RATIONALE OF THE DIELECTROMETRIC METHOD OF DEFINITION OF LUBRICANT OILS' TRIBOLOGICAL CHARACTERISTICS' CHANGES

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В статье на примере исследований отработанных масел продемонстрирована противоречивость обще принятых методик, и вопрос оценки трибологических характеристик масел на основе результатов эксплуатационных исследований, и оценки их эксплуатационной оценки, является особенно актуальным. В статье описываются результаты измерений диэлектрической проницаемости в переменном электрическом поле, полученные при различных условиях эксплуатации. Эти результаты позволяют оценить степень старения масел и их эксплуатационные характеристики. В рамках настоящей работы были проведены исследования на базе различных методик оценки трибологических характеристик масел, включая оценку вязкости, температуры вспышки, кислотного числа и содержания нерастворимых осадков. Результаты показали, что применение диэлектрической проницаемости в переменном электрическом поле может быть использовано для оценки эксплуатационных характеристик масел.

Ключевые слова: олива, трибологические характеристики, реологические характеристики, диэлектрическая проницаемость, нормативные методы.
The article demonstrates the contradiction of generally accepted methods of research of lubricants tribological properties on the example of spent oil studies and critically considers the possibility of using the obtained results as criteria for assessing the serviceability of lubricating oils after a certain service life. In particular, regulatory parameters such as viscosity, flash point, acid value and insoluble sludge content were considered. Viscosity, in particular, was assessed by the Heppler’s and the Ostwald’s methods. As a result, it was found that the first of these methods shows lower values. Similar ambiguity is demonstrated by normative methods for determining the flash point in open and closed crucibles, determining the acid number by potentiometric or calorimetric titration of an oil sample dissolved in various solvents and determining the sludge content by extraction with n-pentane, n-heptane and extraction benzene. As it turned out, the results obtained by different methods are impossible to compare. The analysis of the obtained data also confirms the opinion that the indicators determined in the laboratory have no practical application, because they do not correlate with the real operating conditions of the oil. Such laboratory studies can only be used to compare two or more samples of lubricants. As an objective criterion that would reflect the interaction of the components of lubricating oils and friction units during operation and could serve as an indicator of the degree of aging of the oil, the author proposed to use the dielectric constant in an alternating electric field. These first research results show that changes in dielectric constant as a function of service life can be considered an indicator of the degree of aging of the oil, and the results allow us to estimate the concentration of sludge and mechanical contaminants in oils. However, given the multicomponent nature of modern oils and the influence of other factors on the dielectric penetration of the material, the results obtained should be considered only preliminary and those that require further refinement and processing.

Key words: oil, tribological characteristics, rheological characteristics, dielectric constant, normative methods

Introductions
Settings of technically and economically expedient oils’ operation time is one of the most important issues in the lubricants’ usage [1]. In Ukraine, these problems have become especially relevant. Market demands for petroleum products has led to changes in the current production structure of enterprises, the structure of imports and exports, product range and sales systems. The total range of aviation, motor, transmission, hydraulic, turbine, compressor, electrical-insulation and other oils which are produced at Ukrainian enterprises includes more than 200 items, within motor and transmission oils - more than 65. At the same time, there is a significant increase in the volume of imported lubricants. This influx is due primarily to the fact that domestic refineries can provide Ukraine with lubricating oils by only about 44%. According to various expert estimates, the necessity for lubricating oils up to 900 thousand tons per year can be expected in Ukraine in the coming years, and the need for transmission oils reaches at least 50,000 tons, in particular. With such a wide range of products, the question of the suitability of lubricants by different manufactures, the choice of lubricants in terms of quality and cost, as well as the definition of oils’ optimal operational time in terms of their ability to meet certain operational requirements as to different equipment arises especially important [2].

Setting objectives
Settings of the lubricants’ optimal lifetime deadlines is not only extremely important, but also a complex task, the solution of which must simultaneously satisfy both operational and technological conditions, the purpose of which is to ensure the reliability of lubricated machines and mechanisms; and economical profitability, which consists in choosing a rational approach to the choice and consumption of oils. Therefore, the choice of parameters to characterize the intensity of the oil aging process during operation of the equipment and oils condition assessment has considerable practical interest [2, 3].

Research results and their analysis
The author analyzed well-known standard methods for assessing the quality of lubricating oils. In practice, the aging of lubricating oils is often checked out by the change in their rheological properties, which are determined according to accepted standards by measuring viscosity at different temperatures, depending on the purpose of the oils. However, it should be noted that if the thermochemical mechanisms of the aging process lead to an increasing in the oils viscosity, the dissolving effect of fuel in motor oils or mechanical destruction in transmission oils reduces their viscosity. Thus, changes in the viscosity of the oil during operation are determined by various complex factors, and it is possible that the viscosity of
the working oil is equal to its original value, but in this case the changes in chemical and fractional composition are ignored. In the process of aging, the conditions of the hydro- and elastohydrodynamic regime of lubrication change, despite the fact that the standardized viscosity determined in laboratory conditions is similar to or close to the viscosity of fresh oil [4]. As part of a research program at “Radom Polytechnic” (Radom, Poland), the viscosity for several randomly selected oils after different usage time was determined by the author using different viscometers. The results are given in table 1. The following oils have been investigated:

1. CASTROL EPX (similar to API GL-5, SAE (18) 85W-90) after 113 operating hours.
2. CASTROL EPX (similar to API GL-5, SAE (18) 85W-90) after 312 operating hours.
3. BPDL MP30 (similar to API CC, SAE 30) after 4160 operating hours.
4. MOBILGARD 312 (similar to API CD, SAE 30) after 512 operating hours.
5. MOBIL Delvac 1230 (similar to API CC, SAE 30) after 628 operating hours.

The data given in table 1 demonstrate that the Heppler’s method gives a viscosity value lower than the Ostwald’s one. Studies show that this is probably due to the inhibition of the used oil’s flow through the capillary by means of impurities accumulated in it during the operating time. For this reason, an objective measurement of the oil viscosity by the capillary method is impossible. Thus, the viscosity of the oil can be undoubtedly considered as an indicator that characterizes its rheological properties, but it should be noted that the viscosity can not be the only indicator of the serviceability of oils. Viscosity, as a measure of internal friction of a liquid, is not able to fully characterize the resistance to movement of equipment parts, due, in addition, the type and geometry of conjugate friction pairs, the technology of their processing and method of lubrication [3].

Methods for oil viscosity determining and estimating should be improved taking into account the maximum approximation to the operational effects under real friction units’ conditions. According to ASTM standards, during recent years a Brookfield rotary viscometer for the lubricating oils’ viscous classification has been widely used in many countries [4].

Another well-known standard criterion for assessing the quality of lubricants is the flash point determination in open and closed crucibles. Studies confirmed by the author (see Table 2) show that with a slight change in the viscosity of the lubricating oil, a decrease in the flash point may indicate the depth of oxidation of the oil and the formation of highly viscous condensation products. It was also found that the flash point in the open crucible decreases with the increased sludge content in the lubrication oil. More accurate results can be obtained by determining the flash point in an open crucible. The table 2 shows the flash point values of previously selected oils.

Table 2 – The comparative flash point obtained by various methods

| Sample number | Flash point in open crucible, °C | Flash point in closed crucible, °C |
|---------------|---------------------------------|----------------------------------|
| 1             | 266                             | 239                              |
| 2             | 247                             | 227                              |
| 3             | 278                             | 254                              |
| 4             | 253                             | 230                              |
| 5             | 267                             | 240                              |

The actual flash point is due to many factors. The analysis of the obtained data confirms the opinion that the determination of the flash point in the laboratory, especially in a closed crucible, has no practical application, because it does not correlate with the real operating conditions of the oil. This temperature determination can only be used to compare two or more samples of lubricating oils [4].

Free acids content determination in lubricants is carried out by the acid number determining method, while the determination of free and bound acids – by the method of determining the alkaline number. Both methods are reduced to potentiometric or calorimetric titration of the oil sample dissolved in alcohol (ethyl, isopropyl), gasoline, toluene, isopropanol or other solvent. The results obtained by different methods are impossible to com-
During the operating process of lubricating oils, various sediments accumulate there, they are products of condensation and coking, as well they have the purely mechanical origin. Determining their number can also be considered as a measure of the oils aging level. However, various solvents are used to determine the content of these precipitates. Disregarding external mechanical impurities, which should be determined by the benzene extraction method (so does ESSO), ELF recommends sludge content determination the by extraction with n-pentane, SHELL – n-heptane, and ESSO – gasoline extraction. Thus, it is obvious that, while the sludge content determination by means of pentane, heptane and gasoline, mechanical impurities are also released from the oils in addition to resins. This means only that the sludges are the sum of insoluble in this solvent resins and mechanical impurities. The amount of precipitated resins is determined by the nature of the solvent, its behavior to the oil, temperature, the chemical composition partition coefficient of the resins and their molecular weight. Comparison of the amount of precipitate precipitated with various solvents on the filter plate SETA, is given in table 4.

Thus, it can be stated that the actual sludge content in the lubricant oil corresponds to the content of the precipitate obtained from the oil by means of this solvent, reduced by the content of mechanical impurities, determined with the help of benzene. These methods of the content of sludge determining, due to their differences, do not allow to draw conclusions about the serviceability of lubricating oils. Moreover, a study conducted by the authors at Radom Polytechnic University showed that the introduction of 2% (as to the weight) mechanical impurities and sludge which had been extracted from waste oils into SuperOl SAE 30 motor oil slightly improves its anti-wear properties. The same results were obtained after the adding of these precipitates in the base oil SAE 10, and the anti-wearing properties were determined on a four-
ball friction machine. Thus, the determination of the content of sludge and mechanical impurities, although related to the performance properties of lubricating oils can not serve as a direct indicator of the aging process.

Thus, we can conclude that the normative methods for assessing the protective properties of lubricating oils do not respond to actual operating conditions. Similar conclusions can be made by considering other standardized criteria such as pour point and water amount (not covered in this article) [3].

From the above considerations it follows that the set of standards for oils, as well as methods for determining their properties are based on conventional indicators or on conventional means of determining them with insufficient correlation with the actual operating conditions. In general, only fresh oils can be evaluated by standard test methods, because the procedure for determinations implementing usually requires contamination removal from the tested samples, their dehydration, homogenization, etc., removal the components that accumulate in the oil during operation and, naturally have a significant impact on the determined values. Modern methods of lubricating oils testing are usually developed by oil manufacturers or the authors of their recipes, ie they are clearly production interesting and useful to assess the electrochemical processes and changes in the behavior of oil in an electric field. It is well known that pure fresh lubricating oils of the same grade in intervals (not lower - not higher), this allows the determination of their properties are based on conventional petroleum products properties assessing, much attention has been paid to the study of conductivity (resistance) in a constant electric field. According to the author, such studies characterize the temporal values of these properties in certain solutions. Studies of conductivity, and in fact the potential drop, implemented in an alternating electric field, can characterize the process of changing the state of multicomponent mixtures.

A number of studies have been conducted to confirm this idea. Contaminations had been isolated from the used oil Superol "CC SAE 30" by extraction with benzene. The obtained samples had been dried at a temperature of 105 °C, and after the isolated contaminants were dissolved in an oil base to obtain solutions of 0.01, 0.05, 0.25, 1 and 5%. Similarly, from the benzene solution, after evaporation of the solvent, by extraction with n-pentane were isolated sludge, which were dissolved at the same concentrations in the oil base. Under the above conditions and a certain order of the samples replacement, the changes in the potential drop for a series of solutions of contaminants and sludge of different concentrations have been studied. For the obtained results in the concentrations range up to 1%, the corresponding regression equations have been compiled and graphical dependences have been compiled (see Fig. 1).

Preliminary analysis of the graphical dependences shows that the sharpest changes in the potential drop are observed for strongly polar sludge as oxidation products. When the concentration of sludge above 4%, the value of the potential drop is stabilized.

Conclusions
The described researches have shown that normative methods of estimation of protective
properties of lubricating oils which are based on conditional indicators or on conditional means of their definition do not correlate enough with real operational conditions, and moreover, they show a certain discrepancy in results. It is logical that the described test methods can and should be applied only to fresh oils, and they, unfortunately, can not give an answer about the functional suitability of lubricants after a certain usage. An attempt to use dielectrometric parameters as a criterion that reflects the interaction of the lubricating oils components and friction units demonstrates results that may have practical value. Based on the previous results, it can be stated that changes in dielectric constant as a function of operating time can be considered an indicator of the oil aging degree. The obtained dependences allow to estimate the concentration of sludge and mechanical contaminants in the working oils. However, given the multicomponent nature of modern lubricants and the unconditional influence of other factors on the dielectric penetration of the material, a series of additional and refining experiments should be conducted to obtain more objective mechanisms for assessing the lubricating oils tribological state.

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