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Application of permittivity spectroscopy for screening of motor oils lubricating properties

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Motor oils can be regarded as systems of highly dispersed polarizable dielectric in a matrix of non-polarizable or weakly polarizable dielectric. Taking into account that permittivity defines the ability of dielectrics to be polarized under external electric field and thus, to conduct alternative current, Permittivity Spectroscopy (PS) can be one approach for characterization of motor oils lubricating properties determined by their polarization ability. The analysis is based on measurements of the frequency dependence of the real component of the complex capacitance *C'*. A sharp increase of *C'* at a given frequency is registered. The height of the jump and its starting position in respect to the frequency are accepted as qualitative criterion for the lubricating properties of the oil and used for comparison between different oils in respect to their oiliness. The application of the method is demonstrated and evaluated in testing of technology for production of synthetic motor oil friction modifiers.

Key words: permittivity spectroscopy, motor oils and friction modifiers, polarisation, lubricating properties, oiliness.

INTRODUCTION

The quality of motor oils is essential both for the transport and the economy sectors since high quality oils provide reduced friction and high compression to internal combustion engines. The presence of active additives can significantly increase their lubricating properties. The ability to predict the remaining useful life (RUL) of motor oils could minimise the need for their scheduled changes, providing material saving, labour costs reduction combined with a positive effect on the environmental protection [1].

Motor oils are formulated from base petroleum stocks with about 10-25% additives [2]. The oil forms a film between the surfaces of the adjacent moving parts and thus minimises the direct contact between them, decreasing friction, wear and production of excessive heat. During their use they experience thermal and oxidative stresses which degrade the chemical composition of the base oil and deplete the oil's additive package. Contaminations such as leakage of water, introduction of carbon residues and metal impurities also affect their exploitation life. It is important that motor oils have a high lubricating ability which leads to lower fuel consumption, extended service life of the engine and a direct favourable impact on environment protection efforts. The methods for testing of oils lubricating properties are slow and require time and significant resources. Accurate full analysis is usually performed in specialised laboratories which additionally increases costs and consumes time. The currently used methods performed by major engine and lubricant manufacturers are in fact frequent, repetitive and time-consuming physical, chemical and mechanical tests. They include determination of oil viscosity, total acid number (TAN), total base number (TBN), insoluble (such as soot) content, fuel and water dilution, glycol contamination and metals content, degree of wear etc. [3-5].

Noticeably, the development of new, more simple, convenient, compact and faster non-destructive methods for complex dynamic characterisation of motor oils quality and assessment of the changes in their lubricating properties during exploitation is strongly needed. One promising approach is the application of physicochemical methods.

What makes them appropriate? The lubricating properties of oils are strongly dependent on viscosity and oiliness. While viscosity as a basic physicomechanical parameter is well formulated in the hydrodynamic theory of lubrication and deeply studied [6], oiliness can be regarded as a "hidden" potential quality parameter of the oil and is hence evaluated with a set of properties which ensure lubricating effect at thickness of the film, small enough to eliminate the viscosity effect [7]. The main characterisation factor is the strength of

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attachment of the thin oil layer towards the two moving parts, which preserves them from direct contact. It depends on the oil's polarisation characteristics which ensure the formation of layers with orientated molecules. The oiliness is superior when polarisation is easier [8]. The addition of compounds with high polarisation activity (oxygen-containing compounds such as naphthene, carbonic acids, asphaltenes, tar and compositions with sulphur in their molecules) improves the strength of the fine polarized oil layer. The oiliness is tested on special traction stands where the degree of wear of the standard moving parts (for instance balls) is evaluated. During exploitation oils progressively deteriorate their functional properties until they entirely lose their lubricating ability. The main degradation process is oxidation which changes the chemical composition [4, 9-11]. There is no universal criterion for determination of the moment at which the oil cannot be used further and should be changed. Since lubricating properties and their deterioration during exploitation are closely related to the presence of highly polarizable components, physicochemical methods that analyse the polarisation properties of molecules are an attractive trend. One path which is under exploitation is the evaluation of the relative permittivity changes of motor oils during exploitation [12-14]. However, the accuracy of the developed devices is still rather low [15-16]. Taking into account that the permittivity defines the ability of dielectrics to be polarised under external electric field and thus, to conduct alternative current, Permittivity Spectroscopy (PS) can be one approach for characterization of motor oils. The classical applications of the Permittivity Spectroscopy are typically related to the dipole properties studies of pure gases and liquids. The applied frequency range is from 1000 MHz down to 1 MHz and requires special measurement instrumentation [17-22].

Motor oils can be regarded as systems of highly dispersed polarisable dielectric in a matrix of non-polarisable or weakly polarisable dielectric. They require measurements in different frequency range. Preliminary experience has shown that important interactions between the two media are well observable in the range of 1 MHz down to 0,1 Hz. [23-24]. For that frequency range it is convenient to apply Permittivity Spectroscopy as a branch of Impedance Spectroscopy especially tuned for studies of dielectrics permittivity. This approach ensures contactless measurements in respect to the object's physical behavior and conductivity without the need of a reference electrode. Preliminary screening experiments confirmed the applicability of PS for motor oils [23, 25]. It should be noted that in the applied frequency range the penetration depth of the alternative current signal (A.C.) is much larger than the object's thickness [20]. As a result, the electric field strength is practically equal in the total volume of the sample.

When the A.C. signal is applied in the dielectric, the relative permittivity ε can be expressed as a complex number [20, 26]:

$$\varepsilon = \varepsilon' - j\varepsilon'', \qquad (1)$$

where ε' and ε'' denote the real and the imaginary (loss factor) components of the complex value of ε. The capacitance C can be also presented in a complex form:

$$C = C' - jC'', \qquad (2)$$

since the capacitive impedance $Z(j\omega)$ follows the dependence:

$$Z(j\omega) = -j(\omega C)^{-1}, \qquad (3)$$

where ω is the frequency.

The capacitance of a parallel plate capacitor is [17, 26],

$$C = \frac{\varepsilon\varepsilon_0 S}{d} \qquad (4)$$

where ε_0 is the permittivity of vacuum, S is the surface area of the electrodes and d is the distance between them.

If the impedance is replaced with admittance:

$$Y(j\omega) = 1/Z(j\omega), \qquad (5)$$

then

$$Y(j\omega) = j\omega C = j\omega(C' - jC'') = \omega C' + j\omega C''. \qquad (6)$$

The real component $j\omega C''$ in Eqn. 6 can be regarded as dielectric conductivity [26]. It can be expressed also as equivalent resistance $R = 1/\omega C''$, which can be directly measured and describes energy dissipative effects as ohmic conductivity, dipole's reorientation losses in electric field and others. C' is related to the dielectric permittivity, i.e. to the polarisation ability of the system.

The present study aims at applying Permittivity Spectroscopy as a robust and selective method for rapid characterisation of motor oils quality and degradation state. Its application is demonstrated in testing of technology for production of synthetic motor oil and friction modifiers.

EXPERIMENTAL

The permittivity measurements of motor oils were carried out in a special test cell with two coaxial cylindrical steel electrodes of diameter 49 mm with coplanar working surfaces and added spacer of paper positioned in three places that ensure a constant distance of 0.2 mm between the electrodes spring fixed in the cell. The material (special hardened steel) is identical with the one of the balls used in the traction stands where comparative test of the oiliness are performed. Following a developed oil deposition procedure, all the measured samples had one and the same geometry (surface and thickness). The complex permittivity measurements were performed on Solartron 1260 FRA in the frequency range 1 MHz – 0.1 Hz at room temperature with amplitude of the signal 1 V at density 5 points per decade. The precise determination of the object's permittivity was ensured by a preliminary calibration procedure, which eliminates the parasitic components coming from the test rig [23]. Following Eqn. 6, the most illustrative form for representing the experimental results was selected [27] - the frequency dependence of *C'*, given as log *C'*(F) / log *f*(Hz). More details for the investigated oil samples are given in the next section.

RESULTS AND DISCUSSION

Preliminary measurements have been performed on four different types of motor oils available at the market with preliminary known lubricating quality - oil base, natural, semi-synthetic and synthetic (Table 1). The aim was to define criteria for estimation of the oil quality.

Table 1. Measured oils available at the market.

Sample No	Oil	Type	Status
1	Oil Base SN 500	Base	Fresh
2	Prista M10D	Mineral	Fresh
3	Prista 10W40	Semi-synthetic	Fresh
4	Prista 5W40	Synthetic	Fresh

The results from the permittivity measurements of the fresh samples (Samples 1 - 4 from Table 1) presented as frequency dependence of *C'* are shown in Fig. 1.

For the oil base (Sample 1) no frequency dependence of *C'* was observed. This composition still has no additives that ensure its lubricating properties. For the rest of the samples at a given characteristic frequency a sharp increase is registered. The increase of *C'* is related to the polarisation ability of the oil components, i.e. to their oiliness. Noticeably, molecules that have higher polarisation ability will react on the external polarisation A.C. signal at higher frequencies and will cause higher increase of *C'*. Thus the jump and its starting position in respect to the frequency can be accepted as qualitative criterion for the lubricating properties of the oil and used for comparison between different oils in respect to their oiliness. As seen in Fig. 1, for the mineral oil (Sample 2) the sharp increase of *C'* starts at lower frequency in comparison with that of the semi-synthetic (3) and synthetic (4) samples combined with a lower enhancement of this parameter. The increase of *C'* for sample 4 is more pronounced than that for sample 3. According to the accepted assumption the quality of the oils increases in the following direction: oil base < mineral < semi-synthetic < synthetic, which correlates with the market evaluation of the 4 samples.

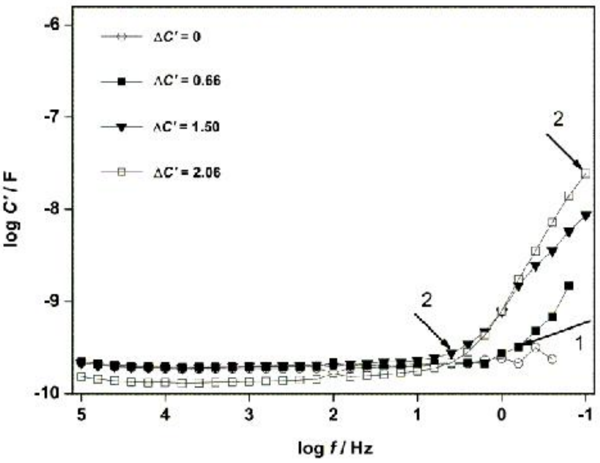

Fig. 1. Frequency dependence of *C'* for Sample 1 (○); Sample 2 (■); Sample 3 (▼) and Sample 4 (□).

It should be emphasized that every type of oil exhibits a typical capacitive diagram which ensures an easy distinction between the synthetic and the natural oils.

According to the performed screening measurements, a two-fold semi-quantity criterion for comparative evaluation of oiliness is defined, based on the capacitive impedance measurements: (i) value of the characteristic frequency f_{ch} of *C'* jump; (ii) enhancement/jump defined as $\Delta C' = \log C'_{max} - \log C'_{fch}$. According to this criterion, in oils with better quality, Δ *C'* is larger and occurs at higher frequencies.

The obtained results were applied for evaluation of the quality of modifiers produced in the frames of a technological project [28].The measurements were performed using mineral oil as an oil base (Table 2).

Table 2. Evaluated samples.

Sample No	Oil/modifier	Type	Status
5	Modifier glyceryl monooleate (MGO) with waste glycerine (process catalyst Y zeolite)	Additive	Fresh
6	Modifier MGO with waste glycerine (process catalyst Zn suktsinid zeolite)	Additive	Fresh
7	Mineral Oil (sample 2) with 0,5 % modifier (sample 6)	Natural motor oil with additive	Fresh
8	Mineral Oil (sample 2) with 0,5 % with modifier (sample 5)	Natural motor oil with additive	Fresh

Fig. 2 presents results performed with pure modifiers. According to the defined criteria both samples have excellent properties in respect to oiliness (*C*' increases more than 4 decades). The comparison of the two modifiers registers a little bit better performance for sample 5, which is marked only in the *C'* enhancement and not in the value of the characteristic frequency.

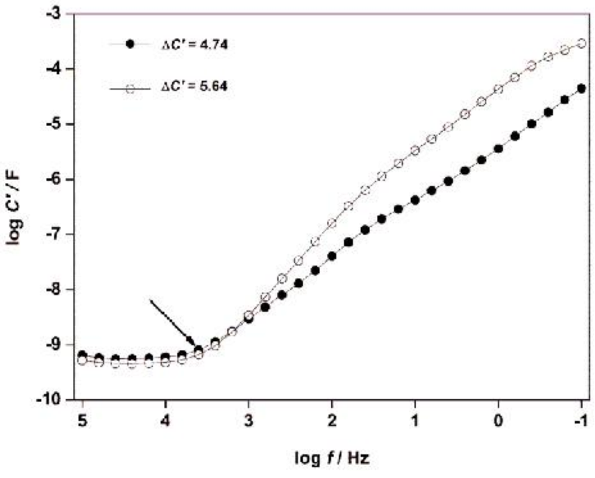

Fig. 2. Frequency dependence of *C'* for: Sample 6 (●) and Sample 5 (○).

The addition of the two modifiers to the base oil shows significant improvement of the motor oil quality (Fig. 3). The additional enhancement of *C'* in respect to the base oil is more than 3 decades and the characteristic frequency of *C'* jump moves from about 1 Hz to 50 Hz. Obviously the presence of the highly polarizable molecules of the modifier in the oil matrix accelerates the formation of the organized dipole thin film and the quality of the micelles structure. The comparison of the results for Samples 7 and 8 shows the same difference which has been obtained for the pure modifiers which is logical, since the oil base is one and the same.

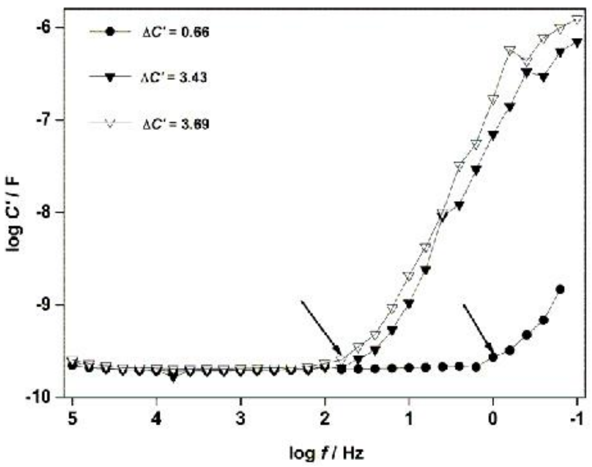

Fig.3. Frequency dependence of *C'* for: Sample 2 (●); Sample 7 (▼) and Sample 8 (∇).

The obtained results confirm the applicability of the developed technology for production of modifiers, as well as the high quality of the modified oils and their practical applications.

To confirm the selectivity of the method, the results obtained with Permittivity Spectroscopy were compared with those performed by the standardized method based on traction stands, which was carried out in a licensed laboratory (Table 3). It is applied for classification of motor oils according to their level of anti-wear properties. The evaluation of the oils is based on optical measurement of the average diameter of wear $\bar{d}$(mm). The smaller the diameter of the spot, the better the anti-wear properties of the tested object. As seen in Table 3, in respect to the quality, the results obtained by the Permittivity Spectroscopy approach are in agreement with those obtained on the traction stand.

For example, the result for Sample 8 obtained by PS shows excellent oiliness properties (Δ *C'*=3.69), which is also proven by the standard method ($\bar{d}$=0.35 mm).

However, the registered differences for oil base and oil with modifier are of about 0.30 mm (quite difficult for optical registration) in combination with time consuming experiments, while in addition to the quick measurement, the PS approach registers differences of more than 1000 times, which confirms the high sensitivity and robustness of the new approach.

Table 3. Comparative analysis.

№	Name of the sample	Results from the conducted testing with Permittivity Spectroscopy (Frequency dependence of the effective capacity *C'*) Δ *C'*	Results from the conducted testing with four-ball machine (Average diameter of wear, at time of testing 1 hour) $\bar{d}$ (mm)
1	Oil base SN 500	0	0.70
2	Prista M10D	0.66	0.60
7	Mineral oil M10D Prista Oil with 0,5 % modifier MGO with waste glycerine with catalyst Zn suktsinid zeolite	3.43	0.39
8	Mineral oil M10D Prista Oil with 0,5 % modifier MGO with waste glycerine with catalyst Y zeolite	3.69	0.35

CONCLUSIONS

The performed studies on motor oils analysis confirms the selectivity and sensitivity of Permittivity Spectroscopy, which registers changes in the measurement parameter (*C')* of several orders, thus ensuring much more reliable and precise classification of oils in terms of their lubricating properties.

The results obtained open a niche for applying the methodology as a quick alternative method for assessing the lubricating properties of oils.

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ПРИЛОЖЕННИЕ НА ДИЕЛЕКТРИЧНАТА ИМПЕДАНСНА СПЕКТРОСКОПИЯ ЗА СКРИНИНГ НА СМАЗОЧНИТЕ СВОЙСТВА НА МОТОРНИ МАСЛА

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(Резюме)

Моторните масла могат да бъдат разглеждани като системи от поляризиран диелектрик в матрица от неполяризиран или слабо поляризиран диелектрик. Като се има предвид, че диелектричната проницаемост определя способността на диелектриците да се поляризират под въздействие на външно електрично поле, Диелектричната импедансна спектроскопия (ДИС) би могла да бъде подходящ метод за охарактеризиране на смазочните свойства на моторните масла, по отношение на тяхната поляризационна способност. Анализът се основава на измерване на честотната зависимост на реалната компонента на ефективния капацитет *C'*. При определена честота е регистрирано рязко увеличение на *C'*. Големината на скока и неговата начална позиция по отношение на честотата са приети като качествени критерии за смазочните свойства на маслата и са използвани за сравняване на различни видове масла по отношение на тяхната масленост. Прилагането на метода е демонстрирано и оценено при разработване на технология за производство на модификатори на триене и синтетични моторни масла.