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Marine Engine Oil Diagnostics by Means of NMR Spectroscopy and Relaxometry of Protons

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Abstract

The goal of this work is to investigate fresh and used marine engine oil by high-resolution ^{1}H nuclear magnetic resonance (NMR) as well as by NMR relaxometry with Laplace transform inversion. The largest decrease in the molar content of CH_3 groups was observed in used 10W40 oil, from 37.7% to 27.3%, and the largest increase in the content of CH groups was observed in 15W40 engine oil, from 8.8% to 11.5%. The inversion method based on standard deviation minimization and regularization (RILT) was used to obtain the distribution of relaxation times. It is demonstrated that the bimodal distributions of the longitudinal relaxation times practically differ very little between fresh and used oils. T_2 relaxation times for the used 10W40 oil (21 ms and 63 ms) shift to shorter values in the bimodal distribution when compared to fresh oil (25 ms and 89 ms). The T_2 relaxation times for the used M-4015 oil increased from 14 ms and 42 ms to 19 ms and 60 ms, respectively. This indicates a change in the mobility of the functional groups of macromolecules caused by a change in the viscosity of the used oil. It is proposed to use the NMR method of proton relaxometry and the distributions of relaxation times to diagnose marine engines using used motor oil.

Keywords: Marine motor oils, Diagnostics, NMR

1. Introduction

One of the primary tasks of the maritime industry is to improve the reliability, durability, and efficiency of machines and units. The global experience of operating marine diesel power plants demonstrates that, in addition to engine design and manufacturing technology advancements, the most important factor determining engine technical life is the quality of the fuels and oils used. Under normal operating conditions, the quality of the oil used for lubrication is one of the few ways to achieve a noticeable increase in engine durability and economy without incurring any tangible costs.

Typically, information on the aging of marine engine oils is usually obtained through a comprehensive laboratory analysis that determines the change in the main indicators typically used to assess the quality of the oil. The main physical and chemical properties determined in the laboratory are: flash point in an open crucible; density; water-soluble acids and alkalis; acidity; acid and alkaline numbers; water content, kinematic viscosity; conditional viscosity; coking capacity; the presence of mechanical impurities and their composition; and ash content.

Motor oils provide lubricating, thermal control, detergent, sealing, and anti-corrosion properties. These are all provided by motor oil. Many factors act on the lubricating oil while the engine is running, including high temperatures, fuel entering. The study of the processes of oil aging and mechanical impurity dispersion is critical for extending the engine's service life. lubrication temperature, the lubrication system, oxygen contained in the air, and foreign impurities. The oil's properties change as a result of the numerous physical and chemical processes that it goes through: the oil "ages" [1]. It darkens during operation, changes in viscosity, flash point, acidity change, molecular

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weight increases, and mechanical impurities of organic and inorganic origin appear. Oil oxidation products reduce reliability and increase engine wear. The engine ages much more rapidly in the engine than it does in the laboratory under artificial oxidation conditions. Studies of the group chemical composition of the oil depending on the duration of the engine operation showed that the contribution of aromatic hydrocarbons remains practically unchanged, but the contribution of resinous substances increases due to the oxidation of alkanic and naphthenic compounds.

Many studies have been conducted to investigate the relationship between changes in the basic physicochemical properties of oils and part wear [2]. This is a review of diagnostic and forecasting methods as well as the development of systems for monitoring the state of lubricating oils. However, the results of these studies are quite contradictory. A wide range of oils and additives used to improve its quality complicates the situation.

The issue of petroleum product quality control is critical because it affects the safety of operating environments and transportation safety. The current control methods are either complex and expensive or do not provide an unambiguous identification of the quality of petroleum products. Furthermore, standard methods for analyzing the quality of petroleum products typically necessitate a significant time investment. It is critical to develop new express methods for quality control and counterfeit detection using compact devices.

The efficient use of fuel and lubricants on ships is dependent on consistent quality control. The rationality of their use and environmental protection are also dependent on their quality. The rationality of their use and environmental protection are also dependent on their quality. The method of proton nuclear magnetic resonance (NMR) relaxometry with the inversion of the Laplace transform can be proposed as a new express method for non-destructive quality control.

The properties of petroleum products are analyzed by various physical and chemical methods, including radio-frequency spectroscopy methods. Most of these methods, however, are quite complex, costly, and time-consuming. The publication [3] is devoted to the creation of intelligent sensor systems for diagnostics and the development of online analysis methods for marine motor oil. A wide range of methods for analyzing oils during operation is presented in the handbook [4].

The work [5] aims to improve ship safety by employing effective methods for diagnosing marine diesel engines. The analysis of used motor oil provides critical information [6] about the condition of the engine.

The thermal degradation of fresh motor oils, base oils, and additives was determined using ^{1}H NMR spectroscopy, relaxometry, and diffusion methods in reference [7]. Only the base oil with no additives exhibits a significant change in the NMR spectrum after thermal treatment. According to low-field NMR relaxometry transverse relaxation is much more sensitive to changes in the dynamic behavior of molecules as temperature increases The T_2 relaxation time decreases during thermal degradation for both the base oil and the oil with additives, indicating that the degraded sample has molecular mobility. In contrast to the oil with additives, additional peaks appear in the base oil spectrum after thermal degradation in the region of 2.2-6 ppm and 7.3-8.8 ppm. These peaks are conditioned by new aromatic and hydrocarbon compounds resulting from the thermal degradation of the oil.

In [8], fresh and used motor oils exposed to the atmosphere were examined by NMR and other methods. The studies revealed new lines in the NMR spectrum for used oil in the range of 2.1-2.7 ppm and 6.8-7.2 ppm, which are due to the formation of new aromatic and aliphatic hydrocarbon products, respectively. The concentration of polycyclic aromatic hydrocarbons in used oil has been shown to be many times higher than in fresh motor oil.

In [9], various NMR results (^{1}H and ^{13}C 1D NMR, 2D correlation spectra, diffusion and relaxation experiments) are discussed and interpreted to gain insight into the aging process of motor oils. The article [10] explores approaches based on the gamma distribution model for processing NMR relaxometry and diffusometry data in the study of engine oil degradation. The work [11] is focused on studying the degradation of lubricating oil by changing the rate of proton spin-lattice relaxation using the magnetic field cycling method. The pros and cons of this technique are discussed.

In [12], we proposed using the NMR relaxation method with the Laplace transform inversion for the express analysis of petroleum products. The distributions of spin-lattice and spin-spin relaxation times T_1 and T_2 for low viscosity marine fuel, diesel fuel, M-100 fuel oil, and SN-150 and SN-500 base oils were determined using low-field NMR. The nature of the distributions for different petroleum products varies significantly, which is explained by the different composition of many hydrocarbons.

A method for determining the spin-spin NMR relaxation time of protons was proposed in publication [13] to estimate the service life of motor oils and control the degree of engine wear.

Several studies have been conducted in order to determine the relationship between changes in a number of the most important physicochemical parameters of oil and engine wear. However, the inconsistency of the obtained results causes us to proceed with caution.

The use of modern oils containing dispersant additives allows for a significantly increased service life in diesel engines. Only timely oil changes can ensure reliable engine operation with minimal wear of friction parts and the lowest consumption of lubricating oils. Premature oil changes also lead to increased engine wear.

In [12], to solve the problem of multicomponent distributions of relaxation times based on the method of minimizing the standard deviation and regularization [14], the generalized inversion algorithm [15] was used to separate the exponential decay of NMR signals.

Relaxometry is a broad category of NMR experiments that focus on measuring nuclear spin relaxation times to characterize the structural and dynamic properties of the sample. The main methodological difference between NMR relaxometry and other methods of relaxation in a weak field is that the data is analyzed in the time domain rather than the frequency domain analysis of the exponential decay or recovery of nuclear magnetization yields relaxation rates. The dynamics of rotational and translational diffusion, as well as chemical exchange processes, influence relaxation times. Multicomponent or multi-phase samples give samples of experimental data, which may contain areas with clearly different T_2 or T_1 values.

The paper [16] discusses various types of compact NMR relaxometers, typical pulse sequences, and applications for studying liquids, polymers, biological tissues, porous materials, etc.

Longitudinal relaxation T_1 relaxation and transverse relaxation T_2 carries information about internuclear distances and molecular motion correlation times. T_2 and the rate of spin-lattice relaxation measurements can be linked to different types of molecular fragment mobility.

At present, the development of various NMR methods in strong inhomogeneous constant and radio-frequency magnetic fields is increasingly progressing. Such NMR applications are offered, among other things, for testing various materials [17].

At the same time, NMR relaxometry provides information about the diffusion and molecular dynamics of substances and at the same time requires a minimum field homogeneity, in contrast to traditional methods of high-resolution NMR spectroscopy. Relaxometry in a weak magnetic field enables the use of small and portable devices as well as a diverse range of applications. In recent years, NMR relaxometry has received a new stimulus in connection with the development of stable algorithms for the numerical inversion of the Laplace transform, allowing it to obtain relaxation time distributions of relaxation times that carry information about the structure and dynamics of macromolecules [18].

The purpose of this work was to study fresh and used marine motor oils by high-resolution ^{1}H NMR as well as NMR relaxometry with Laplace transform inversion. This approach makes it possible to use the capabilities of both methods to determine the changes that occur in engine oil during the operation of a marine engine and solve the problem of engine diagnostics by means of used engine oil.

2. Methodology for Conducting Experimental Studies

High-resolution NMR spectra of hydrogen were obtained using a Varian 400 spectrometer in the Immanuel Kant Baltic Federal University's laboratory and processed with the MestReNova program. The proton NMR relaxation rates were measured on a Tecmag Apollo NMR-NQR spectrometer in a low magnetic field at a frequency of 13.65 MH and processed using the TNMR program. The relaxometer magnet is made up of two magnets that are 60x80x100 mm in size and are connected by a U-shaped magnetic circuit with a 25 mm gap. The magnetic field induction was 300 mT in the gap. The magnetic field inhomogeneity at the probe coil location was 0.1 mT/cm. The working coil of the probe measured 5.5 mm in diameter and 12 mm in length. A standard inversion-recovery pulse sequence was used to determine the distribution of T_1 spin-lattice relaxation times. The Carr-Purcell-Meiboom-Gill sequence was used to determine the distribution of T_2 spin-spin relaxation times. The Carr-Purcell-Meiboom-Gill sequence was used to obtain the distribution of T_2 spin-spin relaxation times. For the standard Carr-Purcell-Meibum-Gill pulse sequence, the NMR signal is described by the expression

$$M(t) = \int_0^\infty f_2\left(T_2\right) exp\left(-\tfrac{t}{T_2}\right) d\,T_2, \tag{1}$$

where $M(t)$ is the measured signal as a function of time. To measure longitudinal relaxation using the inversion-recovery method, the signal can be represented by the expression:

$$M(t) = \int_0^\infty f_1\left(T_1\right)\left[1 - kexp\left(-\tfrac{t}{T_1}\right)\right] d\,T_1, \tag{2}$$

where k=2 only for the case of complete inversion of the magnetization using the first RF pulse, $f_1(T_1)$ and $f_2(T_2)$ are distribution functions of relaxation times.

The study's subjects were marine oil, Total Disola M-4015 marine oil, intended for lubrication of medium and high-speed diesel engines, and engine oils 15W40 and 10W40.-4015 oil has a viscosity of 14cSt at 100 °C and a pour point of -9 °C. The viscosity of 15W40 and 10W40 oils at 100 °C is 12.6-16.3 centistokes, with a winter temperature limit of -20 °C and -25 °C, respectively. Samples of 10W40 and M-4015 oils were used in diesel engines for 300 hours. Samples of 15W40 oil were used for 250 and 500 hours.

The multi-exponential method of inversion of integral transformations according to the algorithm [15] was used in the work, as the samples under study are single-phase systems.

3. Results of Experimental Studies and Their Analysis

Marine lubricants, like other petroleum products, are made up of a diverse range of different substances. These are liquid hydrocarbons, as well as resins, asphaltenes, carbenes, and heteroatomic organic compounds to a lesser extent. in such multicomponent systems of paraffinic [for example, hexadecane (cetane) CH_3-$(CH_2)_{14}$-CH_3], naphthenic C_nH_{2n} series (for example, cyclodecane $C_{10}H_{20}$), and aromatic hydrocarbons (for example, alpha-methylnaphthalene $C_{10}H_7CH_3$) have different structures, molecular weight, and mobility of molecular fragments and molecules as a whole.

Paraffinic hydrocarbons have a linear or branched structure and can have up to forty carbon atoms in the chain. Naphthenes are mono- and polycyclic compounds in which carbon atoms are connected into cyclic structures by a single bond. Aromatic hydrocarbons are cyclic compounds that have an aromatic group attached to them.

Figure 1 shows high-resolution ^{1}H NMR spectra obtained for fresh and used 15W40 oil after 500 hours, respectively. The lines from hydrogen atoms, CH groups of paraffin and naphthenic chains, from CH_2 groups of paraffins, and CH_3 groups of saturated hydrocarbons are visible in the spectra. Both of these spectra (Figure 1), as well as those other petroleum products, are qualitatively similar and differ only in terms of intensity, width, and resolution. The spectra were integrated into the corresponding chemical shift regions to determine the quantitative composition of the samples' functional organic groups.

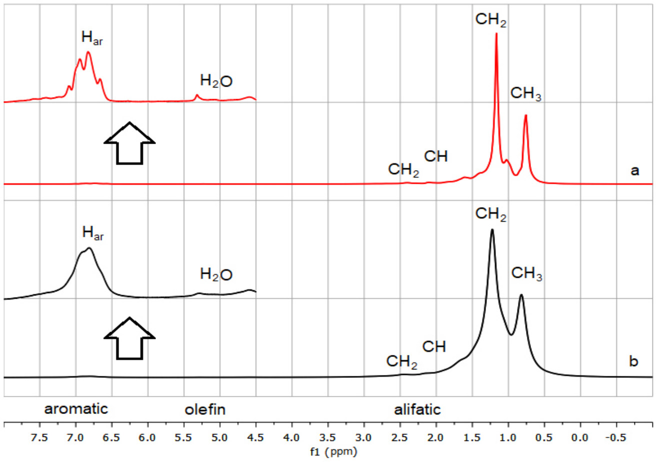

Figure 1. *^{1}H NMR spectrum (400 MHz) of the samples of fresh (a) and used for (500 h). (b) 15W40 marine engine oil. Signals of aromatic protons are shown at an enlarged scale*

As shown in Table 1 and Figure 2, the molar content of CH_3 organic groups decreases and the content of CH groups increases in aliphatic hydrocarbons. Aside from M4015 oil, the content of hydrogen atoms in aromatic har compounds increases in used oils.

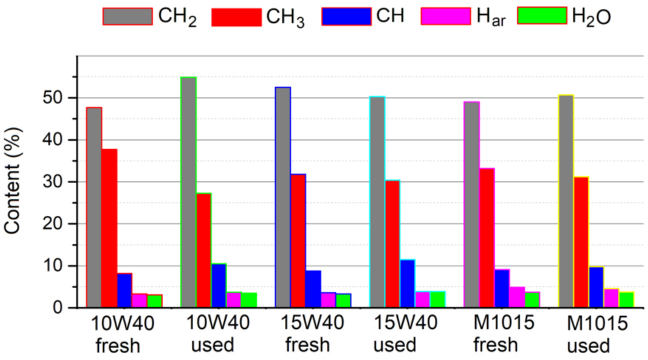

Figure 2. *Changes in the content of various organic groups in ^{1}H NMR spectra of fresh and used motor oils*

Table 1. *Modular content of functional organic groups in samples of fresh and used oils from 1H NMR spectra (400 MHz)*

Sample	H_{ar}	CH_2	CH	CH_3	H_20
Oil 10W40 (fresh)	3.3%	47.7%	8.2%	37.7%	3.1%
Oil 10W40 (used 300 hours)	3.7%	54.9%	10.5%	27.3%	3.5%
Oil 15W40 (fresh)	3.6%	52.5%	8.8%	31.8%	3.3%
Oil 15W40 (used 250 hours)	3.9%	50.3%	11.5%	30.4%	3.9%
Oil 15W40 (used 500 hours)	4.3%	50.3%	11.6%	29.7%	4.1%
Oil M4015 (fresh)	4.9%	49.0%	9.1%	33.2%	3.7%
M4015 oil (used 300 hours)	4.6%	50.7%	9.8%	31.2%	3.8%

The lines of the ^{1}H NMR spectra for fresh and used oils are most intense in the region of protons of aliphatic groups protons. The increase in the width of the lines in used oil is due to a change in its viscosity and density, as well as the fact that ferromagnetic particles appear in the oil during engine operation, changing the local magnetic fields. According to studies, the content of aromatic hydrocarbons in used oil generally increases when compared to fresh oil. There is also a redistribution of the molar content of aliphatic hydrocarbons' functional organic groups CH, CH2, and CH3.

The spectra of fresh and used motor oils show that there are no lines associated with the formation of new aliphatic and aromatic structures in the ranges of 2.2-6 ppm and 7.3-8.8 ppm. Förster et al. of [10] also came to the same result. This confirms the conclusion made in the publication [7] that additives affect the degradation of engine oil during engine operation. The NMR spectra of protons obtained in [10] are similar to the spectra shown in Figure 1. The largest decrease in the molar content of CH_3 groups from 37.7% to 27.3% is observed in used 10W40 oil and the largest increase in the content of CH groups from 8.8% to 11.5% in 15W40 engine oil.

When compared to fresh oil, both measured T_2 relaxation times for used 10W40 oil (21 ms and 63 ms) are shifted to shorter values (25 ms and 89 ms). The T_2 shifts to 15W40 oil. For used M-4015 oil roughly the T_2 relaxation times for used M-4015 oil are changed from 14 ms to 42 ms to 19 ms and 60 ms, respectively. This indicates an increase in the mobility of macromolecule functional groups caused by a decrease in the viscosity of the used oil.

The longitudinal T_1 relaxation times also have bimodal distributions and practically do not change for the studied used oils (30 ms and 100 ms) relative to the T_1 times for fresh oils. The average values of T_1 and T_2 relaxation times for fresh and used oils, obtained in [7] and [10], turned out to be close to those obtained in this study.

The results of studying high-resolution ^{13}C NMR spectra of motor oils show that these spectra have a significantly higher multiplicity than proton spectra. Simultaneously, the spectral lines of the used oil samples broaden insignificantly, and the ratio between the line intensities in the spectra hardly changes.

Engine oil properties change as a result of oxidation, decomposition, and thermal polymerization of hydrocarbons, which results in a change in the molar content of functional organic groups. The oil film oxidizes upon contact with heated parts of the cylinder and other parts. This leads to varnish formation and coking.

The times of longitudinal and transverse relaxation in NMR carries information about the times of correlation of different molecular motions. Measurements of the spin-spin and spin-lattice relaxation rates allow them to be correlated with the corresponding motions and are a reliable and fast NMR method for assessing the properties of materials [16].

Figures 3 and 4 show the results of a study of the distributions of T_1 and T_2 the relaxation times in 15W40 and 10W40 marine engine oils. The distributions of the relaxation times of fresh and used oil can be seen to differ from each other. The ratio of different hydrocarbons determines the relaxation time values. These macromolecules have different structures, molecular weights, and mobility of molecules and their fragments, which determine the relaxation times and the distribution characteristics. The different mobilities of the molecules also determine the multimodality of the distributions of spin-lattice relaxation times. Heavy molecules form short T_1 values, while light molecules cause long ones. The positions, width, and intensities of the peaks in the distributions depend not only on the composition of hydrocarbons but also on the presence and types of additives that improve certain properties of the motor oil, as well as on wear products.

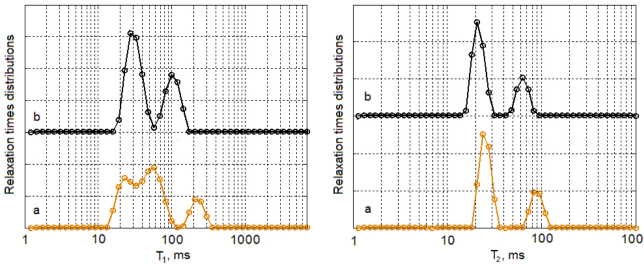

Figure 3. *Distributions of T_1 and T_2 relaxation times for fresh (a) and used for 500 hours (b) 15W40 oil*

In comparison to fresh oils, both peaks in the distribution of T_2 relaxation times shift toward shorter times in used motor oils. This could be due to an increase in the viscosity of used oils, which reduces the mobility of some hydrocarbons. The same happens with T_1 times for used 15W40 oil. The T_1 relaxation time peaks for used 10W40 oil practically do not shift in comparison to the peaks for fresh oil.

When analyzing relaxation times, it is necessary to consider their dependence on motor oil viscosity [10]. R2=1/T2 transverse relaxation rates are proportional to viscosity The higher the viscosity, the higher the transverse relaxation rate. Most often, the viscosity of engine oil typically increases as it degrades during operation. The oil's viscosity can rise for a variety of reasons, including incomplete combustion of the fuel-air mixture in the engine; thermal polymerization; oxidation, evaporation, sludge formation, water ingress into the oil; and mixing with air. The viscosity of the oil may increase due to the soot contamination and the formation of dissolved coke and oxides. This leads to viscous braking, poor lubrication of bearings, a decrease in engine power, a lack of smoothness in the set of revolutions, the appearance of a cavitation process, etc.

At the same time, thermal cracking may cause engine oil viscosity to decrease (destruction of oil molecules under the influence of high temperatures, i.e., the process opposite to polymerization). Shear deformation forces can cause destruction of macromolecules and reduce motor oil viscosity. Fuel can get into the lubricating oil, which also leads to a decrease in its viscosity. At low viscosity, a very thin oil film on rubbing parts leads to their intensive wear, engine overheating, the oil reduces cooling efficiency, and its oxidation increases.

Figure 5 depicts the distributions of T_1 and T_2 relaxation times for fresh and used M-4015 oil The lines shift here the region of longer times, indicating an increase in the mobility of molecular groups containing hydrogen atoms.

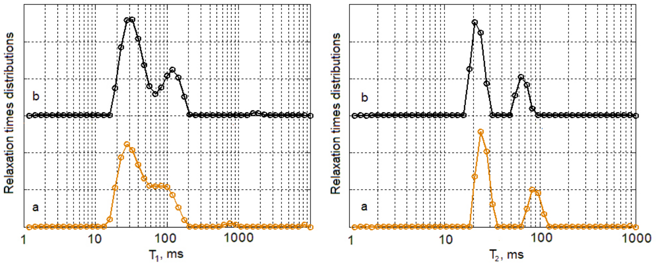

Figure 4. *Distributions of T_1 and T_2 relaxation times for fresh (a) and used for 300 hours (b) 10W40 oil*

Even unused engine oil contains a variety of substances including hydrocarbons blend, a viscosity modifier, additives (detergents, anti-corrosion, and so on.) that improve its properties. In fresh oil, the presence of thickening additives causes the formation of large particles (micelles). The viscosity modifier causes a change in the degree of aggregation in used oil.

Thus, depending on the causes (engine malfunctions), the influence on the distribution of relaxation times can change both in the direction of increasing T_1 and T_2 and in the direction of their decreasing. According to the nature of the T_1 and T_2 distributions, the level of aggregation or micellization of the viscosity modifier polymer decreases.

It can be assumed that the decrease in T_2 relaxation times in used oil is because proton relaxation times are very sensitive to the presence of ferromagnetic particles in liquids that appear in the oil during engine operation. Local magnetic fields change near these particles, which leads to a decrease in the relaxation time of protons of used engine oil molecules.

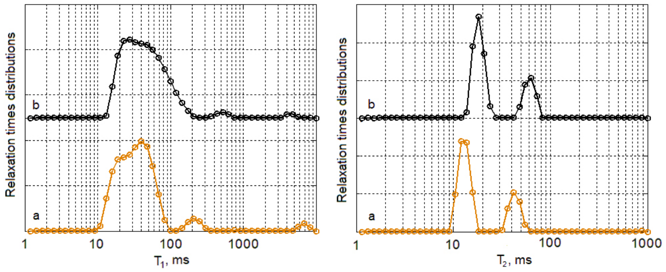

Figure 5. *Distributions of T_1 and T_2 relaxation times for fresh (a) and used for 300 hours (b) M-4015 oil*

4. Conclusion

In this work, samples of some fresh and used marine engine oils were experimentally studied by high-resolution ^{1}H NMR. It is shown that the largest decrease in the molar content of CH_3 groups from 37.7% to 27.3% occurred in used 10W40 oil, and the largest increase in the CH group content from 8.8% to 11.5% was observed in 15W40 engine oil.

Both obtained T_2 relaxation times for used 10W40 oil (21 ms and 63 ms) are shifted to a shorter range in the bimodal distribution when compared to fresh oil (25 ms and 89 ms). T_2 relaxation times for used M-4015 oil increased from 14 ms and 42 ms to 19 ms and 60 ms, respectively. This indicates an increase in the mobility of macromolecular functional groups caused by the decrease in viscosity. The distributions of longitudinal relaxation times also have a bimodal character (30 ms and 100 ms) and differ little between fresh and used oils.

The study's findings indicate that the NMR relaxometry method is appropriate for analyzing the state of engine oil and, as a result, for obtaining diagnostic data on the engine's state. In the future, we intend to use dielectric spectroscopy and magneto-optical methods to study and diagnose marine engine oils.

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Authorship Contributions

Concept design: N. Sinyavsky, Data Collection or Processing: I. Mershiev, Analysis or Interpretation: N. Sinyavsky, Literature Review: I. Mershiev, Writing, Reviewing and Editing: N. Sinyavsky.

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