in exhaust gases on the content of CH (Fig. 5).

Obviously, improving the speed and quality of combustion of fuel provided by the input activator of combustion, leading to reduced fuel consumption, contributes to a more complete combustion of the gasoline in the cylinder which is manifested in the reduction of residual hydrocarbons CH. The maximum effect is achieved in the above defined concentrations, input of additives, in accordance with the composition of the base gasoline. In this case, and the relative effect size also correlates with data obtained in the analysis of the fuel efficiency of an engine working on different fuel samples. Thus, the maximum reduction effect of CH is achieved on the samples of the fuels on the basis of the base gasoline, No. 1 (7.5 %), the minimum — fuel samples based on base gasoline No. 4 (to 3.6 %).



**Fig. 5.** The dependence of the relative content of residual hydrocarbons HC in the exhaust gases from the concentration of input additives

It is obvious that the above results belong to the "instant effects", which excludes the effect of cleaning additives components that manifest themselves only after prolonged operation of the engine. Therefore, in actual operation of the engine numbers relative improvement of its performance can be substantially higher and will depend on the duration of the operating time of the engine on fuel with additive, the initial state of the engine, and its modes of operation.

Thus, this study proved that the optimal input concentration of a multifunctional additive that provides the maximum effect as detergent components and activator of combustion of its constituent depends on the group composition of gasoline, primarily from the content and composition of the oxygen component in the fuel. The increase in the content of oxygenates reduces the efficiency of operation of the additive and increases its concentration. Therefore, in forming the branded fuels of the required individual selection of the concentration of multifunctional additives based on the composition of the base gasoline and set ratio "price—quality".

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