The results of the study of the mechanism of oxidation of motor oil

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Abstract. The results of the study of the oxidation and evaporation of a partially synthetic Total Quartz 10W-40 SL/CF synthetic engine oil in the temperature range from 160 to 190 °C are presented. The rates of increment of the processes of oxidation and evaporation from the time and temperature of the test, as well as the critical temperatures and temperatures of the onset of these processes, are determined. A grapho-analytical model for predicting thermal-oxidative stability indicators in a wider temperature range of test temperatures is proposed.

In scientific papers [1-6], the thermal-oxidative stability of lubricating oils was evaluated by the optical density, volatility and the coefficient of thermo-oxidative stability, taking into account the combined change in optical properties and volatility during thermostating. The oxidation mechanism was determined by the change in these indicators from the time and temperature of the test, which did not take into account the influence of the speed of the processes and temperature of the test on the concentration of oxidation products. Therefore, the goal of this research is to determine the effect of temperature and test time on the rate of oxidation and evaporation.

For the study, the universal multigrade partially synthetic Total Quartz engine oil was selected, which has a viscosity grade of 10W-40 and a group of performance properties SL for gasoline engines and CF for diesel engines.

When examining the oil, the following control and testing tools were used: a thermostatic control device, a photometric device for direct photometric measurements of oxidized oils and electronic scales. The technical characteristics of the devices are given in [7-8].

The research methodology was as follows. An oil sample weighing 100 ± 0.1 g was poured into a glass beaker of a thermostat and tested at temperatures of 190, 180, 170 and 160 °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 was determined, part of the sample was taken for direct photometry and determination of optical density [7].

Based on the data obtained, graphical dependences of the optical density, volatility, and coefficient of thermo-oxidative stability on the time and temperature of the test were constructed and regression equations were determined. The average increment rates of optical density, volatility and coefficient of thermo-oxidative stability were determined by the difference of these indicators for every 10 hours of the test, divided by this time. Next, graphical dependences of the increment rate on the time and
temperature of the test were constructed, by which the temperature of the onset of oxidation, evaporation, and temperature transformations was determined.

Figure 1 shows the dependence of the optical density on the time and temperature of the test oil. It is shown that with decreasing test temperature, the rate of oxidation processes decreases. So, the value of optical density equal to 0.2 is achieved at temperatures: 190 °C in 16 hours; 180 °C - 32 hours; 170 °C - 67 hours and 160 °C - 140 hours, i.e. when the temperature decreases from 190 °C to 160 °C, the oxidation time increases by 8.75 times.

An important operational indicator of the studied engine oil is the critical temperature at which abnormal phenomena occur during oxidation. This temperature was determined when the optical density reached a value of 0.05 by applying a graphical analytical model [7], which provides for the calculation of the decimal logarithm of the time to reach this value at each test temperature. Figure 2 shows the dependence of the decimal logarithm of the time when the optical density reaches 0.05 on the test temperature. This dependence is described by a linear equation:

\[ \lg t_0 = 0.02667(221.5 - T) , \]

where 0.02667 - is a coefficient characterizing the rate of change of the decimal logarithm of time from the test temperature, h⁻¹; 221.5 - critical temperature for the test oil, °C.

At a critical temperature in one hour of testing, the optical density reaches 0.05 and the decimal logarithm = 0. Using formula (1), you can determine the decimal logarithm for any temperature, and by calculating the antilogarithm, determine the time to reach 0.05. For example, at a temperature of 200 °C, the decimal logarithm of time is 0.57, and the antilogarithm of this value is time 3.72 hours.
The value of optical density $D = 0.05$ is recommended to be used constant for comparison of various oils, because a larger value will increase the critical temperature.

Figure 3 shows the dependences of the increment rate of oxidation processes on time and temperature of testing partially synthetic motor oil. It was found that with decreasing test temperature, the rate of oxidation processes decreases. So, after 30 hours of testing, the rate of oxidation processes was at temperatures: $190 \, ^\circ C - 0.0247 \, h^{-1}$; $180 \, ^\circ C - 0.0077 \, h^{-1}$; $170 \, ^\circ C - 0.0031 \, h^{-1}$; $160 \, ^\circ C - 0.0014 \, h^{-1}$, i.e. with decreasing test temperature from 190 to 160 °C, the increment of the oxidation processes decreased by 17.2 times. Moreover, for the test temperature of 190 °C (curve 1), the dependence is described by a linear equation:

$$v_D = 0.000766(t + 3),$$

where $0.000766$ - coefficient characterizing the acceleration of oxidation processes, $h^{-2}$; $t$ - is the test time, h.

For the test temperatures of 180 °C, 170 °C, and 160 °C (curves 2–4), the dependences have two sections with different intensities of changes in the optical density increment rate, which causes the dependencies to bend at a test time of 20 hours. Moreover, after the dependence is bent, the optical density increment rate decreases the more, the lower the test temperature. This can be explained by the presence of two types of products of different energy intensity, which is confirmed by studies [1], [2], [3], [4], [5], [6], according to which primary products are formed in the initial period, which become oxidized when oxidized. The formation of secondary products requires more thermal energy or oxidation time. Therefore, when secondary oxidation products are formed, there is a bending of the dependences of the rate of increments in optical density on the test time. However, this phenomenon appears at certain temperatures. So, for the partially synthetic Total Quartz 10W-40 SL/CF engine oil at a temperature of 190 °C, this phenomenon has not been established, because the processes of formation of primary and secondary oxidation products occur simultaneously. The dependences of the optical density increment rate on the test time for temperatures of 180-160 °C are piecewise linear with a bend at 20 hours of testing. The increments rate of optical density (figure 3 b) determines the temperature of the onset of oxidation processes and is of great importance when comparing various oils and their classification by API operational properties groups. In addition, it was found that at test temperatures of 160 and 170 °C, the optical density increment rates are almost the same.

![Figure 3. Dependences of the optical density increment rate on (a) time and temperature (b) temperature and test time of partially synthetic Total Quartz 10W-40 SL/CF motor oil: 1 - 190 °C; 2 - 180 °C; 3 - 170 °C; 4 - 160 °C; 1' - 10 hours; 2' - 20 hours; 3' - 30 hours; 4' - 40 h.](image)

Great value when evaluating in assessing the volatility of motor oils is the critical temperature, determined by the decimal logarithm of the time to reach the volatility of 2 grams of oil (figure 4). This dependence is described by a linear equation
\[ \lg t_0 = 0.0383(203.5 - T) , \]

where 0.0383 - is a coefficient characterizing the evaporation rate of the test oil, g/h; 203.5 - critical temperature of evaporation, °C.

**Figure 4.** The dependence of the decimal logarithm of the evaporation time of 2 g on the temperature of the test of the partially synthetic Total Quartz 10W-40 SL/CF engine oil.

Using equation (3), you can calculate the decimal logarithm of the evaporation time of 2 grams of oil at other temperatures, and by determining the antilogarithm, the test time. For example, at a temperature of 200 °C, the decimal logarithm of time was 0.16, and the antilogarithm of this value was a time equal to 1.44 hours, i.e. during this time, at a temperature of 200 °C, 2 g of oil will evaporate.

**Figure 5.** Dependences of the evaporation rate increment on (a) time and temperature (b) temperature and test time of partially synthetic Total Quartz 10W-40 SL/CF motor oil: 1 - 190 °C; 2 - 180 °C; 3 - 170 °C; 4 - 160 °C; 1' - 10 hours; 2' - 20 hours; 3' - 30 hours; 4' - 40 h.

With decreasing test temperature, the rate of increments in evaporation decreases. The dependence of the evaporation rate increment at test temperatures of 180 - 160 °C (curves 2 - 4) has two linear sections of different intensity of variation in the evaporation rate increment, which undergo bending dependences at a test time of 20 hours for all temperatures. Within 20 hours of the test, primary oxidation products are formed, requiring a smaller amount of thermal energy, so most of it is absorbed by the evaporation products, while the evaporation increment rate decreases. As the test time increases, primary products turn into secondary, more energy-intensive products, so the rates of optical density increment and evaporation decrease.
The dependences of the evaporation rate increment on the test time for temperatures of 180-160 °C are piecewise linear with a bend at 20 hours of testing. It was established (figure 5 b) that at test temperatures of 160 and 170 °C, the evaporation increment rate slightly depends on the test time, however, at temperatures of 180 and 190 °C and a test time of 40 hours (curve 4), the increment rates are almost the same, although the volatility is different (figure 4). These dependences are described by a second-order polynomial, for each of which a regression equation can be established, for example, for a test time of 10 hours it has the form:

\[
v_G = 3.125 \cdot 10^{-7} T^2 - 0.09713 T + 7.5863
\]

Solving equation (5), the temperature of the onset of evaporation processes is determined, which amounted to 155.4 °C.

Figure 6 shows the dependences of the coefficient of thermo-oxidative stability on the time and temperature of the test oil. The coefficient of thermo-oxidative stability takes into account the processes of oxidation and evaporation. Of great importance in determining the temperature range of the working capacity of engine oils is critical temperature, which is determined by the dependence of the decimal logarithm of the time to reach the coefficient of thermo-oxidative stability of a value equal to 0.05 on the test temperature, acquires an important value in determining the temperature range of operability of motor oils (figure 7). This dependence is described by a linear equation:

\[
\lg t_{K_{tos}} = 0.03(213.5 - T)
\]

where 0.03 - is a coefficient characterizing the rate of change of the decimal logarithm of time from the test temperature, h⁻¹; 213.5 - critical temperature for the test oil, °C.

Using equation (6), it is possible to determine the decimal logarithm of the time to reach the \(K_{tos}\) coefficient of 0.05 for any temperature, and by calculating the antilogarithm, determine the test time. So, for example, the decimal time logarithm for a temperature of 200 °C was 0.39, and the test time was 2.45 hours.
Figure 8a shows the dependences of the increment rate of the thermo-oxidative stability coefficient on the time and temperature of the test oil. The dependence is described by a linear equation for a test temperature of 190 °C (curve 1):

\[ \nu_{\text{Klos}} = 0.001(t + 3), \]  

(7)

where 0.001 - is a coefficient characterizing the acceleration of the processes of oxidation and evaporation, \( \text{h}^{-2} \); \( t \) - test time, \( \text{h} \)

For test temperatures less than 190 °C, the dependences are described by piecewise-linear dependencies with bending at 20 hours of testing.

The dependences shown in figure 8b are described by a second-order polynomial for which regression equations can be established, for example, for a test time of 10 h and temperatures from 160 to 190 °C, has the following form:

\[ \nu_{\text{Klos}} = 0.75 \times 10^{-6} T^2 - 0.0023T + 0.176, \]  

(8)

Solving equation (8), the temperature of the onset of conversion in the test oil is determined, which was 153 °C. It was found that in the initial period of the test (time 10 h, curve 1), the oxidation processes differ from the processes that occur during a longer time (curves 2 - 4). In addition, at test temperatures of 160 and 170 °C, the increment rates of the thermo-oxidative stability coefficient are almost the same. Their significant increase occurs at temperatures above 180 °C.

Conducted experimental studies found:

- The critical temperatures of the partially synthetic Total Quartz 10W-40 SL/CF engine oil were 221.5 °C during oxidation; evaporation - 203.5 °C; temperature transformations, taking into account the processes of oxidation and evaporation - 213.5 °C, which allows you to expand information about the temperature range of application of the studied oil.
- The temperature of the onset of oxidation, evaporation, and temperature transformations, determined by the rates of increase in optical density, volatility, and coefficient of thermo-oxidative stability from temperature during the test for 10 hours, was for: optical density - 160 °C; evaporation - 155.4 °C; coefficient of thermo-oxidative stability - 153 °C.
- The oxidation mechanism in the first hours of testing (\( t < 20 \) hours) is characterized by a sharp increase in the rate of increase in optical density and a sharp drop in the rate of increase in evaporation, as well as a sharp increase in the rate of increase in the coefficient of thermo-
oxidative stability regardless of the temperature of the test. However, there is a temperature at which the rates of optical density increment, evaporation, and temperature transformations change linearly from the beginning of temperature control. This is confirmed by the fact that in the process of temperature control two types of products of different energy intensity are formed, and primary products, less energy-intensive, are the basis for the formation of secondary products, more energy-intensive. From this moment, the dependences of the optical density increment rate, evaporation, and thermal oxidative stability coefficient are described by linear equations.

- The proposed graphoanalytic model for determining the indicators of thermo-oxidative stability during thermostating of lubricants allows us to determine their values at temperatures different from the accepted temperature range of the test.

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