## DETERMINATION OF DISPERSING-STABILIZING PROPERTIES OF MOTOR OILS AND THEIR DIRTINESS IN PERFORMANCE CONDITIONS

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Under the motor oil performance conditions, it is very difficult to determine the dispersing-stabilizing properties and the degree of dirtiness of the oil. These characteristics, however, have a great effect on the performance life of the oil until its replacement and the reliability of tractor and automobile operation. Relationships of changes in dispersing-stabilizing properties of motor oils with the content of additives and performance time in the engine were obtained by theoretical analysis and practical studies. The results of the studies on improvement of paper chromatographic method to determine the dirtiness of the oils under their performance conditions are presented.

Key words: motor oil, performance, dispersing-stabilizing properties, degree of dirtiness, paper chromatography, diffusion, oil spot, control.

Some of the important properties of motor oils that determine their performance life are dispersing-stabilizing properties and degree of dirtiness [1].

The dispersing-stabilizing properties of motor oil stem from the action of additives that inhibit enlargement of dirt particles, their deposition, and formation of deposits in engine channels and parts [2]. Determination of dispersing-stabilizing properties and dirtiness of motor oils by laboratory methods entail use

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of special equipment and a sufficiently high professional level of the executor, which is not always possible in conditions of operation of the machine [3].

A drawback of proximate methods of quality control of oils is relatively high error in determination of values of the parameters. At the same time, if the real performance conditions and the purpose of the proximate methods are considered as a warning of hazardous wear and tear of machine parts and prediction of performance life of oils, under the performance conditions these methods are more preferable to laboratory methods [4].

The simplest method of determination of dispersing-stabilizing properties (DSP) of the working motor oil in the engine is the proximate method where the chromatogram of a drop sample of the oil being analyzed is compared with reference spots [5]. But this method requires a more detailed theoretical and practical analysis and investigations for its improvement.

DSP is a tentative quantity and measured in points. The DSP of an oil has an inversely proportional dependence of the additive content in the motor oil and varies from 0 to 9. Let us assume that an additive has such properties when, at  $n_{dp} = 1$ , DSP = 0 point and upon complete consumption of the additive, i.e. at  $n_{dp} = 0$ , DSP = 9 points (Fig. 1).

Taking account of the linear relationship of the DSP with the quantity of the dispersing additive and the adopted assumptions associated with the change of the parameter, we have:

$$DSP = k \left( 1 - n_{dp} \right) + DSP_0 \tag{1}$$

where DSP,  $DSP_0$  – current and initial content of DSP, points;  $n_{dp}$ ,  $n_{dp_0}$  – current and initial quantity of dispersing additive referred to the entire volume of the oil in the lubricating system, wt. %; k – a coefficient dependent on quality characteristics of the additive (for the adopted assumption, k = 9) [6].

The change in dispersing-stabilizing properties of the motor oil as a function of dirtiness is shown in Fig. 2. To determine the nature of the function that indicates the consumption of the dispersing-stabilizing additive for retention of the dirt in the working motor oil during its performing time t, let us combine DSP(n) and DSP(x) correlation graphs and get  $n_{dn}(x)$  [6].

The dispersing additive is consumed continuously for retention of the dirt in finely dispersed state. The relationship of *DSP* with the dirtiness degree is described by equation of the type

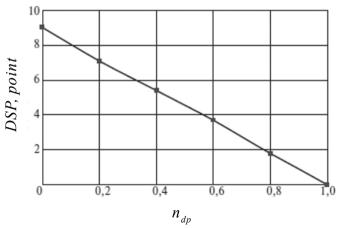


Fig. 1. Dependence of change in DSP of motor oil on additive content.

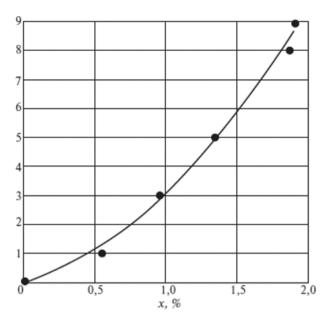


Fig. 2. Dependence of change of DSP in oil on performing time and dirt content.

$$n_{dp} = n_{dp_0} - a_x \cdot x^2 \tag{2}$$

where  $a_x$  – equation coefficient dependent on quality characteristics of the additive; x – quantity of dirt [6, 7].

At  $x = x_{\infty}$  and  $n_{dp} = 0$  we get

$$a_x \cdot x_{\infty}^2 = n_{dp_0} \tag{3}$$

Considering that in equation (2), at  $t \to \infty$  and  $x \to x_{\infty} = a/n_{y}$ , we get

$$a_x = \frac{n_{dp_0}}{a^2} \cdot n_y^2 \tag{4}$$

Putting equation (4) in (3) we get

$$n_{da} = n_{da_0} \left[ 1 - \left( \frac{\upsilon_y \cdot x}{a} \right)^2 \right] \tag{5}$$

where  $v_1$  - rate of oil loss, kg/h; a - rate of dirt accumulation, kg/h.

Let us put equation (5) in (1):

$$DSC = DSC_0 + k \left\{ 1 - n_{da} \left[ 1 - \left( \frac{\upsilon_y \cdot x}{a} \right)^2 \right] \right\}$$
 (6)

Equation (6) expresses dependence of DSP on residual dispersing-stabilizing additive content that decreases due to oil loss and rate of dirt accumulation.

To predict the performance life of the oil based on assessment of the dispersing-stabilizing properties, let us put equation (2) into (6) and express the time as:

$$t = -\frac{q_o}{v_y} \ln \left[ 1 - \sqrt{1 - \left(\frac{DSC - DSC_0}{k}\right)} \right]$$
 (7)

where  $q_{\circ}$  – quantity of oil in the crankcase, kg.

Equation (7) characterizes the pattern of change of dispersing-stabilizing properties of the working motor oil as a function of such parameters as the content of dispersing-stabilizing additive, its quality characteristics and the quantity of dirt and the rate of their accumulation.

The conducted investigations confirmed the validity of the chosen concept and the directions of the investigations on development and refinement of methods of control of dirtiness degree and dispersing-stabilizing properties.

Refinement of the methods of evaluation of the above-noted properties of the working motor oil consisted in investigation and improvement of the paper chromatographic method. This was realized by using regular filter paper with average pore size of  $3.5-10~\mu m$  or denser with pore size of  $1-1.25~\mu m$ . Permeation of an applied oil drop through the paper is a complex process that leads to separation of the oil into its constituent fractions due to adsorption processes. In proximate method of estimation of oil dirtiness, the chromatograms obtained on the paper are visually compared with the scale of standard drop test samples of oil spots. To improve this method of proximate estimation of oil dirtiness, the time needed for getting reliable chromatograms is determined in the first place. As stated above, spreading of an oil drop through the filter paper is a complex physicochemical process, for a description of which it is essential to take account of the laws of capillary absorption and diffusional repartition of the oil medium through the porous sorbent, i.e., through the filter paper [6].

When an oil drop is applied to the filter paper, its liquid phase initially lies on the surface. The time of its existence depends on the rate of absorption of the oil in the material, which, in turn, depends on the action of the capillary forces.

Capillary forces are generated because of pressure difference  $(P_c)$  above the plane and curved phase interfaces:

$$P_k = \frac{2\sigma}{r}\cos\theta\tag{8}$$

where  $\sigma$ - surface tension of the liquid, N/m; r- radius of the capillary, m;  $\theta$ - wetting boundary angle, rad [6]. Motion of a liquid in cylindrical capillaries, which simulates oil absorption in porous materials, obeys the *Poiseuille's law* that describes the speed of motion:

$$\frac{dl}{d\tau} = \frac{P_x \cdot r^2}{8\eta l} \tag{9}$$

where  $P_x$  – moving pressure, Pa;  $\eta$  – liquid viscosity, N/m<sup>2</sup>; l – length of filled section of the capillary, m.

In equation (9), the moving pressure  $P_x$  is the difference between the capillary pressure and the hydrostatic pressure of the absorbing oil column. For horizontal open capillaries (filter paper lies horizontally), the hydrostatic pressure is nil, so, with due regard for (8), equation (9) can be written as:

$$\frac{dl}{d\tau} = \frac{\sigma \cos \theta r}{4nl} \tag{10}$$

For the same oil and porous material (filter paper),  $\sigma$ ,  $\eta$ , and  $\theta$  are constant quantities, so:

$$\frac{dl}{d\tau} = K \frac{r}{l} \tag{11}$$

where K – proportionality constant.

As evident from equation (11), the absorption rate is proportional to the capillary radius and inversely proportional to the length of the filled section. Thus, oil absorption into the filter paper will occur primarily in the large pores. In this case, the speed of motion slows down after filling of the pores of the filter paper right above the oil spot (into the interior) and horizontal repartition of the oil begins. Alongside the described capillary absorption laws, there will also occur diffusional repartitioning processes.

As the oil permeates into the filter paper, diffusion occurs in all directions. However, the basic relationships describing mass transfer caused by concentration difference can be obtained by studying the transfer in one direction (unidimensional linear diffusion).

To calculate the sizes of the oil diffusion spots in the filter paper, use can be made of the approximate equation  $x = (\pi Dt)^{1/2}$  for oil advance through a filter paper layer. Note that in most cases the diffusion coefficient value for clean oils lies in the range  $(1-10)\cdot 10^{-13}$  m<sup>2</sup>/sec at normal temperature.

As the working oil containing "aging" products spreads (is absorbed) across the filter paper, there occurs simultaneous movement of the oil and the "aging" products, but with different diffusion coefficients. Deposition of the "aging" products in the filter paper pores depends on their size: first the large and then the finer particles deposit in the large pores, and last the pores are filled with more mobile oil base, which leads to formation of chromatographic images of the working oil drop on the filter paper. The chromatograms should be analyzed at 20°C 90 min after application of the drop, particularly for determining the dispersing capacity of the oil.

The diffusion processes can be accelerated by heating the oil spot from below using heating elements. In this case, the time for visual evaluation of the chromatogram of the oil spot shortens several folds.

In the course of proximate determination of the degree of dirtiness and *DSP* it was found that the obtained black and white images of the spots do not permit unambiguous interpretation of the change of *DSP* of the oil and determination of the nature of the dirt.

Analysis of numerous samples showed that spots do not allow a sufficiently precise determination of the percentage content of mechanical impurities and provide only a possibility of approximate determination of their quantity. No less important is also the point that the spot color establishes to a large degree the facts of dirtying of the oil with fuel combustion products, accumulation of resins of asphaltenes, carbenes, carboids, and additive functioning products, but not mechanical impurities getting into the oil from the surrounding medium.

Evaluating the method of DSP determination from the chromatogram of an oil spot, it is very difficult to unambiguously characterize the functioning of cleansing-dispersing additives because presence of fuel in the oil distorts the image of the spot and reduces objectivity of the information.

To evaluate the known mechanisms, we analyzed more than 200 chromatograms of spots of oils used in engines of tractors of various types and various technical states and operated under various load conditions. Visual examination, however, does not allow sufficiently accurate evaluation of the pattern of change of dirtiness without additional information about the content of mechanical impurities, insoluble deposit, and fuel (flash point), and additives (base number). In keeping with this, an analysis was made, with due regard for these results of the investigations of the oil of the same tests made in laboratory conditions following standard methods.

Analysis of the oil spots showed that after 50 h of running (after loading or replacement), regardless of the technical state and type of the machine, conditions of its use under condition of high quality of the used oil, all chromatograms have approximately the same structure, color, and shape.

Examining and analyzing the chromatograms of the spots for machines of various types and taking account of their technical state after 100 h of running it can be concluded that in almost all cases the oil is suitable for use. However, in machines with defective fuel systems, the flash point is close to the defective value even though the spot barely shows this discrepancy. After 200 h of running (in some cases, when the machines worked long due to high loads), note must be taken of the change in color of the spot, i.e., the degree of saturation of dark color at the core. Such an oil must be replaced and such parameters as flash point and base number must be controlled additionally after 50 h of running.

The flash point and base number of 70% of the investigated samples changed after about 300 h of running. The shape of the spot and the color of the core changed.

Machines operating for 400 h without change of the oil had chromatographic parameters close to hazardous. At the same time, it must not be claimed unequivocally that parameters of all oils reached the defective values. Detailed analysis showed that motor oils used in new, technically fit machines performing uncomplicated operations had enough margin of functional properties.

To increase the information content of the chromatographic analysis, we have developed an oil spot scale which makes possible more accurate evaluation of the state of the oil for its replacement in terms of the actual state. The change in the spot color may bear information not only about dirtiness of the oil, but also about functioning of the additives, dilution of the oil by the fuel, and dissolution of a portion of the resins. Thus, if the fuel gets into the oil, the spot changes color from yellow-gray to brown or black, depending on the distance from the core.

The arithmetic mean value of the reduced error (error referred to full-scale value) of determination of *DSP* and the degree of dirtiness of the motor oils in the known scale was 15% and in the developed scale, 3.6%. Periodic control of the degree of dirtiness of the working motor oil by analysis of the spot on the filter paper makes it possible under the performance conditions to predict the time of attainment of the oil quality indices to their critical values and thereby prevent hazardous malfunctioning of the internal combustion engine.

## REFERENCES

- 1. A. A. Gureev, I. G. Fuks, and V. l. Lashkhi, *Chemmotology* [in Russian], Khimiya, Moscow (1986), p. 368.
- 2. A. M. Kuliev, *Chemistry and Technology of Additives to Oils and Fuels* [in Russian], Khimiya, Leningrad (1985), p. 312.

- 3. G. P. Lyshko, Fuel and Lubricants [in Russian], Agropromizdat, Moscow (1985), p. 336.
- 4. V. V. Ostrikov and V. V. Belogorskii, Tekhn. Oborud. Dlya Sela, No. 12, 39-40 (2007).
- 5. Yu. A. Gur'yanov, *Proximate Methods and Devices for Diagnosing Machine Units from Oil Parameters* [in Russian], Doctoral dissertation, Chelyabinsk (2007).
- 6. V. V. Belogorskii, Enhancing Efficiency of Proximate Methods and Devices for Control of Motor Oil Quality [in Russian], Candidate's dissertation, Michurinsk (2009).