Substantiation of optical criterions of thermal-oxidative stability of lubricating oil

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Abstract. Research results of criteria of thermal-oxidative stability determined by different combinations of coefficient of absorption of light quantity and optical density with coefficient of evaporation and kinematic viscosity of oxygenated oil are presented. It is shown that the amount of optical density and the coefficient of evaporation divided by coefficient of relative viscosity are the most effective criteria of thermal-oxidative stability of lubricating oils described by second order polynomial with a high correlation coefficient.

1. Introduction
To assess the oxidation of lubricating oils in laboratory conditions and in production, a photometric method has been widely used, which makes it possible to evaluate the effect of temperature conditions on the rate of these processes [1-4].

The following factors are proposed as a criterion for thermal oxidation resistance: the absorption coefficient of the light flux, optical density, evaporation, kinematic viscosity characterizing the amount of absorbed thermal energy by the lubricating oil during the test, however, the effectiveness of each of them is not justified from the point of view of the mathematical description.

The purpose of the present studies is to determine the most effective criterion, taking into account both optical properties, volatility and kinematic viscosity.

2. Materials and methods
The studies were carried out using the example of Rosneft M-10G2K mineral motor oil.

The following testing and control instruments were used for the study: a device for thermostating oils, a photometric device for direct photometry of oxidized oils, a small volume viscosimeter, and electronic scales.

The temperature and the speed of the mixer were maintained automatically during the test. Mineral oil was tested at three temperatures of 180, 170 and 160 °C. After every 8 hours of testing, the beaker with the oxidized oil sample was weighed, the mass of the evaporated oil was determined, a sample was taken for direct photometry at a photometric layer thickness of 2 mm, and the absorption coefficient of the light flux KP and the optical density D.

\[ D = \varphi - \varphi_0, \] (1)
\[ D = \log \frac{\varphi}{\varphi_0}, \quad (2) \]

where \( \varphi \) and \( \varphi_0 \) are, respectively, the light flux was incident on the oil layer in the cuvette and passed through the oxidized oil layer.

A portion of the oxidized oil sample was taken to determine the kinematic viscosity at 100 °C. Selected samples were poured out back into a glass beaker that was then re-weighed. The oil test continued according to the described technology until the absorption coefficient of the light flux achieved \( 0.7 \ldots 0.8 \) units.

According to the obtained experimental data, the following were determined:
- the coefficient of evaporability \( K_G \)
  \[ K_G = \frac{m}{M}, \quad (3) \]
  where \( m \) and \( M \) are, respectively, the mass of the evaporated oil tested for 8 hours and the mass of the remaining oil in the beaker, g;
- coefficient of relative viscosity \( K_\mu \)
  \[ K_\mu = \frac{\mu_o}{\mu_T}, \quad (4) \]
  where \( \mu_o \) and \( \mu_T \) are the kinematic viscosity of oxidized and market grade oils, respectively.

As an indicator of thermal oxidation stability \( \Pi \), the authors studied four variants of combinations of the absorption coefficient of the light flux and the optical density with evaporation coefficients and relative viscosity:
- I variant
  \[ K_{\Pi} = f(t), \quad D = f(t); \quad (5) \]
- II variant
  \[ \Pi_1 = f(K_{\Pi} + K_G), \quad \Pi_2 = f(D + K_G); \quad (6) \]
- III variant
  \[ \Pi_3 = f(K_{\Pi} + K_G) \cdot K_\mu, \quad \Pi_5 = f(D + K_G) \cdot K_\mu; \quad (7) \]
- IV variant
  \[ \Pi_5 = f(K_{\Pi} + K_G) / K_\mu, \quad \Pi_2 = f(D + K_G) / K_\mu. \quad (8) \]

The first variant characterizes the change of the oxidation products concentration during oil thermostating during the test time.

In the second variant, the index of thermal-oxidation stability \( \Pi_1 \) characterizes the amount of absorbed thermal energy at which oxidation and evaporation products are formed [5].

In the third variant, the thermal-oxidation resistance index \( \Pi_2 \) characterizes the effect of the kinematic viscosity at the index \( \Pi_1 \) [6].

In the fourth variant, the index \( \Pi_3 \) determines the ratio between the products of oxidation, evaporation, and kinematic viscosity.

3. The study of oil processes during its testing

Figure 1a shows the dependence of the light flux absorption coefficient (curves 1, 2, 3) and optical density (curves 1', 2', 3') on the time and temperature of the thermostating. It is established that at evaluating the processes of oxidation by optical density, their values are less than the estimations by the absorption of light flux coefficient, irrespective of the temperature of thermostating [7].

The use of the thermal-oxidation stability index (see formula 6) [8], which does not take into account the kinematic viscosity, is the same as in the evaluation of oxidation processes using the coeffi-
cient of the light flux absorption and the optical density (Fig. 1b). However, the values of the index $\Pi_1$ increase due to the coefficient of evaporation $K_G$.

The using of the thermal-oxidative index stability that includes an additional kinematic viscosity [9], expressed by the relative viscosity coefficient $K_\mu$, using formulas 7 and 8, shows that the same trend of the relation between the coefficient of the light flux absorption and the optical density (Figures 2a, 2b), however the viscosity is affected on its value.

To justify the most effective thermal-oxidation stability index according to formulas 5-8 (variants I-IV), the index of the potential resource is introduced, index is determined by the time the index becomes equal to 0.6, taking into account the coefficient of the light flux absorption and the optical density of the oxidized oil, and establish the differences between them.

![Figure 1](image)

**Figure 1.** Dependences of the coefficient of the light flux absorption (curves 1, 2, 3) and the optical density (curves 1', 2', 3') (a) and the index of thermal-oxidizing stability (b) on the time and temperature of the test of mineral motor oil Rosneft M-10G: 1, 1' - 180 °C; 2, 2' - 170 °C; 3, 3' - 160 °C.

The dependences of the potential resource $P$ on the test temperature are shown in figure 3a, taking into account the coefficient of the light flux absorption, and in figure 3b are shown the dependence of the potential resource on the test temperature, taking into account the optical density for variants I-IV.

The analysis of the obtained results showed that irrespectively of the options for determining the thermocline resistance index, the dependence of the potential resource $P$ on the test temperature is described by a polynomial of the second order.
Figure 2. Dependencies of the thermal-oxidation stability index multiplied by the relative viscosity (a) and divided by the relative viscosity (b) on the time and temperature of the test of mineral motor oil Rosneft M-10G2K: 1, 1' - 180 °C; 2, 2' - 170 °C; 3, 3' - 160 °C (curves 1, 2, 3 are taking into account the coefficient of the light flux absorption and the coefficient of evaporation, and curves 1', 2', 3' are taking into account the optical density of the oil during oxidation).

Regression equations of the potential resource dependencies on the oxidation temperature and the coefficient of the light flux absorption for the variants (Fig. 3a):

I variant
\[ D = 0.19\bar{D}^2 - 69.5\bar{D} + 6384 \] (9)
II variant
\[ D = 0.145\bar{D}^2 - 53.35\bar{D} + 4931 \] (10)
III variant
\[ D = 0.13\bar{D}^2 - 47.7\bar{D} + 4397 \] (11)
IV variant
\[ D = 0.185\bar{D}^2 - 67.95\bar{D} + 6267 \] (12)
The correlation coefficient for all equations is equal to one.

Regression equations of dependencies of potential resource on oxidation temperature and optical density for variants (Fig. 3b):

I variant
\[ D = 0.25\bar{D}^2 - 91.5\bar{D} + 8408 \] (13)
II variant
\[ D = 0.205\bar{D}^2 - 75.35\bar{D} + 6957 \] (14)
III variant
\[ D = 0.195\bar{D}^2 - 71.45\bar{D} + 6577 \] (15)
IV variant
\[ D = 0.24\bar{D}^2 - 88\bar{D} + 8104 \] (16)
The correlation coefficient for all equations is equal to one.
Analysis of the dependencies (Figures 3a and b) shows that using formulas 9-12 and 13-16 it is possible to determine the potential resource for a temperature below 160 °C. In addition, when using the variants of formulas 5-8, taking into account the absorption coefficients of the light flux or optical density and the relative viscosity coefficients, practically identical values of the potential resource were shown [10]. In general, to compare the potential resource in the oxidation of motor oils, any of the formulas 5-8 variants I-IV can be used. As a criterion of thermal-oxidation stability, it is recommended to use the indexes $\Pi_2$ and $\Pi_3$, taking into account optical properties, evaporation and relative kinematic viscosity, which are reflecting the processes that are occurring in the lubricating oil during its oxidation.

4. Conclusions
On the basis of the conducted studies it was established that during oxidation of mineral and partially synthetic motor oils at the beginning of oxidation processes, the anti-wear properties of oils are decreasing, and for synthetic oil in the initial period, properties increase and then decrease. The proposed empirical criterion of anti-wear properties of oxidized oils, which characterizes the conditional concentration of oxidation products in the nominal area of the frictional contact, makes it possible to compare different lubricants and improves the classification system by groups of performance properties.
The proposed coefficient of electrical conductivity of the boundary layer separating the friction surfaces makes it possible to determine the boundaries of formation of adsorption layers and their transition to chemisorption layers.

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