Graphoanalytical method for determining the indicators of thermal-oxidative stability of lubricating oils

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Abstract. This article presents the results of a study of the effect of temperature tests on indicators of thermal oxidative stability: optical density, evaporation, coefficient of thermal oxidative stability. A grapho-analytical model is proposed for determining these parameters for a wide range of temperatures without temperature control of oils using experimental results obtained at two temperatures. A comparative evaluation of the experimental data with the calculated ones obtained using the grapho-analytical model has been carried out.

The antioxidant properties of motor oils determine their resistance to aging. The oxidation processes are most intense in thin layers, on surfaces heated to high temperatures. The speed and depth of oxidative processes are significantly influenced by products of incomplete combustion of fuel, particles of metals and contaminants of inorganic origin. To increase the service life of motor oils, it is necessary to know the speed of aging processes and their dependence on temperature, therefore, tests of oils for thermal-oxidative stability are usually carried out in a certain temperature range. To do this, use the methods described in [1-4].

The aim of the research is to substantiate the use of the graph-analytical method for determining the indicators of thermal-oxidative stability in a wide range of temperatures.

For the study selected all-season universal partially synthetic engine oil Mazda Original 10W-40 SL/CF. The following tools are selected as the means of testing and control: a device for temperature control of oils; a photometric device for direct photometry of oxidized oils with a photometric layer thickness of 2 mm and electronic scales. The technical characteristics of the devices are given in the monograph [5].

According to the research method, a sample of oil weighing 100 g was poured into a glass beaker for temperature control at temperatures of 160, 170 and 180 °C at atmospheric pressure with stirring with a glass stirrer with a rotational speed of 300 rpm. The duration of the test was determined by the time to reach the optical density, the oxidized oil value of 0.4 - 0.5. After every eight hours of testing, a glass beaker with a sample of oxidized oil was weighed, the mass of the evaporated oil was determined, a part of the sample (2 g) was taken for direct photometry and the optical density D of the oxidized oil was determined.
The considered method for determining the indicators of thermal-oxidative stability D, G and K<sub>kos</sub> makes it possible to determine these indicators at other temperatures using the graph-analytical model from the results of oil research at two temperatures [6-8].

In figure 1 shows the dependences of optical density on time and temperature of the test of a partially synthetic Mazda Original 10W-40 SL/CF engine oil, with curve 4 constructed for a temperature of 190 °C, calculated from experimental data obtained at temperatures of 180 and 170 °C.

**Figure 1.** The dependence of optical density on the time and temperature of the test partially synthetic engine oil Mazda Original 10W - 40 SL/CF: 1 - 180 °C; 2 - 170 °C; 3 - 160 °C; 4 - 190 °C.

The dependence D = (f, T) (figure 1) is used to determine the time to reach the established values of optical density (D = 0.05; 0.1; 0.2; 0.3) at temperatures of 180, 170 and 160 °C, calculating their decimal logarithms and building the dependencies of the decimal logarithms of the time to reach the set values of optical density from the test temperature (figure 2).

For example, for an optical density of D = 0.05, the time to reach this value corresponds to temperatures: 180 °C - 12 hours; 170 °C - 29.5 hours; 160 °C - 70 hours. The decimal logarithms of this time were for temperatures: 180 °C - 1.08; 170 °C - 1.47; 160 °C - 1.85. In figure 2 built dependence 1 on this data.

The dependences of the decimal logarithm of the time to reach the established values of optical density for D = 0.1 (curve 2), D = 0.2 (curve 3) and D = 0.3 (curve 4) are constructed in a similar way. These dependences are described by linear equations; therefore, it is possible to determine log<sub>t</sub>D for other temperatures, for example, 190 °C, which is 0.68 for D = 0.05 (curve 1). Antilog 0.68 is 4.8 hours. In addition, the dependence (curve 1) intersects the abscissa axis at a temperature of 207 °C, which means that at this temperature in 1 hour of testing the optical density of the oil will be 0.05.

**Figure 2.** Dependence of the decimal logarithm of the time to reach the optical density on the test temperature of a partially synthetic Mazda Original 10W-40 SL/CF motor oil: 1 - D = 0.05; 2 - D = 0.1; 3 - D = 0.2; 4 - D = 0.3.
Important indicators of the temperature conditions of the performance of motor oils are the temperatures of the onset of oxidation processes and the critical temperatures characterizing the temperature range of their performance. In figure 3 shows the dependence of optical density on the test temperature of the test oil after 32 hours of testing for each temperature. This dependence is described by a polynomial of the second degree, and the regression equation is

\[ D = (6.05 \times 10^{-4}) T^2 - 0.19365 T + 15.502 \] (1)

The derivative of equation 1 determines the rate of change of optical density from the test temperature, equating it to zero, you can determine the temperature of the oxidation process, which was 1 °C.

In figure 4 curve 4 is constructed using the graph-analytical model. These dependences are used to determine the time to reach the established values of evaporation (1; 2; 3; 4 and 5 g) of their logarithms and to build the dependencies of the decimal logarithms of the time to reach the set values of evaporation from the test temperature (figure 5). The dependences obtained allow us to determine the evaporation time of the set values for other temperatures. The dependence for evaporation in 1 gram per 1 h (curve 1) intersects the abscissa axis at 215 °C. The dependences \( G = (f, T) \) (figure 4) are used to determine the temperature of the onset of evaporation and the critical temperature of the working capacity of the oil under investigation according to this indicator.

\[ G = 0.002T^2 - 0.624 T + 49.525 \] (2)

The derivative of equation 2 determines the change in speed and evaporation from the test temperature, equating it to zero, you can determine the temperature of the beginning of the evaporation process, which was 156 °C.
Figure 5. Dependence of the decimal logarithm of the time to achieve evaporation on the temperature of testing partially Mazda Original 10W-40 SL/CF synthetic engine oil: 1 - G = 1 g; 2 - G = 2 g; 3 - G = 3 g; 4 - G = 4 g; 5 - G = 5 g.

Figure 6. Dependencies of time and temperature of testing of a partially synthetic Mazda Original 10W-40 SL/CF engine oil (test time 10 hours).

Presented in figure 7 dependencies take into account the processes of oxidation and evaporation and are used to determine the time to reach the set values of the coefficient $K_{tos}$ (0.05; 0.1; 0.2; 0.3 and 0.4) to determine its decimal logarithm and to build a graphical dependence of the decimal logarithm of time achieve the established values of the coefficient of thermo-oxidative stability as a function of the test temperature (figure 8). The presented dependences make it possible to determine the time of change in the $K_{tos}$ coefficient for other temperatures, for example, 190 °C (curve 4, figure 7).

Figure 7. Dependences of the coefficient of thermo-oxidative stability on the time and temperature of testing partially Mazda Original synthetic engine oil: 1 - 180 °C; 2 - 170 °C; 3 - 160 °C; 4 - 190 °C.

In figure 9 shows the dependence of the thermo-oxidative stability coefficient on the test temperature after 16 hours of testing, which allows to determine the temperature of the onset of conversion processes in the oil under study. The regressive equation for this relationship is:

$$K_{tos} = (2,7 \cdot 10^{-4}) T^2 - 0,0865 T + 6,937$$

(3)
Figure 8. Dependence of the decimal logarithm of the time to achieve the coefficient of thermo-oxidative stability on the test temperature of a partially synthetic Mazda Original engine oil: 1 - $K_{tos} = 0.05$; 2 - $K_{tos} = 0.1$; 3 - $K_{tos} = 0.2$; 4 - $K_{tos} = 0.3$; 5 - $K_{tos} = 0.4$.

The derivative of equation 3 determines the rate of change of the coefficient $K_{tos}$ from the test temperature, equating it to zero, you can determine the temperature of the start of conversion processes in oil, which was 1 °C.

Figure 9. Dependence of the coefficient of thermo-oxidative stability on the test temperature of a partially synthetic Mazda Original 10W-40SL/CF engine oil (test time 16 hours).

The reliability of the proposed graph-analytical model for determining the indicators of thermal-oxidative stability D, G and $K_{tos}$ was determined by comparing the experimental and calculated data obtained at a temperature of 160 °C are summarized in Table 1.

The relative error was calculated by the formula:

$$
\epsilon = \frac{Q_E - Q_C}{Q_E} \cdot 100 \%
$$

(4)

where $Q_E$ and $Q_C$ – respectively, the values of the indicators obtained experimentally and by calculation.

According to the data table, 1 relative error when calculating the optical density does not exceed 1%, evaporation is not more than 3.8% and the coefficient $K_{tos}$ is not more than 2%.

Table 1. Comparative evaluation of experimental and calculated data indicators of thermo-oxidative stability.

| Value of the indicator | Experiment | Calculation | Relative error,% |
|------------------------|------------|-------------|-----------------|
|                        | Time of achievement, hour | Time of achievement, hour |                   |
| Optical density        |            |             |                 |
| 0,05                   | 71         | 70,8        | 0,28            |
| 0,1                    | 99         | 100         | 1,0             |
| 0,2                    | 139        | 138         | 0,72            |
| 0,3                    | 166        | 165         | 0,6             |
| Evaporability          |            |             |                 |
| 1,0                    | 13         | 12,5        | 3,8             |
| 2,0                    | 38         | 369         | 2,6             |
Conducted experimental studies found:

1. The use of a grapho-analytical model for calculating indicators of thermal-oxidative stability allows reducing the laboriousness of the tests and expanding information about the temperature range of the performance of lubricating oils.

2. Proposed new indicators of thermal-oxidative stability, including the onset temperature of the processes of oxidation, evaporation and temperature transformations in the studied oils, as well as critical temperatures of these processes, allowing to determine the temperature range of their performance and compare different lubricating oils.

Reference

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