Theoretical study of motor oil chromatogram in express diagnostics using the drop test

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Abstract. The quality and compliance with the requirements of motor oils used in operation is one of the key factors determining durability and reliability of the internal combustion engine (ICE). The operating conditions of motor oils in ICE have changed significantly with an improvement in the design of the engine, the increase in power, the increase in pressure in cylinders and the change in the torque of the crankshaft. The requirements to motor oils during operation are constantly increasing, the specified terms of oil drain interval are increased. The composition of motor oils has also changed, and the technologists are adjusting their finished oil compositions to increasing requirements. Thus, it is necessary to constantly monitor the state of oil during ICE operation, the use of traditional express methods of oil quality verification is not always possible for new brands. The study considers the theoretical justification for the application of the drop test for the brands of strongly alkaline oils – Vanellus C6 Global “BP” (U) 15W-40 and Neste Tyrbo LXE.

1. Introduction

The reliability of ICE operation depends on the quality of lubricants and technical fluids used in operation. In the process of operation, motor oils are subjected to various thermal and mechanical loads caused by the change of the chemical formula, they are contaminated with mechanical impurities, water, used fuel, and at certain values of the rejection parameters they lose their properties. As noted in the works of Korneev S.V., if you use motor oils that meet the requirements of the technical regulations, then the probability of ICE failure increases and the costs of maintenance and repair are reduced [1]. Therefore, it is necessary to regularly monitor the condition of motor oils during their operation [2]. The analysis of express diagnostic methods of oils revealed the drop test, which is considered the most suitable and which makes it possible to quite easily and with due accuracy determine some key parameters of motor oils during ICE operation [3]. This method was effectively used to diagnose the parameters of medium-alkaline and low-alkaline oils. When trying to use the method for the analysis of strongly alkaline oils, the chromatogram on filter paper was not distributed into characteristic zones, the diameter and ratio of which determined the oil shelf life factors for further operation. The chromatogram showed a uniform spot of a drop distributed evenly over the filter with the manifestation of its structure.

It is necessary to study whether the formation of concentric zones is possible when analyzing strongly alkaline oils by the drop test. The study theoretically proves the process of oil drop spreading through the filter, the mechanism of formation of concentric zones of the chromatogram by the ratio, which determines oil operability during engine operation.
2. Materials and methods
The theoretical study was based on a physical model that represents the cross section of an oil drop, with two zones of surface layer and the volume of the drop being distinguished. Free energy equations of the system were used to determine the pressure forces on the drop surface. The interaction of impurity particles in the physical model of strongly alkaline oils – Vanellus C6 Global “BP” (U) 15W-40 and Neste Tyrbo LXE – is considered.

3. Results and discussion
A sample of operating motor oil (a drop taken from the engine) is a complex heterogeneous system, including oil, a package of unfinished additives, chemical elements of operated additives (oil destruction) and impurities that are formed during engine operation. These impurities have different shape, structure, size, density, and chemical composition. When the drop is applied to the filter, the impurities in the spreading drop move along certain patterns. Oil spreads over the surface of the filter and fills its pores, the largest mechanical impurities are primarily deposited on the filter, they almost do not move in the flowing oil. Soluble additive elements are very small in size, so they move over the volume of the spreading oil drop. Depending on the wear of the engine parts, the period of oil use and deviation from the ICE adjustments recommended by the manufacturer, the content of additive oil and impurities in the drop will differ. The mechanisms of indicated chromatogram zones lead to different diameters of zones and their ratio to each other. Due to the fact that mechanical impurities have large size and large density, which is higher than the density of the oil and additive, they precipitate in the center of the chromatogram and form the core zone – 1 (Figure 1). The additive forms the diffusion zone – 2, and the oil filling filter pores forms the pure oil zone – 3 [4]. The zones of the chromatogram are defined by the radius \( r \), the radius value will depend on the number of contamination or additive components in the controlled oil, as well as the density of the impurity or additive \( \rho_k \), density of the oil itself \( \rho_o \), its initial viscosity \( \nu_k \), filter porosity \( \varphi \), sample volume \( V_k \), sample heating temperature \( t \), and the oil spreading rate on the filter surface \( W \).

![Figure 1. Diagram of distribution of concentric zones on the filter surface depending on the density difference of oil components: 1 – core zone, 2 – additive diffusion zone, 3 – pure oil zone.](image)

The analytical description of the concentric zones model caused by the influence of a large number of factors is a difficult task. The dissociation of additive components in the analysis of strongly alkaline motor oils complicates the formation of concentric zones. The dissociation process leads to electrostatic forces that affect the nature of the force interaction of particles in the analyzed sample [5]. To assess the contamination of oils with various impurities, it is necessary to create a mathematical model, to describe the distribution of additive components and impurities, which makes it possible to calculate the number of components based on their content in the zones of the chromatogram.

To solve this problem, the motion of components in concentric zones is described by the system of equations. The physical model shown in Figure 2 was used in the mathematical description of the chromatogram. The model is represented by the cross section of the oil drop flowing along the filter and contains two zones:

1 – surface layer 1 with a thickness of 10-9 m, which is the boundary of the oil sample. The
particles of oil and impurities in the surface layer interact with oil and with air molecules.

2 – internal volume of the oil sample, which contains engine oil itself and components of additive, mechanical impurities, as well as the elements of additive destruction – oil destruction.

The precipitation of impurities in the oil surface layer and inside the sample was considered separately due to different force interactions.

Figure 2. Physical model of oil sample spreading on filter surface:
1 – surface layer; 2 – oil drop; 3 – impurity particles; 4 – filter; 5 – filter pores.

The equilibrium is disturbed in the surface (boundary) layer between ambient air and the sample (oil drop) due to different density of air and oil. This leads to the transfer of part of the movement across the contact boundary and the transfer is ensured through the interaction from the air and an oil drop. At the same time, the hypothesis of Batchelor J. states that in the surface layer the total free energy depends not only on the volume of the drop, but also on the contact area of different media and is determined by the formula [6]:

\[ d \Pi = -p_1 \, dv_1 - p_2 \, dv_2 + 2 \sigma F \] (1)

where \( F \) – total surface area of the sample; \( \sigma \) – surface tension; \( p_1, p_2 \) – air and oil pressure; \( P \) – free energy.

At equilibrium position of the system the free energy differential \( dP = 0 \) 

\[ \sigma \, dF = p_1 \, dv_1 + p_2 \, dv_2 . \] (2)

When solving the equation (2), the pressure change at different points of the boundary layer can be determined by the following equation:

\[ p_1 - p_2 = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \] (3)

In this equation, the radii of curvature \( r_1 \) and \( r_2 \) are determined at the intersection of the sample surface by two orthogonal planes along the axis \( z \). If the surface shape is symmetrical, spherical \( r_1 = r_2 \), then the equation (3) is as follows:

\[ p_1 - p_2 = \frac{2 \sigma}{r} \] (4)

\( r \) – radius of sphere surface change.

If the drop surface becomes flat, the radii \( r_1 \) and \( r_2 \rightarrow \infty \), then the surface tension is determined by the formula:

\[ \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) = 0 \] (5)

The ratio of air-oil pressure shall be defined by the following expressions:

\[ p_1 - p_2 = 0 \] and \( p_1 = p_2 \).

Assuming that the oil density is constant and the pressure change depends only on the height of the drop surface layer, the pressure difference depending on (4) is determined by the following equation:

\[ p_1 - p_2 = \rho g z , \] which can be converted as follows:
\[ \rho g z = \frac{2 \sigma}{r} \]  
(6)

where \( g \) – gravity of the sample; \( \rho \) – density of oil drop; \( z \) – height of the top layer of the oil drop.

When considering the equation (6), it is possible to determine the effect of gravity and surface tension on the change of the shape of the surface shape of the two media – air-oil, and the surface tension and gravity of the oil drop have the same effect. From the expression \( \rho g z \sigma \rho z \), it can be concluded that the effect of surface tension on the change of the surface shape of the spreading oil sample can be neglected. Next, the order of values in equation (6) was determined under normal air conditions \( \rho = 1.225 \frac{kg}{m^3}; \ r = 10^{-3} m; \ \sigma = 0.0294 \frac{N}{m} \). In this case \( \rho g z = 101325 Pa \) and \( \frac{2\sigma}{r} = 2 \times 0.0294 \times 10^{-3} = 58.8 Pa \), and it is clear from the expression and the values of coefficients that when considering the physical model of chromatogram, the value of the tension force cannot be neglected.

With a slight increase of surface d\( F \), the free phase energy can be determined from the following relation:

\[ dF = \sigma dF + \sum \mu_i dN_i, \]  
(7)

where \( \mu_i \) – chemical potential of \( i \) components; \( F \) – sample surface; \( N_i \) – number of particles of \( i \) components.

The expression \( \sum \mu_i N_i \) of the right part of the equation (7) can be presented in the following constraint:

\[ \sum \mu_i dN_i = d \sum \mu_i N_i - \sum d \mu_i N_i \]  
(8)

As a result of substitution in the equation (7) the dependence (8), the equality was obtained:

\[ d(F - d \sum \mu_i N_i) = \sigma dF - \sum d \mu_i N_i \]  
(9)

Part of this equation (left) is a complete differential, so it can be presented by the following expression:

\[ \frac{d \sigma}{d \mu_i} = \frac{dN_i}{dF} = K_i \]  
(10)

here \( K_i = \left[ \frac{dN_i}{d \mu_i} \right] \) – excess density of components in the surface unit;

The chemical potential of \( i \) components can be represented by a linear dependence on the concentration of these components according to the following formula:

\[ \mu_i = \mu_0 + aT \ln C_i, \]  
(11)

wherein the expression is as follows:

\[ d \mu_i = aT \frac{dC_i}{C_i}. \]  
(11)

converting the dependency (11) we get:

\[ K_i = - \frac{C_i}{dT} \left( \frac{d \sigma}{dC_i} \right), \]  
(12)

where \( a \) – constant value. If we consider an ideal gas, then \( a = K \), where \( K \) – constant value given by Boltzmann.
After analyzing the relation (12), it can be concluded that the ratio \( \frac{dC_i}{dT} \) will be positive at positive \( dT \), and at \( \frac{dC_i}{dT} < 0 \) there is an excess of component concentrations, thus \( K_i > 0 \). As the concentration increases, the components that are in the surface layer reduce the surface tension, and hence are called coagulators.

At positive \( dT \) and if the ratio \( \frac{dC_i}{dT} \) is also positive, then at \( \frac{dC_i}{d\sigma} > 0 \) there is a decrease in the concentration of components, i.e. when \( K_i < 0 \) these components will be displaced from the upper layer due to the fact that they will determine the increase of the free energy of the system.

Thus, the upper (boundary) layer of the sample contains particles that reduce the surface tension, these include usually dark soot and additive destruction products in oil. The density of these impurities will be proportional to the density of the motor oil, and therefore their distribution through the filter under the influence of gravity can be described by the Stokes law. The molecules in strongly alkaline oils dissociate into positive and negative ions, and hence the energy of particle interaction in the boundary layer will change and look as follows:

\[
V(r) = V_e + V_v, \tag{13}
\]

where \( V_v \) – Van der Waals gravity force of various impurities; \( V_e \) – electrical energy of impurities repulsion.

This expression (13) describes the total interaction energy of spherical colloidal impurities of a certain radius \( r_0 \) as a function of the distance between the center of the impurity.

Assuming that the distribution of impurities in the surface layer will take place by diffusion, the stationary diffusion flow of impurities to the conventional stationary particle with radius \( r_0 \) can be written by the following relation:

\[
I = 4\pi r^2 \left( D \frac{dC}{dr} + \frac{C}{\mu} \frac{dV}{dr} (r) \right), \tag{14}
\]

where \( D \) – diffusion coefficient of impurities; \( C \) – concentration of impurities at a distance \( r \) from the conditional fixed particle; \( \mu \) – oil resistance depending on viscosity, \( \mu \) and \( D \) are connected among themselves by the Einstein relation.

\[
\mu D = kT, \tag{15}
\]

where the coefficient \( k = 1,380662 \cdot 10^{-23} \frac{J}{K} \) – constant proposed by Boltzmann; \( T \) – absolute temperature.

Deryagin B.V. established that the process of particle approximation in case of a constant potential of the filter surface \( \Psi \) is the electric repulsion energy \( V_e \), which is defined by the formula [7]:

\[
V_e = \frac{\varepsilon \Psi r_o}{2} \ln(1 + e^{-\tau a}), \tag{16}
\]

where \( \varepsilon \) – constant of the dielectric energy medium, \( \tau = \beta r_0, \beta \) – Debye inverse radius.

The Van der Wals gravity force was calculated by the formula:

\[
V_a = -\frac{A}{12} \left( \frac{1}{u^2 / 4 + u} + \frac{1}{u^2 / 4 + u + 1} + 2 \ln \left( \frac{u^2 / 4 + u}{u^2 / 4 + u + 1} \right) \right), \tag{17}
\]

where \( A \) – constant proposed by Gamaker; \( u \) – potential of impurities interaction, \( u = r - 2r_0^2 \).

Thus, the functions defined by equations (16) and (17) take the following graphical form (Figure 3):
The presence of the Um component when determining the total interaction energy of particles leads to their repulsion when the oil drop flows through the filter, as well as when the oil is operating in the engine. This explains the mechanism of action of dispersing additives contained in the oil having the alkaline medium [8]. In order to diagnose strongly alkaline oils using the drop test, it is necessary to reduce the influence of the Um value by adding acid component to the oil or to the surface of the filter, which will neutralize the alkaline number. To use this technique with a certain sensitivity, there is a need to calculate the correction coefficients. The use of this technique during ICE operation will increase reliability and durability of units and assemblies, reduce maintenance costs [9, 10].

4. Conclusion

Scientific research was carried out using the equipment of the collective use center of Omsk SAU Additive Technologies and Material Processing. The theoretical study of the physical model of the oil drop flowing over the surface of the filter paper made it possible to conclude the following:

1. In strongly alkaline oils the process of distributing mechanical impurities takes place with the same patterns as in low-alkaline and medium-alkaline oils.

2. The formation of concentric zones of the chromatogram determining the suitability of the motor oil for further operation is associated with the presence of the electrostatic repulsion potential of particles caused by the alkaline medium in the oil sample. This prevents the enlargement of impurities and their coagulation with the development of concentric zones of the chromatogram.

3. It is necessary to reduce the repulsion potential of impurity particles to develop a chromatogram pattern with concentric zones. This can be done by applying a dielectric layer to the filter surface to neutralize the alkaline medium.

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