УДК 621.89
DOI: 10.31471/1993-9965-2021-2(51)-16-22

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

I. I. Shostakivskyi*, V. R. Kharun

Ivano-Frankivsk National Technical University of Oil and Gas;
15, Karpatska Str., Ivano-Frankivsk, Ukraine, 76019, e-mail: s h o s t a k i v s k y @ g m a i l . c o m

В статті на прикладі досліджень відпрацьованих олив продемонстрована протирічливість загальноприйнятих методик досліджень трибологічних властивостей мастильних матеріалів та критично розглянута можливість використання отриманих результатів в якості критеріїв оцінювання експлуатаційної придатності мастильних олив після певного терміну експлуатації. Зокрема, були розглянуті такі нормативні показники як в'язкість, температура спалаху, кислотне число та вміст нерозчинних осадів. В'язкість, зокрема, оцінювалася за методом Гепплера та методом Оствальда. В результаті було встановлено, що перший із зазначених методів демонструє нижчі значення. Аналогічну неоднозначність демонструють і нормативні методики визначення температури спалаху у відкритому та закритому тиглях, визначення кислотного числа шляхом потенціометричного або калориметричного титрування зразка оливи, розчиненого різними розчинниками та визначення вмісту шламів методом екстракції н-пентаном, н-гептаном та екстракційним бензином. Як виявилося результати, отримані різними методами, порівнювати неможливо. Аналіз отриманих даних також підтверджує думку про те, що показники, визначені в лабораторних умовах не мають практичного застосування, тому, що вони не корелюються із реальними умовами роботи оливи. Такі дослідження можуть бути використані лише для відносного зіставлення двох або більше зразків мастильних матеріалів. В якості об'єктивного критерія, який би відображав процеси взаємодії компонентів змащувальних олив і вузлів тертя в процесі експлуатації та міг би слугувати показником ступеня старіння оливи автором запропоновано використовувати діелектричну проникність у змінному електричному полі. Приведені перші результати досліджень демонструють, що зміни діелектричної проникності як функція часу експлуатації, можуть вважатися показником міри старіння оливи, а отримані результати дозволяють наближено оцінювати концентрацію шламів та механічних забруднень в оливах. Проте, враховуючи багатокомпонентність сучасних олив та вплив інших чинників на діелектричну проникніть матеріалу отримані результати слід вважати лише попередніми і такими, що потребують подальшого уточнення та опрацювання.

Ключові слова: олива, трибологічні характеристики, реологічні характеристики, діелектрична проникність, нормативні методи.

В статье на примере исследований отработанных масел продемонстрирована противоречивость общепринятых методик исследований трибологических свойств смазочных материалов и критически рассмотрена возможность использования полученных результатов в качестве критериев оценки эксплуатационной пригодности смазочных масел после определенного срока эксплуатации. В частности, были рассмотрены такие нормативные показатели, как вязкость, температура вспышки, кислотное число и содержание нерастворимых осадков. Вязкость, в частности, оценивалась по методу Гепплера и методу Оствальда. В результате было установлено, что первый из указанных методов демонстрирует более низкие значения. Аналогичную неоднозначность демонстрируют и нормативные методики определения температуры вспышки в открытом и закрытом тиглях, определение кислотного числа путем потенциометрического или калориметрического титрования образца масла, растворенного различными растворителями и определения содержания шламов методом экстракции н-пентаном, н-гептаном и экстракцией. Как оказалось, результаты, полученные разными методами, сравнивать невозможно. Анализ полученных данных также подтверждает мнение о том, что показатели, определенные в лабораторных условиях, не имеют практического применения, потому что они не коррелируются с реальными условиями работы масла. Такие исследования могут быть использованы только для относительного сопоставления двух или более образцов смазочных материалов. В качестве объективного критерия, который бы отражал процессы взаимодействия компонентов смазочных масел и узлов трения в процессе эксплуатации и мог бы служить показателем степени старения масла автором предложено использовать диэлектрическую проницаемость в переменном электрическом поле. Приведенные первые результаты исследований демонстрируют, что изменения диэлектрической проницаемости как функция времени эксплуатации могут считаться показателем степени старения масла, а полученные результаты позволяют приближенно оценивать концентрацию

шламов и механических загрязнений в оливках. Однако, учитывая многокомпонентность современных масел и влияние других факторов на диэлектрическую проникновение материала полученные результаты следует считать только предварительными и требующими дальнейшего уточнения и обработки.

Ключевые слова: масло смазочное, 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. At the same time, 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].

Table 1 – Comparative viscosity of lubricating oils obtained by different methods

Sample number	Temperature 40 °C		Temperature 50 °C	
	Method			
	Ostwald's (mm^2/s)	Heppler's (mm^2/s)	Ostwald's (mm^2/s)	Heppler's (mm^2/s)
1	108,6	106,2	66,0	65,2
2	-	115,2	-	70,0
3	112,5	110,7	68,2	66,0
4	102,8	100,1	63,2	62,4
5	98,5	94,9	61,3	59,1

« - » – measurement is impossible

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-

ISSN 1993–9965 print
ISSN 2415–3524 online
Науковий вісник ІФНТУНГ
2021. № 2(51)

pare. In many publications concerning the machines operation, the acid number increasing is considered as a measure of the lubricating oils corrosive effect intensity. Such assumptions are not always confirmed. The results of the acid number measuring by means of standard methods show only the total number of acid groups per unit mass of oil, but it is not known with which radicals these groups are associated and what is the total amount of these acids [4]. The determination of the acid number is associated with a large subjective error in manual calorimetric titration and with the difficulty of accurately determining the inflection point in potentiometric titration, because the real neutralization curves differ from the theoretical characteristics of this process. The table 3 shows the values of acid numbers for previously selected samples of oils determined by calorimetric and potentiometric titration.

Table 3 – Comparison of the acid number values, determined by different methods

Sample number	Potentiometric titration method, mg/KOH/g	Calorimetric titration method, mg/KOH/g
1	1,91	2,01
2	1,31	1,83
3	1,26	1,31
4	1,98	2,02
5	2,34	2,78

Thus, the acid number can be considered a conditional criterion for assessing the oxidation of lubricating oils until the appearance of acidic compounds. The deepening of this process leads to the neutralization and precipitation of the formed esters. Therefore, the scope of the acid number is quite limited.

In turn, changes in the alkaline number determined by alkaline hydrolysis of esters can characterize the intensity of the lubricating oils oxidation process. These tests are quite complex and require expensive special equipment, and the results do not correspond to the real operating conditions. Sludge extraction, as an indicator of the degree of oxidation carried out by means of various solvents, does not give comparable results. Thus, as to the methods for determining the alkaline and acid numbers can be summarized: the determined intensity of the corrosion effect of solutions on materials does not always correspond to changes in acid and alkaline numbers. Therefore, the value of the acid number can not be considered a measure of the corrosive activity of lubricating oils [3].

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.

Table 4 – Comparative percentage of insoluble precipitates determined by different solvents

Sample number	The amount of insoluble precipitates, %		
	in n-pentane	in n-heptane	in extraction gasoline
1	1,49	1,25	3,19
2	1,65	1,34	3,71
3	1,53	1,26	3,21
4	1,79	1,54	3,60
5	1,21	1,01	3,05

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 response 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 in nature. Based on the same set of its own standards, the manufacturer of lubricating oils relatively simply meets their requirements, without paying attention to the behavior of products in real operating conditions and friction units. Moreover, the values of the criticized evaluation properties in the product standards are usually in the tolerance intervals (not lower - not higher), this allows the production of lubricating oils of the same grade in a wide range of compositions.

Analyzing the process of the lubricating oils state changing, we can say that the criteria for assessing this state should be such one that reflects the actual interaction process of lubricating oils components and friction units that actively interact. From this point of view, it may be practically 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 oil is a non-polar liquid. Thermochemical processes that take place under the real operation, lead to the emergence of oxidation products, which in turn should cause polarity increasing. Among petroleum products, dielectric parameters are important primarily for hydrocarbons, which are used to fill electric switches, for the manufacture of capacitors and transformer oils. Only during recent years have been published works on the usage of fast and accurate dielectric methods for the lubricating oils condition assessment. The gradual accumulation of polar products, still soluble in unchanged hydrocarbons, depending on the temperature can bring their concentration to one at which significant changes in dielectric constant can be expected, which in turn becomes critical at critical concentrations and temperatures.

Since lubricating oils are a complex mixture of dozens of different compounds that react with each other, in applied research there is no need to determine the chemical composition of the oils in operation. At the same time, it is necessary to determine the relative changes in the state of these oils, which is understood as a result of changes in the state of chemical composition and, accordingly, fractional composition [4].

In the up to date researching works dealt with 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

ISSN 1993–9965 print
ISSN 2415–3524 online
Науковий вісник ІФНТУНГ
2021. № 2(51)

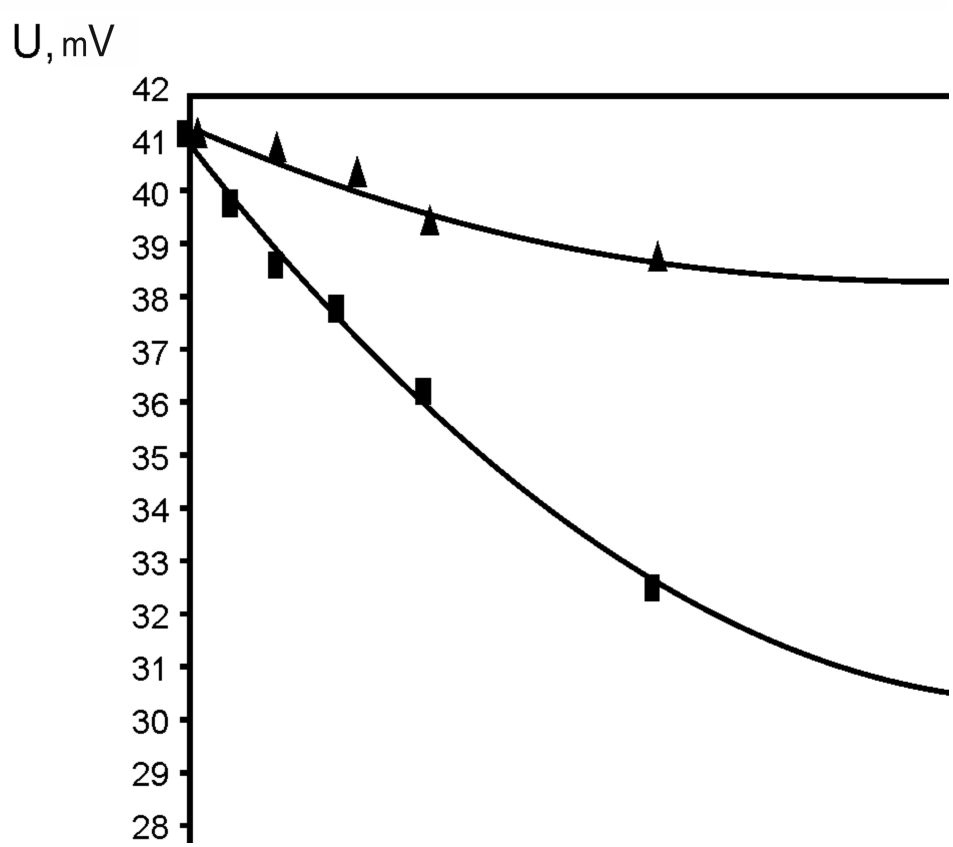

Figure 1 – Dependences of the potential drop on the concentration of sludge and mechanical contaminants

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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