Investigation of changes in the properties of engine oil depending on the sulfur content in gasoline

A Khaziev and A Laushkin
Moscow Automobile and Road Construction State Technical University (MADI), 64, Leningradsky ave., Moscow, 125319, Russia
E-mail: madi-chim@mail.ru

Abstract. In exploitation of modern cars, there are cases of power unit failure due to a sharp deterioration in the properties of engine oil and loss of performance of the lubricant. The article describes the causes of failures of the engines of modern cars associated with the loss of the resource of oil in the engine and the processes occurring in the lubricant. They are increase of kinematic viscosity, decrease of Total Base Number, increase of the acid number, decrease of flash point, increase of water content, decrease of additives content, increase of wear products. Decrease in properties and motor oils lifetime was caused primarily by the deviation of the physicochemical parameters of applied motor gasoline beside regulatory petrol. The process and chemical reaction of sulfurous acid formation during engine operation are described. We have established a pattern of changes in physico-chemical parameters of motor oils in automotive gasoline sulfur compounds. Made quantification is produced by the combustion of 1 kg of gasoline sulfur acid. The low values of the loss of the alkaline number of motor oil, caused by the low sulfur content of the ecological class 5 gasoline, are a prerequisite for an increase periodicity of oil change in the operation of modern cars.

Keywords: car, engine, motor oil, operating conditions, sulfur content, sulfur acid, sulfur dioxide, additive package, base number, the neutralization of the acid.

1. Introduction
In exploitation of modern cars, there are cases of power unit failure due to a sharp deterioration in the properties of engine oil and loss of performance of the lubricant. These processes occur in the normal operation of cars, most often in the winter at low ambient temperatures and are not accompanied by extreme loads on the vehicle's engine.

Tests of samples of motor oils, taken from the lubrication system of failed power units and tested in the MADI-CHIM laboratory, allow us to conclude that there are significant deviations of oil properties:
- increase of kinematic viscosity;
- decrease of TBN;
- increase acid number;
- decrease of flash point;
- increase of water content;
- decrease of additives content;
- increase of wear products.
Result of experimental studies of the MADI-CHIM test laboratory is decrease properties and motor oils lifetime was caused primarily by the deviation of the physicochemical parameters of applied motor gasoline beside regulatory petrol [1]. A significant increase in the viscosity of the engine oil, accompanied by a loss of fluidity of the lubricant in the positive temperature range is the main cause of oil starvation and a reduction (or loss) of the engine life and occurs due to the ingress of motor gasoline into the oil [2].

These processes are accompanied by a decrease of lubricant viscosity, oxidation of oil additives, the evaporation of gasoline from the oil, the accumulation of low-temperature sludge on engine parts, which is formed in conditions of low temperatures of the power unit in the interaction of crankcase gases containing gasoline, water etc. and oil residues rapid response of additives, deterioration of the physico-chemical properties of the lubricant, indicated by TBN decreasing and the growth of TAN, increased density, viscosity and freezing point of the engine oil.

TBN decreasing is usually associated with the ingress of sulfuric acid produced at the combustion of sulfur compounds contained in gasoline. Oil produced in the Russian Federation is rich in sulfur compounds. For example, sulfur content for the Volga and Ural fields reaches 6 % [3].

Most often sulfur is contained in oil and oil products in compounds [4]:
- elemental sulfur (S);
- hydrogen sulphide (H₂S);
- mercaptans (R-SH);
- sulfides (R'-S-R);
- disulphides (R'-S-S-R);
- thiophene derivatives (C₄H₄S);
- high-molecular sulfur compounds;
- complex compounds containing also oxygen, nitrogen, etc.

The presence of sulfur affects the quality of commercial petroleum products and requires additional technological operations to remove it from motor gasolines.

So, the combustion of sulfur contained in motor gasoline generates sulfur dioxide (SO₂), which is very toxic, can cause human poisoning, affect the environment and lead to the formation of acid rain [5–8].

Technical regulations of the Customs Union TP TC 013/2011 “The requirements for automobile and aviation gasoline, diesel and marine gasoline, jet fuel and fuel oil” [9] establishes a gradual reduction of the sulfur content for motor gasoline. Since July 1, 2016 in the Russian Federation, there should be motor gasoline of ecological class K5 with sulfur concentration less than 10 ppm in circulation.

2. Formation of sulfuric acid during engine operation

In the operating of the internal combustion engine, its fuel cylinders are supplied with a certain ratio of automobile fuel and air. At the same time, a working mixture is formed which ignites from the spark of the spark plug and performs useful work during combustion.

Along with automobile gasoline, sulfur compounds are also burned in the engine.

The reaction of sulfur combustion is as follows:

\[ S + O_2 = SO_2, \]

where S is a sulfur;
O₂ is oxygen;
SO₂ – sulfur oxide (sulfur dioxide, sulfurous anhydride) [10].

Let us calculate the amount of sulfur dioxide formed by burning 1 kg of motor gasoline of ecological class 5.

We will describe the molar masses of the compounds participating in the combustion reaction:

\[ M_S = 32 \text{ g/mol}, \]
\[ M_{SO_2} = 32 + 16 \cdot 2 = 64 \text{ g/mol}. \]

Let's compose the proportion:

\[ M_S = 32 \text{ g/mol} - M_{SO_2} = 64 \text{ g/mol} \]
then $X = (10 \times 64)/32 = 20$ mg, that is, when 1 kg of motor gasoline of ecological class 5 burns, 20 mg of SO₂ is formed.

Sulfuric anhydride, when reacted with water, forms sulphurous acid:

$$\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3.$$ (2)

Taking into account the fact that both sulfuric anhydride and water compounds participate in the chemical reaction represented, water is formed in a large amount at burning gasoline [11], then we calculate the amount of acid formed as a result of combustion of gasoline by sulfur dioxide:

$$M_{\text{SO}_2} = 64 \text{ g/mol} \quad \Rightarrow \quad M_{\text{H}_2\text{SO}_3} = 1 \cdot 2 + 32 + 16 \cdot 3 = 82 \text{ g/mol}$$

$$m_{\text{SO}_2} = 20 \text{ mg} \quad \Rightarrow \quad m_{\text{H}_2\text{SO}_3} = Y \text{ mg}$$

$$Y = 20 \cdot 82/64 = 25.625 \text{ m.}$$

Thus, when burning 1 kg of automobile gasoline (ecological class 5), 25.625 mg of sulfuric acid is formed.

3. Neutralization of the acid formed during the combustion of motor gasoline

Sulfuric acid, formed during the combustion of gasoline, enters the engine oil and is neutralized with an additive package. Various additive packages will react with the acid in different ways. To assess the neutralizing ability of motor oils, the indicator "neutralization number" or otherwise "TBN" is used [12]. When it is determined in laboratory conditions, the oil is oxidized with hydrochloric acid HCl and the amount of acid spent on titration is recalculated into an equivalent alkali – KOH [13].

By neutralization reaction $\text{H}_2\text{SO}_3 + 2\text{KOH} = \text{K}_2\text{SO}_3 + 2\text{H}_2\text{O}$ we calculate the amount of equivalent alkali needed to neutralize 1 g of sulfuric acid:

$$M_{\text{H}_2\text{SO}_3} = 82 \text{ g/mol} \quad \Rightarrow \quad 2 \cdot M_{\text{KOH}} = 2 \cdot (39 + 16 + 1) = 112 \text{ g/mol}$$

$$m_{\text{H}_2\text{SO}_3} = 1 \text{ g} \quad \Rightarrow \quad m_{\text{KOH}} = Z \text{ g},$$

then to neutralize 1 g of conditionally taken $\text{H}_2\text{SO}_3$ it will be required:

$$Z = 1 \cdot 112/82 = 1.366 \text{ g of potassium hydroxide.}$$

4. Neutralization of sulfuric acid during engine operation

Not all acid, which is formed during the combustion of motor gasoline, causes its oxidation. Most of it is taken out with the exhausted gases into the engine neutralization system. According to the results of previous studies at maximum engine revolutions under load, with a gasoline consumption of 20 liters per hour, 16 m³ of exhaust gas are emitted during the combustion of one liter of gasoline. Breakdown of gases into the crankcase of the engine depends on many factors and is from 16 to 28 l/min [14]. As a percentage, this is 0.3...0.53 %. In the same ratio, sulfuric acid will enter the crankcase.

We calculate the amount of sulfuric acid that enters the engine oil when the engine is running. The consumption of gasoline with a modern car is 5l / 100 km. For the service interval, which is usually in the Russian Federation 15000 km, the car will consume 750 liters (=555 kg) of gasoline of ecological class 5. In this case, 555·25.625 = 14221.9 mg or about 14.2 g of sulfuric acid will be released. And the crankcase will get: $(14.2\cdot(0.3...0.53))/100 = (0.0426...0.0753)$ g of sulfuric acid.

To neutralize sulfuric acid, it will be necessary to do the following: $(0.0426 ... 0.0753) \cdot 1.366 = (0.058 ... 0.103)$ g KOH.

In the car engine's carter, volume is 3.5 liters (=3 kg) of motor oil, the total alkaline value is 8 mg KOH/1 g, then there will be 20.4 grams of equivalent alkali in the crankcase.

Under normal vehicle operating conditions (automobile gasoline corresponding to GOST 32513-2013 [1], engine oil recommended by the manufacturer, technically sound engine of the car, observance of service intervals of maintenance), only 0.3–0.5 % of the total alkaline number goes to neutralize the acid formed. Taking into account that mainly acidic detergents have the property of neutralizing acids, the resulting acid has practically no effect on the detergent and other properties of the motor oil [15].

5. Conclusions

The low values of the loss of the alkaline number of motor oil, caused by the low sulfur content of the ecological class 5 gasoline, are a prerequisite for an increase periodicity of oil change in the operation of modern cars.
Using of motor gasoline in cars that does not comply with the normative and technical document [1, 9] in terms of sulfur content accelerates the process of triggering additives and reduces the life of engine oil, which negatively affects engine reliability and its resource.

To ensure the declared services intervals for the lubricant, the operating conditions of the cars should be monitored: use automotive materials that meet the manufacturer's requirements automotive equipment, follow the instructions for maintenance intervals, monitor the level and condition of engine oil in the engine. In the event of a change in the operating conditions of the car, it is necessary to adjust the frequency of the engine oil change.

References

[1] GOST 32513-2013 Motor fuels. Gasoline unleaded. Technical conditions 2014 (Moscow: Standartinform)
[2] Khaziev A A, Laushkin A V and Gorina E B 2013 The reasons for changing the properties of engine oil Grusovik 6 15–6
[3] Ogorodnikov S K 1978 Petrochemist handbook (Leningrad: Chimia)
[4] Kalechits I V 1973 Cimistry of hydrogenation processes (Moscow: Chimia)
[5] Tian H 2014 Advances in the study on endogenous sulfur dioxide in the cardiovascular system Chin. Med. J. 127(21) 3803–7
[6] Liu D 2010 Sulfur dioxide: a novel gaseous signal in the regulation of cardiovascular functions Mini-Reviews in Med. Chem. 11 1039–45
[7] Kowalski B I, Abasin D D and Petrov O N 2016 Method of Control the Effect of Temperature for the Oxidation Process of Partially Synthetic Motor Oils Procedia Engineer. 150 480–5
[8] Izrael Yu A, Nazarov I M, Pressman A Ya et al 1989 Acid rain (Leningrad)
[9] TR CU 013/2011 2014 Technical regulations of the customs union “Requirements for automobile and aviation gasoline, diesel and marine fuel, jet fuel and fuel oil” (Moscow: Standartinform)
[10] Harlampidi H E 2000 Seraorganic compounds of oil, methods of purification and modification Sorosovsky Educational magazine 6(7) 42–6
[11] Laushkin A V and Khaziev A A 2012 Causes of watering of motor oil in exploitation Bull. of MADI 1(28) 63–7
[12] Vasileva L S 2004 Automobile Exploitation Materials (Moscow: Nauka-Press)
[13] GOST 11362-96 Petroleum products and lubricants. Neutralization number, Potentiometric titration method (Minsk)
[14] Kuznetsov E S et al 2001 Technical exploitation of automobiles: a textbook for universities ed. E S Kuznetsov 4rd ed Pererab. and additional (Moscow: Nauka)
[15] Laushkin A V and Khaziev A A 2014 Theoretical aspects of the change in the alkaline number of engine oil during the operation of the power plant Coll. Sci. papers on the mater. of the int. sci. and pract. Conf. “Modernization and scientific research in the transport complex” (Perm, PIDU) pp 140–4