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Thermal-oxidative stability control of motor oils by thermal energy with cyclic temperature change

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Thermal-oxidative stability control of motor oils by thermal energy with cyclic temperature change

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Abstract. The results of the study of the thermo-oxidative stability of Castrol Magnatec R 10W-40 SL/CF partially synthetic engine oil with cyclic test temperature changes from 150 to 180 °C and from 180 to 150 °C taking into account the thermal energy absorbed by the products of oxidation and evaporation are presented. The graphical dependences of the decimal logarithm of the thermal energy absorbed by thermostatic products on the decimal logarithm of the test time are obtained, which are described by linear equations in the cycles of increasing and lowering the test temperature, which made it possible to determine the effect of time on the indicators of thermo-oxidative stability.

Thermal oxidative processes in lubricating oil are the cause of aging and are complex multi-stage reactions of hydrocarbons with oxygen. The oxidation process includes the following stages [1-4]. At the first stage, molecules are initiated by thermal energy, which leads to dissociation and breaking of chemical bonds with the formation of free radicals R, at the end of which there is an unpaired electron. The further stages are [1] the interaction of activated molecular fragments in the form of a chain reaction of autooxidation, while they intensively react with oxygen to form radicals of RO_2 peroxides, which react with the original hydrocarbon molecules, and form hydrocarbon radicals R and hydroxy acids, esters that increase acidity oils and optical density.

Autoxidation reactions are significantly slowed down by the presence of antioxidant additives in the oil, the role of which is to interrupt chain reactions and turn active radicals and hydroperoxides into stable products. The mathematical description of the process of oil oxidation due to the variety of chemical structure of additives and differences in the nature of their interaction with the surface of parts and oxidation products is associated with significant difficulties. In this regard, various experimental methods are used to evaluate the thermo-oxidative stability of lubricants.

The purpose of this research is to determine the effect of test time on the thermal oxidative stability of motor oils during cyclic temperature changes, taking into account the thermal energy absorbed by thermostatic products.

The properties of the lubricant are determined not by products that are determined in volume by various physical methods, but by the state of the excited substance during temperature control. Since the amount of accumulated energy in the lubricant is finite, a stationary or periodic discharge of excess energy is necessary [5], the volume of which is equivalent to the concentration of oxidation and evaporation products.

Partly synthetic, multigrade, universal Castrol Magnatec R 10W-40 SL/CF engine oil was selected for the study. As a means of testing control were used: a device for thermostating of oils, a photometric device and electronic scales.

The research methodology was as follows. A 100 g oil sample was poured into a glass beaker of the thermostating device and thermostatically controlled at temperatures of 150, 160, 170 and 180 °C for 6 hours at each temperature with stirring with a glass stirrer with a rotation speed of 300 rpm. After every 6 hours of testing, the sample of oxidized oil was weighed, the mass of the evaporated oil and the coefficient of evaporation K_G [6]. A part of the sample of oxidized oil (2 g) was taken for direct photometry at a thickness of the photometric layer of 2 mm and determination of optical density D [6-8]. According to the data of optical density and evaporation, the coefficient of thermo-oxidative stability K_{tos} [6-8]. After the measurement, the oil from the cuvette of the photometer was poured into a glass cup of a thermostating device, which was weighed and thermostated at a temperature of 10 °C higher. The oil test ended at a temperature of 180 °C and was called a cycle of temperature increase from 150 to 180 °C. A new oil sample weighing 100 g was tested using the same technology, but in a cycle of lowering the test temperature from 180 to 150 °C.

Using similar technologies, the test oil was tested in cycles of increasing and lowering the test temperature, but the test duration was 10 hours. From the data obtained, the amount of thermal energy Q absorbed by the test oil was determined

$$Q = T \cdot t, \tag{1}$$

where - test temperature, °C; - test time, h

The amount of absorbed thermal energy Q_D by oxidation products was determined by the formula

$$Q_D = T \cdot t \cdot D\,, \tag{2}$$

and absorbed by evaporation products Q_G,

$$Q_G = T \cdot t \cdot G\,, \tag{3}$$

The total thermal energy absorbed by the products of oxidation and evaporation $Q_{\Pi_{\mathrm{TOC}}}$, determined by the formula

$$Q_{Ktos} = T \cdot t \cdot K_{tos} \tag{4}$$

According to the data obtained, the decimal logarithms of the thermal energy absorbed by the products of oxidation $\lg Q_D$, evaporation $\lg Q_G$ and the total thermal energy absorbed by the products of oxidation and evaporation were calculated $\lg Q_{K\mathrm{tos}}$. Graphical dependences of the decimal logarithms of thermal energy absorbed by the products of oxidation, evaporation and total thermal energy on the decimal logarithm of the test time $\lg t$ in the cycles of increasing and lowering the test temperature were determined, which determined the effect of time on the indicators of thermo-oxidative stability.

In figures 1*a* and 1*b* show the dependences of the decimal logarithm of the thermal energy absorbed by the oxidation products in the cycles of increasing and lowering the test temperature on the decimal logarithm of time (six and ten hours).

These dependencies are described by linear equations for a test time of 6 hours: temperature increase cycle (direct 1)

$$\lg Q_D = 4.2 \cdot (\lg t - 0.9) \tag{5}$$

temperature lowering cycle (direct 2)

$$\lg Q_D = 1.74 \cdot (\lg t - 0.24) \tag{6}$$

where 4.2, 1.74 - coefficients characterizing the rate of change of the decimal logarithm of thermal energy absorbed by the products of oxidation in cycles of increasing and decreasing temperature from the decimal logarithm of the test time, h^{-1}; 0.9 and 0.24 - coefficients that determine the start time of the change in the decimal logarithm of thermal energy in cycles of increasing and decreasing the temperature of the test.

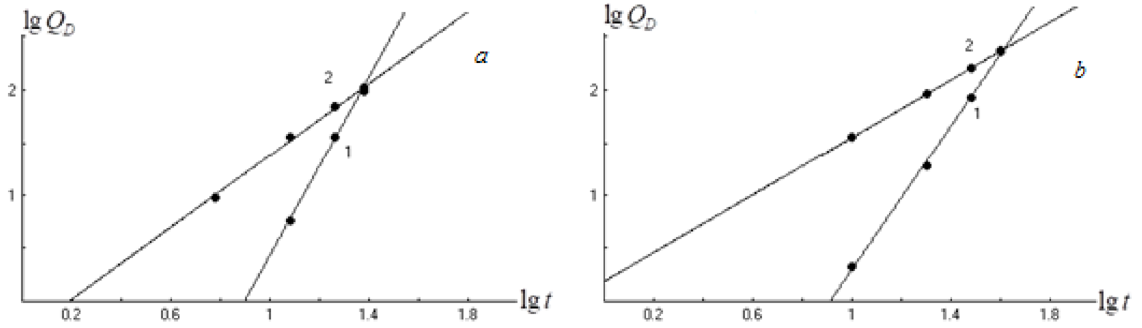

Figure 1. Dependences of the decimal logarithm of the thermal energy absorbed by the oxidation products on the decimal logarithm of the test time of Castrol Magnatec R 10W-40 SL/CF partially synthetic engine oil: (*a* - test time of 6 hours, *b* - also oil test time of 10 hours): 1 - temperature increase cycle from 150 to 180 °C; 2 - temperature lowering cycle from 180 to 150 °C.

Test time 10 hours, temperature increase cycle (direct 1)

$$\lg Q_D = 3.37 \cdot (\lg t - 0.9) \tag{7}$$

temperature lowering cycle (direct 2)

$$\lg Q_D = 1.41 \cdot (\lg t + 0.1) \tag{8}$$

where 3.37, 1.41 - coefficients characterizing the rate of change of the decimal logarithm of the thermal energy absorbed by the oxidation products in cycles of increasing and decreasing temperature from the decimal logarithm of the test time, h^{-1}; 0.9 - coefficient determining the start time of the change in the decimal logarithm of thermal energy in the cycle of increasing the test temperature, h; 0.1 - coefficient determining the value of the decimal logarithm of the thermal energy absorbed by the oxidation products in the decimal logarithm of time, h; lg$t$ = 0, or t = 1, h.

According to the data obtained, in the cycle of increasing the test temperature, the rate of change of the decimal logarithm of thermal energy is higher when testing the test oil for 6 hours at each temperature. Moreover, it should be noted that the start time of the change in the decimal logarithm of thermal energy lgQ_D does not depend on the test time and is lg$t$ = 0.9 or 7.94, h.

In the cycle of lowering the test temperature, the rate of change of the decimal logarithm of thermal energy from the test time is also higher when testing oils for 6 hours and is respectively 1.74 versus 1.41 for 10-hour tests. In addition, in the test temperature reduction cycle, the decimal logarithm of the thermal energy lgQ_D absorbed by the oxidation products during the 6-hour test is lg$t$ = 0.24 or 1.74, h.

If we equate equations 8 and 9, as well as 10 and 11, then we can determine the coordinates of the point of intersection of the dependences of the decimal logarithm of the thermal energy absorbed by the oxidation products in cycles of increasing and decreasing the test temperature of the test oil.

For a test time of 6 hours:

$$4.2 \cdot (\lg t - 0.9) = 1.74 \cdot (\lg t - 0.24) \tag{9}$$

Having solved this equality, we define the decimal logarithm of the time of the intersection of dependencies, which amounted to lg1.36 or 23.32, h.

For a test time of 10 hours:

$$3.37 \cdot (\lg t - 0.9) = 1.41 \cdot \lg t + 0.1 \tag{10}$$

Having solved this equality, we define the decimal logarithm of the time of the intersection of dependencies, which amounted to lg1.6 or 40.29, h.

According to the data obtained, when testing the test oil at each temperature for 10 hours, the intersection time of the lines in the cycles of increasing and lowering the test temperature increases from 23.32 at 6 hours to 40.29 hours, i.e., 1.73 times.

If we substitute the values of the decimal logarithm of time in formulas 8 and 10, then we can determine the coordinates of the point of intersection of the lines by the decimal logarithm of the thermal energy absorbed by the oxidation products for a test time of 6 hours at each temperature:

$$\lg Q_D = 4.2(\lg t1.36 - 0.9) = 1.96 \text{ or } 93.03 \tag{11}$$

For a test time of 10 hours at each temperature:

$$\lg Q_D = 3.37(\lg t1.6 - 0.9) = 2.37 \text{ or } 238.78 \tag{12}$$

According to the data obtained, the amount of thermal energy absorbed by the oxidation products during 10-hour tests of the studied oil at each temperature and the intersection of the straight lines in cycles of temperature increase and decrease is 2.5 times greater.

In figure 2 shows the dependences of the decimal logarithm of the thermal energy absorbed by the evaporation products on the decimal logarithm of the test time at 6 and 10 hours in cycles of increasing and decreasing temperature. It was found that these dependences are described by linear equations for a test time of 6 hours at each temperature.

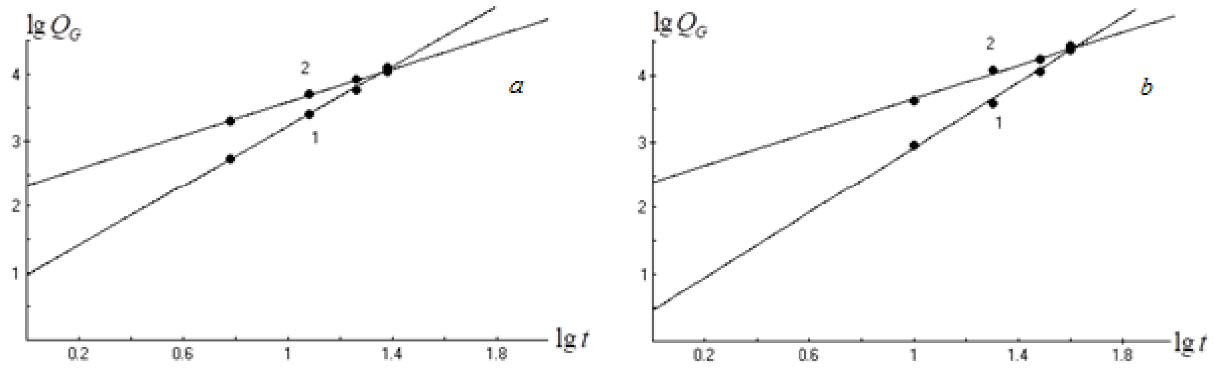

Figure 2. Dependences of the decimal logarithm of the thermal energy absorbed by the evaporation products on the decimal logarithm of time when testing Castrol Magnatec R 10W-40 SL/CF partially synthetic engine oil: (*a* - test time of 6 hours, *b* - also oil test time of 10 hours): 1 - temperature increase cycle from 150 to 180 °C; 2 - temperature lowering cycle from 180 to 150 °C.

For a cycle of temperature increase, (direct 1)

$$\lg Q_G = 2.24 \lg t + 1 \tag{13}$$

temperature lowering cycle, (direct 2)

$$\lg Q_G = 1.34 \lg t + 2.25 \tag{14}$$

Test time 10 hours, temperature increase cycle (direct 1)

$$\lg Q_G = 2.5 \lg t + 0.43 \tag{15}$$

temperature lowering cycle (direct 2)

$$\lg Q_G = 1.31 \lg t + 2.27 \quad (16)$$

According to the data obtained, in the test temperature increase cycle, the decimal logarithm of thermal energy is higher when testing the test oil for 10 hours at each temperature of 2.5063 versus 2.24 at 6 hours of testing. In the cycle of lowering the test temperature, the decimal logarithm of thermal energy $\lg Q_G$ is higher at a 6-hour test of 1.34 versus 1.31 in a 10-hour test. Moreover, the values of the decimal logarithm of thermal energy $\lg Q_G$ are less than (0.43) in 10 hour tests (1 in 6 hours) in cycles of temperature increase $\lg t = 0$. However, in the cycles of decreasing temperature, these values are almost identical 2.25 and 2.27. If we equate equations 13 and 14, as well as 15 and 16, then we can determine the coordinates of the intersection point of the decimal logarithm of the thermal energy absorbed by the products of evaporation in the increase and lowering the test temperature. So for a test time of 6 hours:

$$2.24 \lg t + 1 = 1.34 \lg t + 2.25 \quad (17)$$

Having solved equality (17), we define the decimal logarithm of the time of the intersection of dependencies, which amounted lg1.38 to 24 hours

For a test time of 10 hours:

$$2.5 \lg t + 0.43 = 1.31 \lg t + 2.27 \quad (18)$$

Having solved equality (18), we define the decimal logarithm of the time of the intersection of dependencies, which amounted lg1.54 to 34.78 hours.

According to the data obtained, when testing the test oil with a duration of 10 hours for each temperature, the intersection time of the lines in the cycles of increasing and lowering the test temperature increases from 24 at 6 hours to 34.78 hours, i.e., 1.45 times. If we substitute the values of the decimal logarithm of time into formulas 13 and 15, then we can determine the coordinates of the point of intersection of the lines by the decimal logarithm of the thermal energy absorbed by the evaporation products. So, for a test time of 6 hours:

$$\lg Q_G = 2.24 gt 1.38 + 1 = 4.1 \text{ or } 12589.25 \quad (19)$$

For a test time of 10 hours at each temperature:

$$\lg Q_G = 2.5 \lg t 1.54 + 0.42 = 4.29 \text{ or } 19633.6 \quad (20)$$

According to the data obtained, the amount of thermal energy absorbed by the evaporation products during 10-hour tests of the test oil in cycles of temperature increase and decrease is 1.56 times greater.

In figure 3 shows the dependences of the decimal logarithm of the total thermal energy absorbed by the products of oxidation and evaporation on the decimal logarithm of the test time (6 and 10 hours) in cycles of increasing and decreasing temperature.

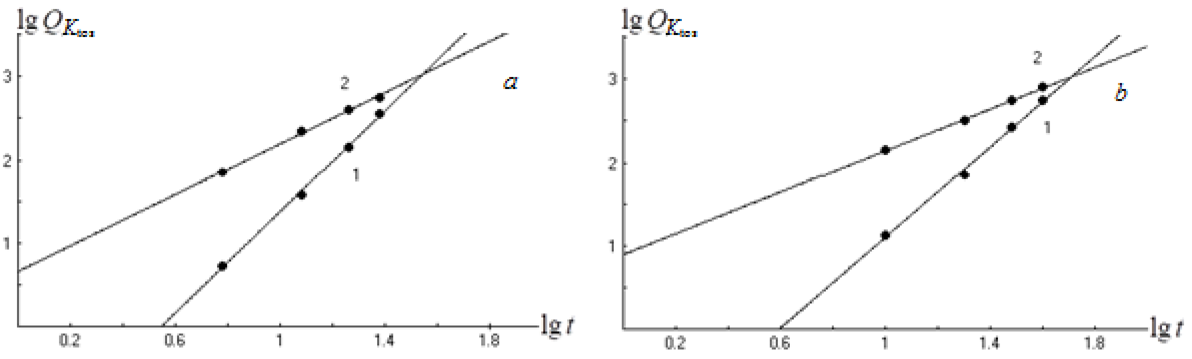

Figure 3. Dependences of the decimal logarithm of the total thermal energy absorbed by the products of oxidation and evaporation from the decimal logarithm of the test time of Castrol Magnatec R 10W-40 SL/CF engine oil: *(a)* - test time of 6 hours, *(b)* - also oil test time of 10 hours: 1 - temperature increase cycle from 150 to 180 °C; 2 - temperature lowering cycle from 180 to 150 °C.

These dependences are described by linear equations. For a test time of 6 hours: temperature increase cycle, (direct 1)

$$\lg Q_{Ktos} = 3.12 \cdot (\lg t - 0.56) \tag{21}$$

temperature lowering cycle, (direct 2)

$$\lg Q_{Ktos} = 1.55 \cdot \lg t + 0.6 \tag{22}$$

Test time 10 hours: temperature increase cycle, (direct 1)

$$\lg Q_{Ktos} = 2.75 \cdot (\lg t - 0.6) \tag{23}$$

temperature lowering cycle, (direct 2)

$$\lg Q_{Ktos} = 1.28 \cdot \lg t + 0.85 \tag{24}$$

According to the data obtained, in cycles of increasing and decreasing the test temperature, the rate of the decimal logarithm of the total thermal energy is higher when testing the test oil for 6 hours at each temperature. Moreover, the value of the decimal logarithm of the total thermal energy $\lg t = 0$ is less at 6 hours of testing in cycles of lowering the test temperature. If we equate equations 24 and 25, as well as 26 and 27, then you can determine the coordinates of the point of intersection of the dependences of the decimal logarithm of the total thermal energy in the cycles of increasing and decreasing the test temperature. So for a test time of 6 hours:

$$3.12 \cdot (\lg t - 0.56) = 1.55 \lg t + 0.6 \tag{25}$$

Having solved equality (25), we define the decimal logarithm of the time of the intersection of dependencies, which amounted lg1.5 to or 31.7 hours

For a test time of 10 hours:

$$2.75 \cdot (\lg t - 0.6) = 1.28 \lg t + 0.85 \tag{26}$$

Having solved equality (26), we define the decimal logarithm of the time of the intersection of dependencies, which amounted lg1.7 to 50.35 hours. According to the data obtained, when testing the test oil for 10 hours at each temperature, the intersection time of the straight lines in the cycles of increasing and lowering the test temperature increases from 31.7 at 6 hours to 50.35 at 10 hours of test, i.e., at 1.59 times.

If we substitute the values of the decimal logarithm of time into formulas 24 and 26, then we can determine the coordinates of the point of intersection of the lines by the decimal logarithm of the total heat energy absorbed by the products of oxidation and evaporation.

For a test time of 6 hours:

$$\lg Q_{Ktos} = 3.1 \cdot (1.5 - 0.56) = 2.91 \text{ or } 866.96 \text{ h °C} \tag{27}$$

For a test time of 10 hours:

$$Q_{Ktos} = 2.7 \cdot (1.7 - 0.6) = 3.03 \text{ or } 1072.75 \text{ h °C} \tag{28}$$

According to the data, the amount of total thermal energy absorbed by the products of oxidation and evaporation in the cycles of increasing and lowering the test temperature is 1.24 times greater.

Conducted experimental studies found:

To compare different oils for the same purpose in terms of thermal oxidative stability, taking into account the thermal energy absorbed by thermostatic products, it is necessary to take the test time at each temperature in the increase and decrease cycles the same.

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