

Correlation of the Dielectric Constant and Conductivity of Marine Motor Oils

✉ Oksana Synashenko¹, ✉ Evgenia Rabenok², ✉ Mikhail Gapanovich², ✉ Nikolay Sinyavsky¹

¹Kaliningrad State Technical University, Department of Physics, Kaliningrad, Russia

²Federal Research Center of Problems of Chemical Physics and Medicinal Chemistry RAS, Chernogolovka, Russia

Abstract

The study of marine lubricants using modern methods for quality control and diagnostics of engine conditions is an important task. The solution to this task determines the technical condition of ships, their performance, and accident-free operation in maritime transport. In this study, the properties of several marine motor oils were studied using broadband dielectric spectroscopy. The complex dielectric constant, conductivity, and loss tangent of base oil, Shell Rimula 15W40 oil fresh and used for 250 and 500 h were studied. The influence of the test voltage frequency and temperature on the selected electrical parameters was determined. In used oils, the DC conductivity decreases slightly, which is apparently due to the depletion of additives. The increase in the conductivity of all studied oils with increasing current frequency is caused by the displacement current. It is shown that dielectric losses increase with frequency as long as the polarization has time to follow the change in the field. A shift in the frequency at which the maximum loss occurs with a change in temperature was discovered. The activation energies of polarization and conductivity were determined. The thermal activation energies obtained from the conductivity and dielectric constant are not significantly different. For the first time, the distributions of the dielectric constant relaxation times for the studied lubricating oils have been obtained. The dielectric relaxation time distribution function depends on the composition of additives in the oil, wear particles, contaminants, and the chemical degradation of the oil during operation. For the first time, correlations have been established between conductivity and dielectric constant at different temperatures and frequencies. These correlations can be used to select frequency ranges that provide stable parameter values and maximum diagnostic ability.

Keywords: Dielectric constant, conductivity, dielectric loss tangent, marine motor oils

1. Introduction

Motor oils are based on base oil and additive systems to reduce wear of parts, protect against gearboxes, remove contaminants, heat removal, and primary foam formation. Lubricating oil undergoes gradual degradation under the influence of high temperatures, water, air, and acidic contaminants (oil oxidation products). Accurate monitoring of oil wear is necessary for both technical and economic reasons.

Standard physicochemical testing methods used to control the quality and safety of motor oils are typically labor-intensive, expensive, destructive, and require multiple sampling. Electrical methods have some advantages over other methods: speed of measurement, low cost, and high testing efficiency. The electrical properties of technical

materials are among the least studied. Several research centers around the world deal specifically with this area of research [1].

Kardoš and Pietriková [2] showed interest in monitoring the condition of motor oils from the point of view of determining degradation factors and diagnostics. The use of sensors and systems for real-time characteristic monitoring to control engine oil aging. For analysis, the dielectric constant and conductivity were examined. These characteristics are discussed as the basis for continuous oil diagnostics.

Schober et al. [3] investigated the conductivity of insulating oil, which is an important quantity for the design, diagnosis, and evaluation of the insulation condition of high-voltage DC systems. The paper presents and discusses conductivity estimates for the condition of insulation systems at various



Address for Correspondence: Oksana Synashenko, Kaliningrad State Technical University, Department of Physics, Kaliningrad, Russia

E-mail: oksanasynashenko@gmail.com

ORCID ID: orcid.org/0009-0004-3149-0345

Received: 13.02.2024

Last Revision Received: 17.05.2024

Accepted: 05.06.2024

To cite this article: O. Synashenko, E. Rabenok, M. Gapanovich, and N. Sinyavsky, "Correlation of the Dielectric Constant and Conductivity of Marine Motor Oils." *Journal of ETA Maritime Science*, [Epub Ahead of Print]



Copyright© 2024 the Author. Published by Galenos Publishing House on behalf of UCTEA Chamber of Marine Engineers. This is an open access article under the Creative Commons AttributionNonCommercial 4.0 International (CC BY-NC 4.0) License

temperatures, field strengths, and for various types of oils. It has been established that electrical insulating oil has conductivity that depends nonlinearly on field strength, temperature, water content, and aging. In addition, its conductivity depends on time because of the drift of charge carriers.

Measurements of fresh and old oil are compared and taken into account when diagnosing oil-filled HVDC systems. Baturlyya et al. [4] presented the results of a study of used motor oils using dielectric spectroscopy. A method for diagnosing oil using capacitive sensors is proposed, which is also suitable for mobile units.

Xu et al. [5] investigated the electrical conductivity of an oil film used in displays. Their study showed that the electrical conductivity of the oil film varies from pixel to pixel. This work shows that it is possible to characterize oil film resistance and heterogeneity using electrical impedance spectroscopy.

Barnoss et al. [6] studied the mechanisms of electrical conductivity of nanofluids based on motor oil saturated with graphite and multi-walled carbon nanotubes in different concentrations by the impedance spectroscopy method. The measurements were carried out at temperatures of 300-400 K in the frequency range 100 Hz-1 MHz. This work shows that the presence of carbon nanotubes significantly affects the electrical properties of motor oil. Analysis of the temperature dependence of direct current conductivity and relaxation time showed that the addition of carbon nanotubes increases the activation energy.

Popov et al. [7] proposed some criteria that can be used to check the analytical results of an expression describing data related to complex conductivity. It is shown that the polarization of the electrode is indirectly related to the relaxation phenomenon. The theoretical and experimental foundations of dielectric spectroscopy were considered by Sidambarompoulé et al. [8]. The main focus here is on insulating liquids and the study of diffusion and ion mobility. Wolak et al. [9] assessed the suitability of the capacity and conductivity of fresh motor oils tested in a wide range of frequencies to determine the quality of the oil and its identification by physicochemical properties. Frequency ranges that provide maximum diagnostic efficiency have been identified.

Polarization caused by the injection current was studied by Zhou et al. [10]. A new model was proposed that considers the injection current. The frequency responses of the three different types of mineral oil were measured, and this new polarization model was used to interpret the experimental data. The new model allows us to better understand the phenomenon of electrical conductivity in mineral oil.

Izmestyev and Konyaev [11] the dielectric characteristics of some automotive motor oils were studied in the frequency range from 100 Hz to 3 MHz. The maximum in the frequency dependence of the dielectric loss tangent of used oil is due to the oxidation of hydrocarbons and is proposed to be used as a rejection indicator.

The polarization, conductivity, and dielectric losses of synthetic motor oils were studied by Izmet'sev and Kozhevnikova [12]. It is concluded that these oils are non-polar dielectrics in which electronic polarization occurs at high frequencies. In this study, the activation energy of conductivity, which depends on both viscosity and the presence of additives, is determined.

A review of studies of fresh and used marine motor oils conducted at the Kaliningrad Technical University using various optical and radio spectroscopic methods is given by Sinyavsky [13]. The possibilities of diagnosing a marine engine based on the characteristics of the used oil and the presence of wear products in it are discussed. Sinyavsky et al. [14] analyzed the distributions of dielectric relaxation times of some fresh and used marine motor oils. A connection between the distributions, the content of additives, and the presence of wear particles has been established. Thus, from a review of the literature, the electrical parameters of fresh and used motor oils can be successfully used to determine their physicochemical properties and diagnose their condition.

The purpose of this study was to assess the possibility of using the dielectric constant, spectrum of relaxation times, conductivity, and loss tangent measured over a wide frequency range to assess the quality of marine motor oil and its identification. A key step toward achieving this goal is to determine the effect of frequency on electrical parameters and to test whether there is a correlation between these parameters at different frequencies and temperatures. This will allow determining the optimal frequency range of the test voltage in future research.

2. Experimental Technique

The measurements were performed on a broadband dielectric spectrometer "Novokontrol" in the frequency range $f=10^2$ - 10^5 Hz and at temperatures from -30 to 200 °C. The sample temperature during the measurements was controlled with an accuracy of 0.5 °C. The measuring cell consisted of two gold-plated copper electrodes. The gap between the electrodes was 50 μ m and was fixed using quartz spacers. The diameter of the electrodes was 20 mm. The voltage between the electrodes was 1 V.

For simple liquids, polarization decreases with increasing frequency with one characteristic relaxation time. In this case, the Debye equation for the complex relative dielectric constant has the following form [1]:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega T_r} \quad (1)$$

where ω - cyclic frequency, ε_∞ - dielectric permittivity at $\omega \rightarrow \infty$, ε_s - dielectric permittivity at $\omega \rightarrow 0$, T_r - dielectric relaxation time.

Motor oil is a complex mixture of dipole molecules that relax with different relaxation times. If the distribution function of these relaxation times is denoted as $G(T_r)$, the real dielectric permittivity for motor oil can be written as follows:

$$\varepsilon'(\omega) = \int_0^\infty G(T_r) \frac{\varepsilon_s + \varepsilon_\infty \omega^2 T_r^2}{1 + \omega^2 T_r^2} dT_r \quad (2)$$

The spectrum of dielectric relaxation times $G(T_r)$ is determined both by the degradation of oil hydrocarbons, the additive package, and the presence of wear products. The function $G(T_r)$ was obtained by finding the inverse transformation of Equation (2), similar to [14].

3. Results and Discussion

Fresh motor oils are non-polar dielectrics. The polar component occurs after the oxidation of oil hydrocarbons.

The temperature and frequency dependence of the dielectric permittivity contain information about the polarization mechanisms and their relative contribution to the resulting polarization of the medium.

The dependence of the real part of the dielectric constant on frequency at different temperatures for the four oils is shown in Figure 1. At low frequencies of voltage applied to the sample, molecular dipoles follow changes in the electric field.

Motor oils contain several additives, and the charge carriers can be ions formed as a result of the dissociation of hydrocarbon molecules or impurity molecules. As the degree of dissociation increases, the dielectric permittivity increases. However, ionic electrical conductivity is determined mainly by additives because dissociation of the main oil molecules is unlikely. When oil degrades, its conductivity increases because of moisture absorption, formation of polymerization products, and oil oxidation.

The dependence of the real part of the conductivity and the loss tangent on the frequency at different temperatures are illustrated in Figure 2 and 3. On the graph $\log(\sigma') = \varphi(\log(f))$ a plateau is observed in the low frequency range. As the

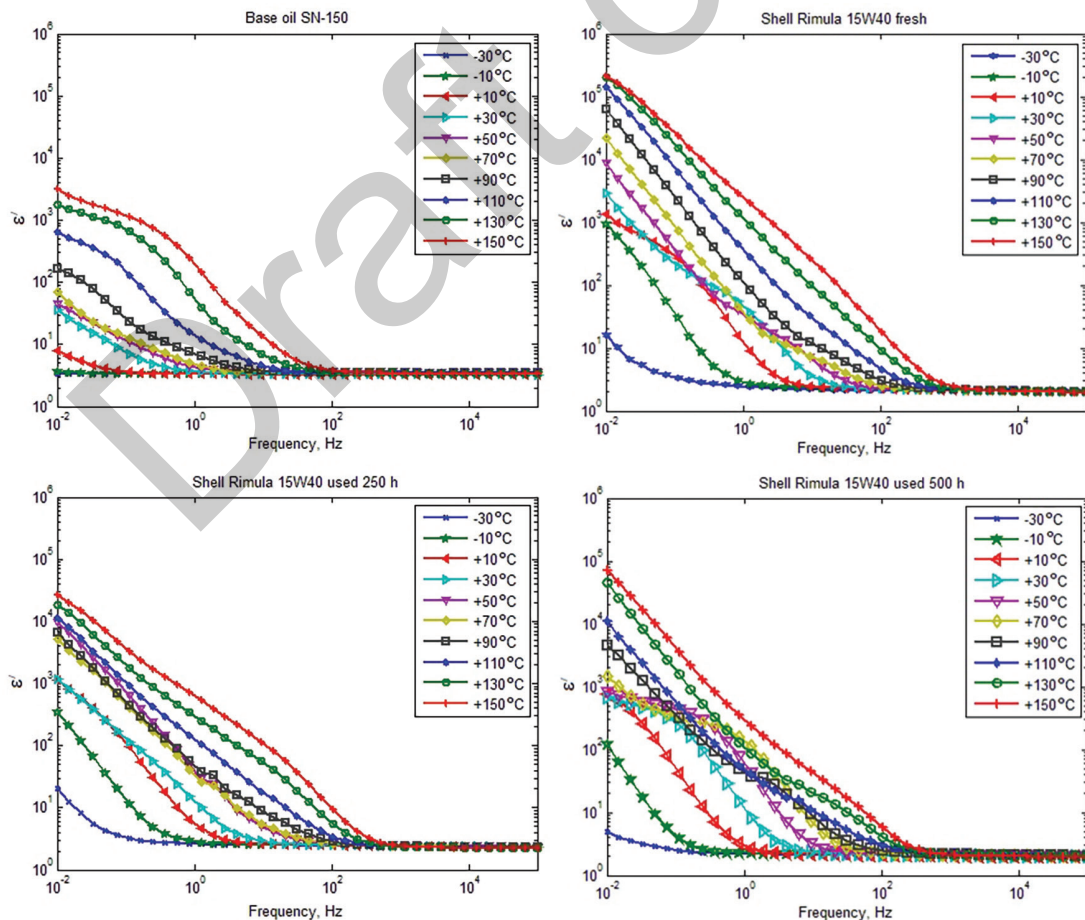


Figure 1. Dependences of the real part of the complex dielectric permittivity ε' of oils with frequency for different temperatures

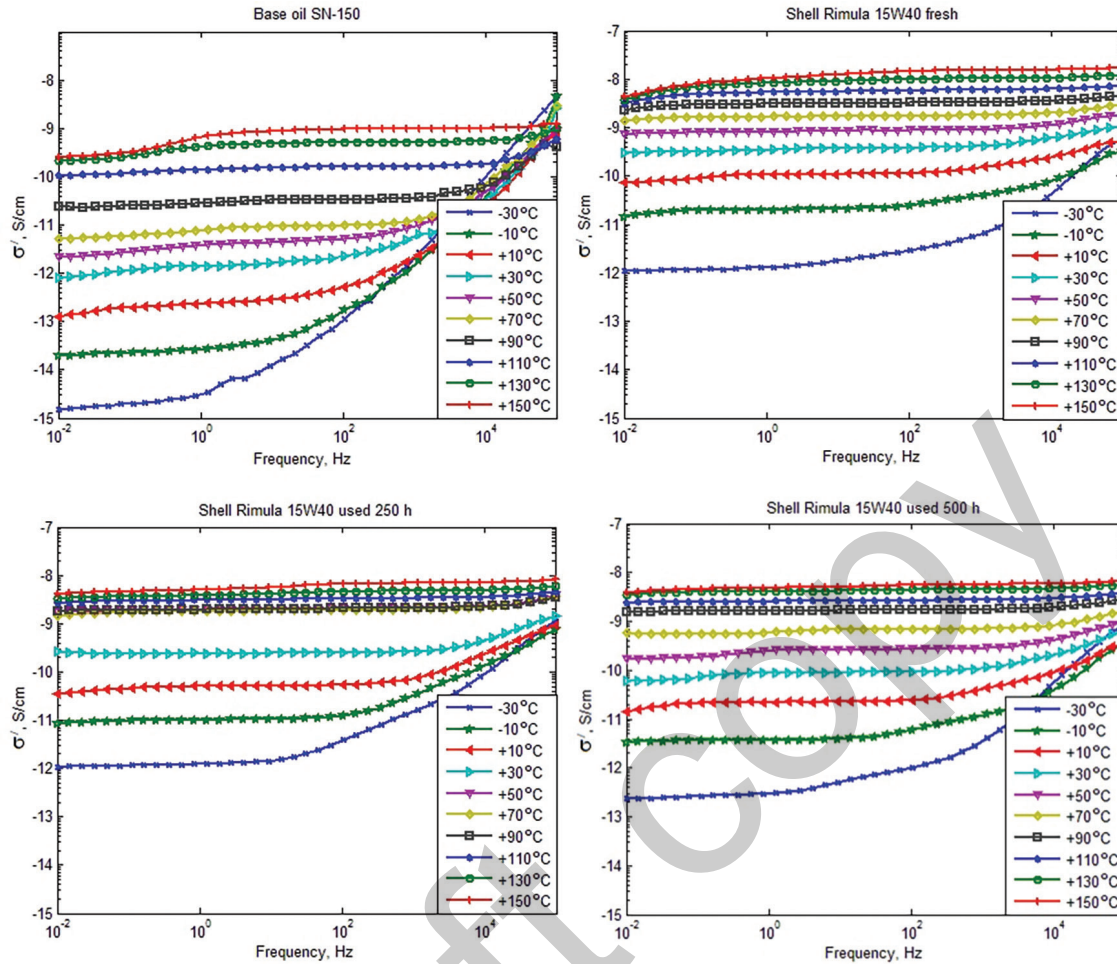


Figure 2. Dependence of the real part of the specific conductivity σ' of oils on the frequency at different temperatures

temperature increases, the plateau also extends into the high-frequency region. The presence of a plateau is related to the transport of free charges [15,16]. The transition from a plateau to a change in σ'_{ac} from frequency indicates a change in the conduction mechanism. By observing the dielectric constant of oil ϵ' in the low frequency region, where it is constant, it is possible to determine the static conductivity σ_s . Figure 2 shows the effect of temperature on the conductivity of the oil samples at different current frequencies. At temperature ($t=30^\circ\text{C}$), the conductivity of the base oil is much lower than that of fresh ShellRimula 15W40 oil and gradually increases with temperature. This is due to the presence of a package of improving additives in ShellRimula 15W40 oil. One would expect the conductivity of used oils to increase because of waste metal wear particles and soot (carbon) particles, but this does not happen. In used oils, the DC conductivity decreases somewhat, which is apparently due to the depletion of additives. At low frequencies, the behavior of electrical conductivity is almost independent of frequency and is described by direct current conductivity. The

increase in the conductivity of all studied oils with increasing current frequency is caused by the displacement current. In addition, at high frequencies, electrical conductivity occurs as a result of translational motion with sudden jumps in the electron. As the temperature increases, the polar group of the molecules becomes oriented, which facilitates the transfer of electrons, leading to an increase in conductivity.

In an alternating electric field, oil losses depend on frequency as follows. At low frequencies, they decrease with increasing frequency. As the frequency increases, losses increase, reach a maximum, and decrease, tending to low values.

In polar dielectrics, power dissipation is mainly determined by frictional losses due to the orientation of the dipole molecules. Therefore, dielectric losses increase with frequency until the polarization has time to follow the change in the field, and $\text{tg}\delta$ also increases (Figure 3). When the frequency becomes so high that the dipole molecules no longer have time to completely orient themselves in the direction of the field, $\text{tg}\delta$ drops and the losses become constant.

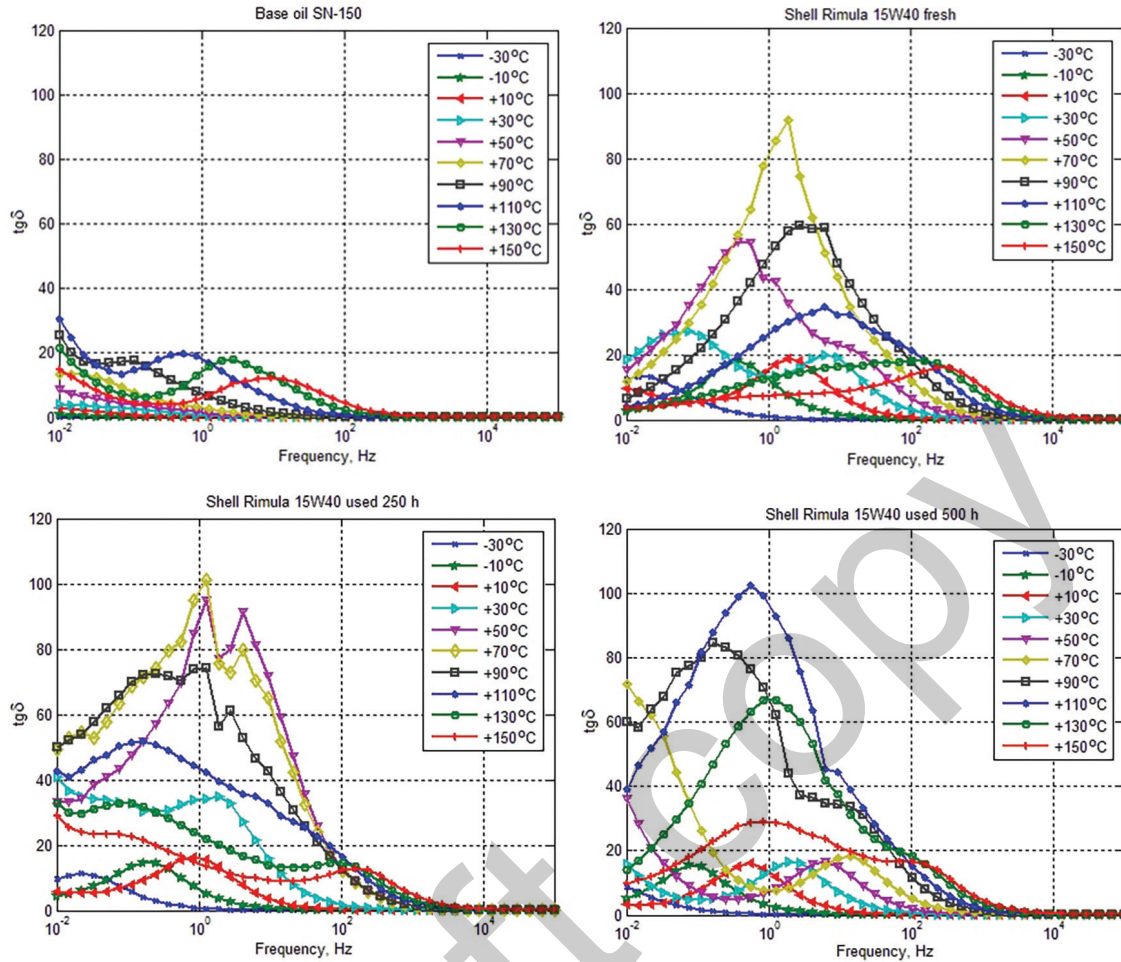


Figure 3. Dependence of the dielectric loss tangent $\text{tg}(\delta)$ of oils on frequency at different temperatures

The dielectric loss tangent for the Debye model can be written as follows:

$$\text{tg}\delta(\omega) = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty)\omega T_r}{\varepsilon_s + \varepsilon_\infty \omega^2 T_r^2} \quad (3)$$

The frequency at which the maximum dielectric loss occurs is found from Equation (3) and has the form:

$$\omega_{\max} = \frac{1}{T_r} \sqrt{\frac{\varepsilon_s}{\varepsilon_\infty}} \quad (4)$$

A shift in the frequency at which the maximum losses occur with a change in temperature is observed in all graphs in Figure 3. For the base oil, the $\text{tg}\delta(\omega)$ spectra are single-humped; for Shell Rimula 15W40 oil, at some temperatures, they are more complex because of the presence of several relaxation times for different oil components. The dielectric loss tangent is determined by the presence of acidic and alkaline additive ions. With

increasing oil operating time, the value of the Debye loss maximum increases and shifts to lower frequencies, which is caused by the appearance of dipole molecules and an increase in their content.

All oils are non-polar dielectrics with ionic conductivity and an exponential increase in conductivity with increasing temperature.

The polarization of non-polar dielectrics occurs as a result of charge displacement under the influence of an applied voltage. As can be seen from the experiments, with increasing temperature, the real part of the dielectric constant increases.

The activation energy of conductivity at direct current is determined using the Arrhenius formula:

$$\sigma_s = \sigma_{s0} \exp\left(-\frac{E_{a\sigma}}{kT}\right) \quad (5)$$

The activation energy of polarizability (dielectric constant) is determined using a formula similar to (5). Figure 4

shows the plots used to fit the linear equation to the above equation. On the conductivity graph, we can observe that changes occur at the critical temperature $T_c = 400$ K, which indicates a transition in the conductivity mechanism. On the one hand, the thermal activation energies obtained from the conductivity and dielectric constant do not differ significantly.

However, the conductivity activation energy of used oils increases from 0.389 eV to 0.480 eV compared with fresh oil (Table 1). In contrast, the activation energy of the dielectric constant of waste oils decreases from 0.423 eV to 0.394 eV. The activation energy of conductivity below 0.5 eV indicates that the samples have higher electrical conductivity than ionic conductivity [6].

The activation energies of ionic conductivity in the studied oils are determined not only by the viscosity of the dispersion medium, which limits the mobility of electric current carriers, but also by the dissociation energy of additives [13].

Application of Equation (3) and inversion of the integral transformation made it possible to find the distribution functions $G(T_i)$ of dielectric relaxation times for all studied oils at different temperatures (Figure 5). The relaxation time distribution functions are unimodal only at low temperatures. With increasing temperature, the distributions become multimodal because of the appearance of different polar molecules after the oxidation of oil hydrocarbons. These molecules have different relaxation rates, which are

also found in the complex form of Debye peaks in the $\text{tg}\delta(\omega)$ dependence (Figure 3).

By excluding the frequency ω from the dependence $\sigma(\omega)$ and $\epsilon(\omega)$, we can obtain a relationship between σ and ϵ for Shell Rimula 15W40 oil fresh and used at different temperatures (Figure 6).

From Figure 6 it can be seen that in various dielectric constants ϵ , conductivity σ does not depend on ϵ . The only exceptions are very small and numerous values of ϵ . The dependence curves for fresh and used oils at different temperatures are similar.

Excluding temperature from the dependences $\sigma(T)$ and $\epsilon(T)$, we obtain a relationship between σ and ϵ for Shell Rimula 15W40 oil fresh and used at different current frequencies (Figure 7). Here, the conductivity also changes sharply only at large and small values of ϵ . At intermediate values of ϵ , the conductivity changes, but not so much. The curves for fresh and used oils are similar to shape.

In the future, it is planned to study the concentration of wear particles in used motor oil using proton NMR spectroscopy and determine the elemental composition of oils using atomic emission spectroscopy for engine diagnostics.

4. Conclusion

Using broadband dielectric spectroscopy, the electrical characteristics of marine diesel lubricants were determined

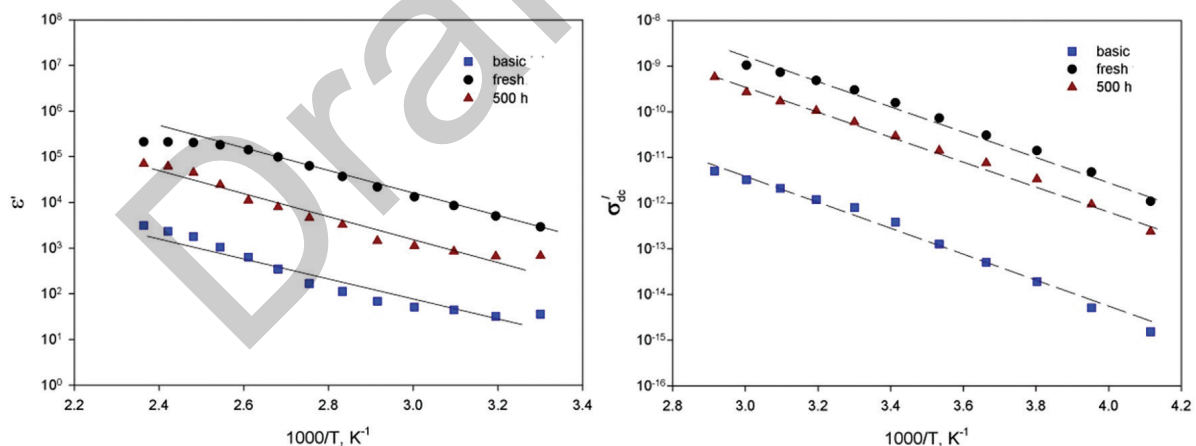


Figure 4. Dependences of dielectric constant ϵ (a) and specific conductivity σ (b) on temperature for base oil SN-150 (1), oil Shell Rimula 15W40 fresh (2), and oil Shell Rimula 15W40 used for 500 h (3)

Table 1. Activation energies of the DC conductivity and polarizability of oils

No	Activation energy	Base oil SN-150	Shell Rimula 15W40 fresh	Shell Rimula 15W40 used 250 h	Shell Rimula 15W40 used 500 h
1	E_{ac}, eV	0.605 ± 0.019	0.525 ± 0.020	0.406 ± 0.030	0.480 ± 0.015
2	E_{ac}, eV	0.466 ± 0.036	0.431 ± 0.020	0.293 ± 0.023	0.394 ± 0.028

at different temperatures and frequencies. The methods used in this study made it possible to study changes in the electrical parameters of used motor oil and establish a correlation between them.

- The presented results show good agreement with the available literature data and confirm the contribution that the proposed methods can make to the study of the characteristics of dielectric liquids.

- Analysis of the data obtained in the work made it possible to determine the distributions of the dielectric constant, electrical conductivity, and dielectric loss tangent.

- The correlations identified during the study can be used to select frequency ranges that will provide stable parameter values and maximum diagnostic ability.

- Establishing a connection between electrical and physicochemical parameters will allow us to create an effective algorithm for testing motor oils.

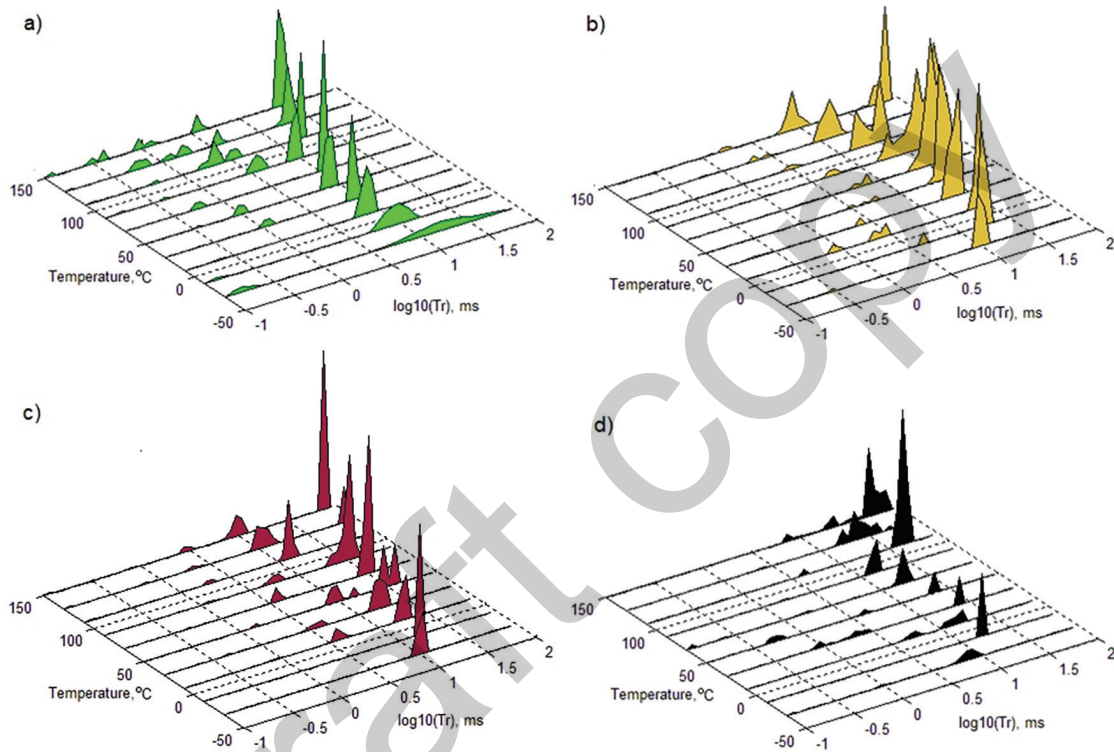


Figure 5. Distributions of relaxation times T_r depending on temperature: base oil SN-150 (a), Shell Rimula 15W40 fresh (b), Shell Rimula 15W40 used for 250 h (c), Shell Rimula 15W40 used for 500 h (d)

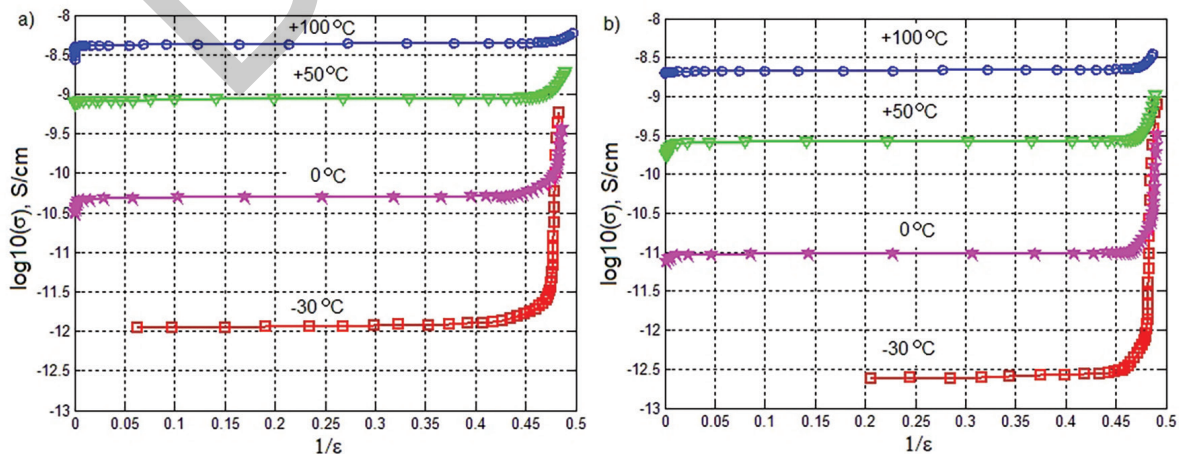


Figure 6. Relationship between the specific conductivity and dielectric constant for oil Shell Rimula 15W40 fresh (a) and used for 500 h (b) at different temperatures

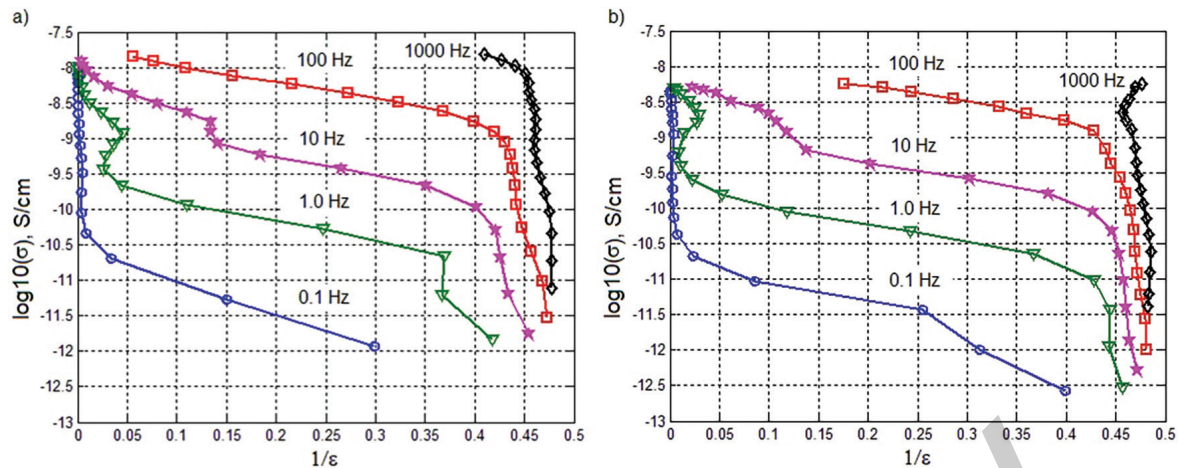


Figure 7. Relationship between the specific conductivity and dielectric constant for oil Shell Rimula 15W40 fresh (a) and used for 500 h (b) at different frequencies

Authorship Contributions

Concept design: M. Gapanovich, Data Collection or Processing: E. Rabenok, Analysis or Interpretation: O. Synashenko, E. Rabenok, M. Gapanovich, and N. Sinyavsky, Literature Review: N. Sinyavsky, Writing, Reviewing and Editing: N. Sinyavsky.

Funding: The research was conducted with the financial support of the Federal Agency for Fisheries of the Russian Federation (project no.: 122030900056-4) and state assignment no FFSG-2024-0003.

References

- [1] F. Kremer, and A. Schönals, *Broadband dielectric spectroscopy*, Springer Berlin Heidelberg, 2003.
- [2] S. Kardoš, and A. Pietriková, "Evaluation of motor oil characteristics and degradation factors for possibilities of continuous diagnostics". *Acta Electrotechnica et Informatica*, vsol. 16, pp. 20-24, Jun 2016
- [3] Fabian Schober, Andreas Küchler, Christoph Krause. "Oil conductivity - an important quantity for the design and the condition assessment of HVDC insulation systems". *FHWS Science Journal*, vol. 1, pp. 59-78, 2013.
- [4] I. V. Baturlya et al. "Dielectric characteristics of engine oils for power units, as measured by a capacitive sensor". *Reports of BSUIR (Belarusian State University of Informatics and Radioelectronics)*, vol. 3, pp. 103-106, 2016.
- [5] B. Xu, et al. "Impedance analysis of oil conductivity and pixel non-uniformity in electrowetting displays". *Results in Physics*, vol. 18, 103223, Sep 2020.
- [6] S. Barnoss, B. Melo, M. El Hasnaoui, M. Graça, M. Achour, and L. Costa, "Investigation of dielectric relaxation phenomena and AC electrical conductivity in graphite/carbon nanotubes/engine oil nanofluids". *Journal of Reinforced Plastics and Composites*, Aug 2020.
- [7] I. I. Popov, R. R. Nigmatullin, A. A. Khamzin, and I. V. Lounev, "Conductivity in disordered structures: Verification of the generalized Jonscher's law on experimental data". *Journal of Applied Physics*, vol. 112, 094107, Nov 2012.
- [8] X. Sidambarompoulé, P. Notinger, T. Paillat, J.-C. Laurentie, and P. Leblanc, "Study of electrical properties and estimation of average mobility and diffusion coefficients in several insulating liquids by dielectric spectroscopy". *International Journal of Plasma Environmental Science and Technology*, vol. 14, pp. 1-18, Dec 2020.
- [9] A. Wolak, R. Z'ywica, J. Molenda, and J. K. Banach, "Electrical parameters as diagnostics of fresh engine oil condition—correlation with test voltage frequency". *Sensors*, vol. 23, 3981, Apr 2023.
- [10] Y. Zhou, M. Hao, G. Chen, G. Wilson, and P. Jarman, "Study of the dielectric response in mineral oil using frequency-domain measurement". *Journal of Applied Physics*, vol. 115, 124105, Mar 2014.
- [11] I. V. Izmetstev, S.A. Konyaev, Changes in the dielectric properties of some motor oils during their destruction, *Bulletin of Perm University, 2012 Series: Physics Vol. 1 (19)* pp. 85-90.
- [12] Izmetstev I.V., Kozhevnikova O.A. Polarization and electrical conductivity of some motor oils as dispersed systems // *Bulletin of Perm University. Series: Physics*. 2016. No. 1 (32). pp. 43–50. doi: 10.17072/1994-3598-2016-1-43-50.
- [13] Sinyavsky N.Ya. Study of marine motor oils by radio spectroscopic and optical methods, *Materials of the VIII International Baltic Maritime Forum: in 6 volumes. Volume 1. Kaliningrad, 2020, Publisher: Kaliningrad State Technical University (Kaliningrad)*
- [14] N. Sinyavsky, O. Synashenko, and N. Kostrikova, "Application of relaxation times distribution of dielectric permittivity for marine engine oils analysis". *Journal of Eta Maritime Science*, vol. 11, pp. 209-216, Sep 2023.
- [15] G.F. Novikov, E.V. Rabenok, Ya.I. Estrin, Yu.A. Olkhov, E.R. Badamshina, Influence of low concentrations of carbon nanotubes on the electrical conductivity of polyurethane elastomer. // *Journal of Physical Chemistry*. 2014. t. 88. No. 10 P. 1605-1609
- [16] G. F. Novikov, E. V. Rabenok, L. M. Bogdanova, and V. I. Irzhak, "Dielectric properties of epoxy Ag-ED20 nanocomposite films synthesized in situ. Temperature dependence of through conductivity, "High-molecular compounds. Series A"". *Macromolecular Compounds (Series A)*, vol. 59, pp. 711-720, 2017.