Research of motor oil oxidation processes

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Abstract. The research results of oxidation, evaporation and changes in the coefficient of thermal-oxidative stability, which takes into account these processes by the increment rate of semi-synthetic motor oil Rosneft Maximum 10W-40 SL/CF in the temperature range from 170 to 150 °C, are presented. The increment rates of oxidation and evaporation processes from time and temperature of testing these processes are determined. The graphical and analytical model is proposed for predicting the indicators of thermo-oxidative stability at a wider temperature range for testing oils based on the results obtained at three temperatures.

1. Introduction
Thermo-oxidative stability is an important operational indicator of motor oils, as the products formed during oxidation affect the corrosion, anti-wear and viscosity properties. The mechanism of oxidation of engine oil is determined by the change of such indicators as the absorption coefficient of the light flux or optical density, volatility and the coefficient of thermo-oxidative stability, which takes into account the change in optical properties and volatility during thermostation, from the time and temperature of the test [1-6]. However, the effect of temperature on the rate of these processes and the concentration of the products of oxidation and evaporation is not well understood. The purpose of this research is to determine the effect of temperature and test time on the increment rate of oxidation and evaporation processes at individual time sections.

Rosneft Maximum 10W-40 SL/CF universal multigrade, semi-synthetic engine oil, viscosity grade 10W-40 (SAE), SL - group of operational properties of motor oils for gasoline engines, CF - for diesel engines were selected for the research.

During the test, the following controls and test devices were used: a thermostatic control device, a photometric device for direct photometry with a photometric layer thickness of 2 mm and electronic scales. The technical characteristics of the devices are given in [7].

2. Method and results of research
An oil sample weighing 100 ± 0.15 was poured into a glass beaker of the thermostating device and tested at temperatures of 170, 160, and 150 °C with stirring with a glass stirrer with a rotation speed of 300 rpm. After every 10 hours of testing, the sample of oxidized oil was weighed, the mass of evaporated oil G was determined, part of the sample (2 g) was taken for direct photometry and determination of optical density using the formula

\[ D = \log(300/P), \] (1)
where 300 is the photometer reading in the absence of oil in the cuvette, μA; P - photometer readings when the cell is filled with oxidized oil, μA.

From the experimental data on optical density and volatility at each test temperature, the coefficient of thermal oxidative stability \( P_{\text{tos}} \) is determined, which is equal to the sum of the optical density \( D \) and the coefficient of evaporation \( K_G \), determined by the ratio of the mass of evaporated oil during the test to the mass of the oil sample before the test.

Based on the data obtained, graphical dependences of the optical density, volatility, and the coefficient of thermo-oxidative stability on the time and temperature of the test were constructed, regression equations were determined by which the critical temperature of the test oil was calculated using a graph-analytical model.

The average increment rates of optical density, volatility, and thermal oxidative stability coefficient were determined by the difference of these indicators for every 10 hours of testing divided by this time. After that, graphical dependences of the obtained average values of the increment rate of optical density, volatility and the coefficient of thermo-oxidative stability on the time and temperature of the test were created, from which determined the temperature of the onset of oxidation, evaporation and temperature transformations.

Figure 1 shows the dependences of the optical density on the time and temperature of the test of the studied engine oil. The dependencies are described by a second-order polynomial. It is shown that with decreasing test temperature, the rates of oxidation processes decrease. So, the optical density value equal to \( D = 0.4 \) is achieved at temperatures: 170 °C in 36 hours; 160 °C - 77 hours; 150 °C - 170 hours, i.e. with decreasing test temperature from 170 to 150 °C, the oxidation time increases by 4.72 times.

![Figure 1](image)

Figure 1. Dependences of optical density on time and temperature of testing semi-synthetic motor oil Rosneft Maximum 10W-40 SL/CF:
1 - 170 °C, 2 - 160 °C, 3 - 150 °C.

Figure 2 shows dependences of volatility on time and temperature of the test engine oil. These dependences are described by a second-order polynomial. It was found that with decreasing test temperature, the rate of evaporation processes decreases. For example, six grams of oil evaporates at temperatures: 170 °C in 46 hours, 160 °C - 82 hours, 150 °C - 146 hours, i.e. with decreasing test temperature from 170 to 150 °C, the evaporation time increases by 3.17 times.

Critical temperature is an important operational indicator of engine oils, at which intense evaporation of oil occurs on the surfaces of heated parts. This temperature was determined during the evaporation of one gram of oil using a graph-analytical model [8], which provides for the calculation of the decimal logarithm of the time to reach evaporation of this value at each temperature (figure 3). This dependence is determined by the linear equation

\[
\lg t_G = 0.018(220 - T)
\]

where 0.018 is a coefficient characterizing the evaporation rate of the test temperature, g/h; 220 - critical temperature of the test oil, °C.
Figure 2. Dependences of volatility on time and temperature of testing semi-synthetic motor oil Rosneft Maximum 10W-40 SL/CF: 1 - 170 °C, 2 - 160 °C, 3 - 150 °C.

Figure 3. Dependences of the decimal logarithm of the time to reach an evaporation value of one gram on the temperature of the test of semi-synthetic Rosneft Maximum 10W-40 SL/CF motor oil: 1 - 170 °C, 2 - 160 °C, 3 - 150 °C.

At a critical temperature, one gram of the test oil evaporates in one hour of testing. Using formula (2), you can determine the decimal logarithm of time for any temperature, and by calculating the antilogarithm to determine the evaporation time of one gram of oil. For example, for a temperature of 180 °C, the decimal logarithm of the time to reach evaporation in one gram was 0.71, and the test time was 5.13 hours.

Figure 4 shows the dependences of the coefficient of thermo-oxidative stability on the time and temperature of testing the test oil, which are described by a second-order polynomial. It is shown that with decreasing test temperature the rate of change of the \( P_{\text{os}} \) coefficient decreases, i.e. in general, oxidation and evaporation rates decrease. So, the coefficient \( P_{\text{os}} = 0.45 \) is reached at temperatures: 170 °C in 36 hours, 160 °C in 78 hours, 150 °C in 166 hours, i.e. with a decrease in temperature from 170 to 150 °C, the time of transformations in the test oil increases by 4.61 times.

An important performance indicator for engine oils is critical temperature. This temperature was determined when the coefficient of thermo-oxidative stability was reached equal to \( P_{\text{os}} = 0.05 \) using the graph-analytical model [8], which provides for calculating the decimal logarithm of the time to reach this value at each test temperature and plotting the graphical dependence (figure 5). The dependence \( \log t_{P_{\text{os}}} = f(T) \) is described by the linear equation

\[
\log t_{P_{\text{os}}} = 0.022(219 - T)
\]

where 0.022 is a coefficient characterizing the rate of change \( \log t_{P_{\text{os}}} \) of the test temperature, 1/hour; 219 - critical temperature of the test oil, °C.

The intersection point of the dependence \( \log t_{P_{\text{os}}} = f(T) \) with the abscissa axis determines the critical temperature for the test oil, which amounted to 219 °C.
Figure 4. Dependences of the coefficient of thermal oxidative stability on the time and temperature of testing semi-synthetic Rosneft Maximum 10W-40 SL/CF motor oil: 1 - 170 °C, 2 - 160 °C, 3 - 150 °C.

Using equation (3), you can calculate the decimal logarithm of the time to reach the $P_{tos}$ coefficient value of 0.05 for any temperature. For example, for a test temperature of 180 °C, the decimal logarithm of time was 0.85, and the antilogarithm was 7.08 hours, i.e. during this test, the $P_{tos}$ coefficient will reach a value of 0.05. At a critical temperature of 219 °C for one hour of testing, the $P_{tos}$ coefficient will be 0.05.

Figure 5. The dependence of the decimal logarithm of the time to reach the coefficient of thermo-oxidative stability of a value equal to $P_{tos} = 0.05$ on the test temperature of the semi-synthetic Rosneft Maximum 10W-40 SL/CF motor oil.

Figure 6 shows the dependences of the increment rate of the thermo-oxidative stability coefficient on the time and temperature of the test of the studied engine oil. It was found that for the test temperature of 170 °C (curve 1), the dependence of $V_{tos}$ is described by a second-order polynomial. For test temperatures of 160 and 150 °C, the dependences of the rate of increase of the $P_{tos}$ coefficient have two sections of different rates of change in speed. The first sections are characterized by a high increment rate of the $P_{tos}$ coefficient, and with decreasing test temperature, the increment rate decreases.

According to the data of [1-6], the first sections are characterized by the period of formation of primary oxidation products with low energy intensity, and the second sections are characterized by the formation of secondary products of more energy-intensive. Moreover, the second sections are characterized by large fluctuations in the increment rate, which is explained by the processes of redistribution of thermal energy between the products of oxidation and evaporation. At the moment...
when the secondary products are formed “darker”, the increment rate of $V_{\text{Ptos}}$ increases, it increases with the evaporation of oil, but at the time of formation of the primary products of lighter, the increment rate decreases. Moreover, secondary products are formed when the concentration of primary oxidation products reaches a limit level. Such a mechanism of oxidation of lubricating oils explains the impossibility of a mathematical description of the joint manifestation of oxidation and evaporation processes.

![Figure 6](image1.png)

**Figure 6.** Dependences of the increment rate of the coefficient of thermal oxidative stability on time and temperature of testing semi-synthetic Rosneft Maximum 10W-40 SL/CF motor oil: 1 - 170 °C, 2 - 160 °C, 3 - 150 °C.

Figure 7 shows the dependences of the increment rate of the thermo-oxidative stability coefficient on temperature and test time of the studied engine oil. To determine the temperature of the beginning of the conversion processes, we use the dependence obtained after 10 hours of testing the test oil (curve 1), which is described by a second-order polynomial, and the regression equation has the form

$$V_{\text{Ptos}} = 3.7 \cdot 10^{-5} t^2 - 0.01107t + 0.83$$

(4)

![Figure 7](image2.png)

**Figure 7.** Dependences of the increment rate of the coefficient of thermo-oxidative stability on temperature and time of testing semi-synthetic Rosneft Maximum 10W-40 SL/CF motor oil: 1 - 10 hours, 2 - 20 hours, 3 - 30 hours.

Solving equation (4), the temperature of the beginning of the conversion processes in the test oil is determined at an increment rate of $V_{\text{Ptos}} = 0$, which amounted to 148.
3. Conclusions
The proposed research technique allows you to expand information on the temperature region of the studied oil by providing data on changes in optical density, volatility, coefficient of thermo-oxidative stability, temperatures of the onset of oxidation processes, evaporation and temperature transformations, critical temperature of these processes and rates of increase in optical density, volatility and temperature transformations from the time and temperature of the test.

Graphic-analytical model for predicting thermo-oxidative stability is proposed, which allows, using known data obtained at three temperatures, to determine indicators at other temperatures without conducting labor-intensive tests and calculate critical temperatures.

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