Problems of sediment formation in internal combustion engines

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Abstract. The present article deals with some complex problems of sedimentation in internal combustion engines. The chemical composition of carbon deposits is determined and a multiparametric equation of the carbon deposit formation rate is made, taking into account the thermal mode of the unit. The solution of the problem under consideration is possible by means of some modern methods of analytical chemistry, which will contribute to the development of new formulations of effective anti-carbon and detergent additives.

During the operation of internal combustion engines there is an accumulation of deposits - carbon, varnish and sludge, which further leads to a significant decrease in efficiency and a reduction of engine life, caused primarily by the deterioration of parts and mechanisms due to their local overheating. Therefore, the study of the causes and mechanisms of sediment formation in engines is of great interest.

It is proved that the processes of engine oil aging in the engine, as well as thermal transformation of fuel and oil components in high temperature zones are the cause of sedimentation phenomena [1]. These processes mainly determine the range of problems related to the reliability of the DVS. Measures related to the reduction of thermal transformation of the components of operating fluids in high-temperature zones significantly reduce sedimentation.

Simplifying, the main types of deposits can be conveniently represented in the following Table 1.

Studies show that especially intense deposits are formed on the parts of the cylinder group, in the intake manifold, as well as on the critical parts of the power system. The main point of localization of the deposits is shown on Figure 1.

Each type of the above deposits can cause a number of interrelated conditions that accelerate the wear and destruction of parts and systems of the engine, but the greatest research interest is the study of the mechanism of carbon formation, which is caused by the following factors:

- the process of varnish formation is the deposition of a high-temperature lacquer film on the parts of the cylinder-piston group (CPG), due to the incorrectly selected grade of motor oil, which has low thermal oxidative stability;
- the process of sedimentation in the crankcase part of the engine and under the valve cover is nothing but the formation of a mixture of hydrocarbon oxidation products with the products of contamination of the crankcase oil with emulsions and water.
### Table 1. The nature and classification of sediments in the automotive internal combustion engine

| Name and illustration | Physical and chemical properties of deposits |
|------------------------|---------------------------------------------|
| **1) Carbon**<br>The bottom of the piston<br>Combusion chamber | Solid carbonaceous substances. Carbon deposits can vary in color, hardness and structure. The chemical composition of carbon deposits depends on the quality of oil and fuel, and on the mode of operation of the engine, air dust, the presence of additives, etc. The main part of the carbon deposits are carbenes and carbides (50-70%), resins and oils (15-40%), asphaltenes and oxides (3-6%), ash (1-10%). |
| **2) Varnish**<br>The surface of the piston | Oxidation product of thin oil films spreading and covering engine parts under high temperatures. It differs in color and nature of its surface, as well as in chemical composition. Varnish deposits are a product of condensation of oxy-acids. The chemical composition of the varnish includes carbon (about 80%), oxygen (10-15%) and hydrogen (up to 7-9%), as well as a certain amount of ash (solid fireproof compounds). |
| **3) Precipitation (sludge)**<br>Crankcase | A mixture of hydrocarbon oxidation products with products of contamination of crankcase oil with emulsions and water. Resins, carbon particles, water vapor, heavy fuel fractions, acids and other compounds condense, coagulate into larger particles and form in the oil sludge, the so-called black sludge. |

**Figure 1.** Localization of the main points of sediment formation: 1 - injectors; 2 - channels of the intake manifold and valve seats; 3 – details of the cylinder group; 4,5 – details of the crank mechanism; 6 – wall of the crankcase
Analysis of the above facts shows that the mechanisms of formation of varnish and sludge on the parts of the DVS are directly related to the illiterate operation of vehicles and violations of the basic provisions on the technical maintenance and repair of vehicles (TM and R).

The use of modern synthetic motor oils has significantly reduced the formation of varnish on the working surface of the parts and almost completely eliminate the deposition of sludge in the crankcase of the engine and under the valve cover. Correctly selected modern engine oil and its timely replacement once and for all closes a question of emergence of a significant amount of slime in the specified places.

The mechanism of carbon formation is the most versatile and interesting for the research. Practical experience has shown that even the use of modern fuels and lubricants (FL) leaves the question of intensive formation of carbon deposits in the engine open. That is why the study of the mechanism of carbon formation is relevant at the present time.

Focusing on the process of carbon formation, first of all it is necessary to analyze the mechanism of the process. Most of the gasoline is completely evaporated in the intake pipe of the engine. In the vapor state, gasoline hydrocarbons are not subjected to chemical transformations in the pre-ignition period and burn, without forming a large amount of carbon. Some of the gasoline does not have time to evaporate in the intake pipeline and in the form of individual droplets, sometimes in the form of fog enters the combustion chamber. Being in the liquid phase, high-boiling hydrocarbons under the action of temperature in the pre-ignition stages can undergo chemical changes. Such changes associated with the oxidation of hydrocarbons and their subsequent condensation, polymerization and compaction of oxidation products, lead to the appearance of high-molecular products that subsequently form carbon deposits.

Studies have shown that in the operation of an automobile engine, carbon deposits are formed unevenly over time. The main amount of carbon deposits is deposited at the beginning of operation of the vehicle. It has been experimentally established that after a run of 10-16 thousand km a certain equilibrium state occurs and the amount of carbon deposits changes slightly during further operation of the engine. Equilibrium is achieved due to the fact that chemical reactions and thermal effects together with gas flows cause the combustion and removal of carbon deposits from the combustion chamber at about the same rate at which they are formed at the moment. This phenomenon is known as self-cleaning of the combustion chamber.

On the basis of these studies, a mechanism for the formation of carbon deposits was proposed. The phase diagram of the mechanism of formation of carbon deposits is shown in Figure 2.

The initial stage of carbon formation is the liquid-phase oxidation of high-boiling hydrocarbons entering the combustion chamber in the form of individual small droplets. Subsequent condensation, polymerization and compaction of oxidation products form a material for the formation of carbon deposits in certain areas of its existence, depending, in turn, on the temperature and gas-dynamic conditions in the combustion chamber. Outside these zones, the residue burns out.

To study the mechanism of carbonation, it is assumed to apply an integrated approach, including modern methods of analytical chemistry – IR spectroscopy to determine the main functional groups of the carbon monoxide substance.

The method of infrared spectroscopy makes it possible to obtain information about the relative positions of molecules for very short periods of time, as well as to assess the nature of the relationship between them, which is fundamentally important in the study of structural and information properties of various substances. In addition, the logical step in the study of the mechanism of carbon formation is to determine the main performance characteristics of fuels and lubricants.
Figure 2. Diagram of the phases of the mechanism of soot formation: 1 – the beginning of soot formation; 1–2 – phase growth of carbon; 2–3 phase equilibrium of carbon; 3–4 final growth phase of soot; 4 – cessation of operation of the engine. (Mass of carbon/Engine running time)

Typical spectrum of carbon deposits obtained on the device IRAffinity-1 (Figure 3) in tablets KBr (aperture 8 mm) in the frequency range 400-4000 cm⁻¹, shown in Figure 4.

Figure 3. The Ft-IR spectrometer IRAffinity-1

Figure 4. Range of carbon deposits from the intake valve DVS

Decoding of spectra is carried out in two ways: by means of the generalized tables of characteristic peaks given in the literature [3], or by a method of comparison of the received spectrum with the available in the database of the software of the device. The method of IR spectroscopy allows to identify chemical composition of carbon deposits with high accuracy.

Despite the entire array of studies of the problem of sedimentation, relatively little attention was paid to operational factors affecting the occurrence of the process in question, i.e. sedimentation such as:

- Poor quality of motor fuel;
- The incompatibility of components of a motor oil with low-quality motor fuel;
- Severe operating conditions of the vehicle;
- Increased thermal stress of high-loaded engine parts.

The quality of motor fuel and the thermal regime of heat-loaded parts have a decisive influence on the processes of sediment formation and the efficiency of the internal combustion engine. The optimal thermal mode of the engine parts can be achieved only by structural changes of certain parts of the unit.

In this regard, promising operational ways to solve the problem of sedimentation are two main directions:

1) application of modern methods of analytical chemistry for the development of new anti-carbon and detergent additives for fuels and lubricants, taking into account the study of the mechanism of carbon formation, increasing the quality and efficiency of fuel and engine oil;

2) creation of a set of techniques to improve the operating conditions of vehicles for new drivers.
The study of new formulations of anti-carbon and detergent additives, as well as the study of their behavior in operation entail a detailed study of the composition and quality of the production of modern motor fuel.

According to the data of the MADI-CHEM testing laboratory, there has been a steady trend of deterioration in the quality of motor gasoline in recent years. So, in 2011 40% of samples of motor gasoline received for testing in the laboratory did not meet the regulatory and technical documentation [4]. The reasons for this process are related to the lack of system control over the quality of motor gasoline during its storage and sale.

Technical regulations for quality control of motor fuel reflects the Table 2. Control over the quality of fuel in the country at the moment is significantly reduced – only 4 parameters out of 11 previously tested are controlled [5].

**Table 2 Technical regulations for quality control of motor fuel**

| №  | Fuel parameter                                         | GOST 2084 (1979 y.) | GOST R 51105 (1999 y.) | TR (2014 y.) |
|----|-------------------------------------------------------|----------------------|------------------------|--------------|
| 1  | Octane number by research and motor methods           | normalizes           | normalizes             | doesn't normalize |
|    | Fractional composition                                |                      |                        |               |
| 2  | Saturated steam pressure                              | normalizes           | normalizes             | doesn't normalize |
| 3  | Actual resin content                                  | normalizes           | normalizes             | normalizes   |
| 4  | Induction period of gasoline                          | normalizes           | doesn't normalize       | doesn't normalize |
| 5  | Copper plate test                                     | normalizes           | normalizes             | doesn't normalize |
| 6  | Octane number by research and motor methods           | normalizes           | normalizes             | doesn't normalize |
|    | Fractional composition                                |                      |                        |               |
| 7  | Acidity                                               | normalizes           | doesn't normalize       | doesn't normalize |
| 8  | Mechanical impurities and water                       | normalizes           | doesn't normalize       | doesn't normalize |
| 9  | Density                                               | doesn't normalize    | normalizes             | doesn't normalize |
| 10 | Lead content                                          | normalizes           | normalizes             | prohibited    |
| 11 | Manganese content                                     | in the previously used gasoline wasn't presented | normalizes for low-octane gasoline | prohibited |
| 12 | Benzene content                                       | normalizes           | normalizes             | normalizes |
| 13 | Sulfur content                                        | normalizes           | normalizes             | normalizes |
| 14 | Mass fraction of oxygen                               | doesn't normalize    | doesn't normalize       | normalizes |

Currently, nickel-based fuel additives are being actively investigated, which in the course of laboratory and field tests have shown good results in the fight against carbon deposits. For example, studies of the effect of Ni(OOCR)2 on carbon formation in diesel engine showed that at the concentration of 9.25⋅10-4 % (1 mg Ni / kg of gasoline), the carbon deposition is reduced by 90-95 % (based on the candle formation is eliminated entirely), reduced the emissions of gaseous toxic substances (CO, CxHy and NO2). Another advantage of nickel-based additives is the reduction of specific fuel consumption by 4-10 %, which is confirmed by road tests on cars of different brands. Studies have been conducted on the effect of nickel additives on carbon formation in diesel engines. For bench testing during the first 9 h of engine operation, the soot was eliminated by 70-90 %. The introduction of 27.75 mg/kg additive into diesel fuel reduces the coking ability of 10% of the residue, the toxicity of emissions in all modes of operation of the ice and the specific fuel consumption.

To date, the use of additives based on nickel is one of the most promising areas in improving the quality of motor fuel. In the future, this will bring the quality of conventional fuel with additives to the quality of fuel with an environmental standard not lower than EURO-5.
Innovative interaction of such disciplines as analytical chemistry, computer programming and technical operation of cars allowed to advance in the study of the mechanism of formation of carbon deposits in the engine. At this stage of research, the analysis of the chemical composition of carbon deposits, studied the chemical compositions and the main characteristics of fuels and lubricants, operating conditions and temperature conditions of the units. On the basis of the obtained regularities, a multi-parametric model of the carbon formation rate equation is formed.

The diagnostic program is formed on the basis of the data obtained during the experiments on the variation of these parameters. The principle is this: you enter the source characteristics – properties of the fuel, the anticipated operating conditions, temperature conditions. The program on the basis of the built-in equations gives the mileage of the vehicle, in which it is not too late to take action – that is, to enter into the system the necessary anti-carbon or detergent additives. A preliminary view of the diagnostic program is shown in the Table 3.

Table 3 Type of diagnostic program to warn the car owner about the beginning of carbon formation in the engine

| Automobiles of GSM | Combination GSM № 1 | Combination GSM № 2 | Combination GSM № 3 | Combination GSM № 4 |
|--------------------|---------------------|---------------------|---------------------|---------------------|
| Base number mg KOH/g | 8,4 | 7,5 | 5,1 | 3,2 |
| Content of actual resins, mg per100 ml of fuel | 70 | 80 | 90 | 100 |
| Opacity(light attenuation coefficient), % | 11 | 14 | 19 | 25 |
| Amount of carbon, mg | 22 | 28 | 35 | 42 |
| Mileage, taking measures to eliminate deposits carbon, km | X | X | X | X |

The developed program will be proposed for inclusion in the maintenance regulations at service stations, as well as in large freight and passenger transport companies.

Working with such software will allow specialists in car maintenance and repair to prevent the formation of deposits in the engine, thereby preserving its life, laid down by the manufacturer, and in some cases to achieve its increase.

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