Study of used marine oils by the photon correlation spectroscopy method

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Abstract. In this paper, we investigate the possibility of using the method of photon correlation spectroscopy for diagnostics of marine engines based on used engine oil in order to improve efficiency and safety of operation of sea vessels. The study used the dynamic light scattering (DLS) method to measure correlation functions and then to obtain distributions of correlation times, diffusion coefficients and particle sizes. To invert the Laplace transform, a method based on standard deviation minimization and regularization (RILT) was used, modified to find the distribution of correlation times. It has been found that the distributions of the hydrodynamic radii of the particles for fresh and used oils differ significantly. By the nature of the distribution of large particles, it has been found that the level of aggregation or micelle formation of the polymer of the viscosity modifier decreases in waste oils. It is shown that the dynamic light scattering method makes it possible to obtain parameters suitable for analyzing the state of engine oil and for obtaining diagnostic data on the state of the engine for used oil.

1. Introduction

The overwhelming majority of ship traffic and marine power engineering is based on turbocharged piston diesel engines. Marine engines are very complex technical objects with many important functional systems that affect the current technical condition of a marine engine, including fuel consumption and failures that threaten the safety of the ship. There is a direct link between reliability of these engines, safety of navigation and operating costs. Improving diagnostic methods can improve and increase reliability of ship engines, maintenance, economic operation, as well as affect safe operation of ships.

Marine diesel engine oil can be used as a medium for diagnosing component malfunctions since it contains particles resulting from wear. Knowledge of the materials of mechanism construction based on the results of the analysis of used oil makes it possible to identify a unit that needs repair or replacement. Changes in the properties of the oil and its composition, depending on the duration of engine operation, make it possible to use them for troubleshooting. At the same time, delivery of equipment to the place of repair, dismantling of units and assemblies is not required. The presence of lead, tin and iron in the waste oil indicates wear on the plain bearings and the crankshaft. Engine overheating, fuel entering the oil, and the presence of abrasive particles in it cause wear on pistons and cylinders. Piston ring wear is detected by the presence of chromium in the engine oil, etc.
The work (Zhu et al. 2013) is devoted to a review of methods and systems for monitoring the condition of lubricating oils, diagnostics and forecasting. The considered methods are analyzed and divided into four categories: electrical (magnetic), physical, chemical and optical methods. The ultimate goal of all sensor systems under development is to achieve online monitoring of the condition of the lubricating oil on board and predict the remaining service life. The development of online analysis of marine lubricating oil and the development of intelligent sensor systems in diagnostics is discussed in the publication (Knowles and Baglee 2012). The article describes a developed system that includes real-time condition monitoring sensors that monitor the properties of the lubricating oil and special monitoring software.

A wide range of in-service oil analysis methods are presented in the handbook (Zhao 2014). In (Berestova 2002), a technique for monitoring the condition of a diesel engine by the parameters of engine oil measured by infrared spectroscopy and ferrography is proposed.

The work (Witkowski 2017) is devoted to improving the operational safety of ships by improving diagnostic methods for a marine diesel engine. In this work, to diagnose diesel injection systems, the author used the heat release characteristics of ship engines. The work (Sinyavsky et al. 2018) investigated possibilities of using NMR relaxometry with the Laplace transform for quality control and identification of marine fuels and oils. The specificity of the distributions of the relaxation times of the studied petroleum products is shown; recommendations are formulated for the creation of promising control and measuring equipment.

Photon correlation spectroscopy is an indirect method for measuring the physical parameters of a medium. In order to determine the quantities of interest, for example, the particle size distribution in a liquid or the diffusion coefficient distribution, the measured autocorrelation of the scattered light intensity fluctuations must be subjected to further mathematical processing.

Dynamic Light Scattering (DLS) (User's manual 2020) is a widely used method for determining particle size in colloidal systems. The resolution of the simple one-angle method is limited by the low information content of the initial data and the ambiguous nature of their analysis.

A multi-angle approach proposed in (Bryant and Thomas 1995) provides significantly more reliable particle size determination, allowing better resolution of closely spaced components in multimodal distributions. Multi-angle dynamic light scattering (MDLS) can provide more accurate particle size distribution information than single angle dynamic light scattering. In MDLS data analysis, the intensities of the autocorrelation functions of light for each scattering angle are combined with the appropriate weighting factors.

Used engine oil is a polydisperse system, for which the photon correlation spectroscopy method allows one to obtain distribution of the effective particle radii of each component and contribution of each component of the system to the scattering signal (Sinyavsky et al. 2020). By the nature of the decay of the autocorrelation function for radiation scattered by impurity particles in oil, one can determine the self-diffusion coefficients of the particles and calculate their hydrodynamic radii. Since the used oil contains a suspension of particles with different effective radii, a special mathematical algorithm can be used to determine the particle size distribution curve. This algorithm must find a solution to the ill-posed inverse problem.

The DynaLS program (Goldin 2002) uses the SVD (Singular Value Decomposition) method as the main analysis tool. Singular value expansion is an effective tool for solving unstable systems of linear equations (ill-conditioned problems). To limit the solution to non-negative values, it is also very important to use the non-negative least squares (NNLS) algorithm.

The most famous program using the Tikhonov regularization method for processing experimental data in the dynamic light scattering method is a program using the CONTIN algorithm (Provencher 1982). To determine the distribution of effective particle radii from the experimental correlogram, Danovich and Serdyuk (1983) also proposes Tikhonov's regularization in the SIPP (Solution Ill-Posed Problems) program.

The purpose of this work was to study some fresh and used oils by the method of dynamic light scattering to determine the changes occurring with oil during the operation of ship equipment, and to
clarify the relationship of these changes with malfunctions of the units. There are no publications on such studies in the literature.

2. Experimental research procedure

The scattered light of a single-mode helium-neon laser was recorded in real time using a photomultiplier tube. A Photocor-FC correlator was used to measure the scattered light autocorrelation function. Photocor software (User’s manual 2020) was used to control the measurement process and processing of measurement results. The correlation function for light scattering at an angle $\theta$ will have the following form for a polydisperse medium:

$$ G(t) = \int_0^{\infty} P(T_d) \exp \left(-\frac{t}{T_d}\right) dT_d, $$

where $T_d$ – decay time. The particle diffusion coefficient was found as:

$$ D = \frac{1}{T_d q^2}, $$

where the scattering vector

$$ q = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}, $$

$\Theta$ – scattering angle, $n$ – refraction index, $\lambda$ – emission wave length. The effective radius of a particle is determined by a well-known formula, which depends on temperature, diffusion coefficients, and fluid viscosity:

$$ R_h = \frac{kT}{6\pi \eta \bar{D}}. $$

where $\eta$ - dynamic viscosity. Integral equation (1) actually describes the relationship between the measured data obtained during the experiment and the physical properties of the investigated liquid. If the distribution of decay times $T_d$ is known, then the distribution of the diffusion coefficient or the particle size distribution can be easily calculated using formulas (2) and (4).

Formula (1) can be represented as:

$$ G(t, \theta) = \int_0^{\infty} f(R_h) \exp \left[-\frac{\Omega(\theta) t}{R_h}\right] dR_h, $$

where $\Omega(\theta) = \frac{16\pi kT (\frac{\eta}{\lambda})^2}{3\eta} \sin^2 \frac{\theta}{2}$. Formula (5) is written without taking into account the constant component and the fraction of light scattered at an angle $\theta$ according to the Mie scattering theory (Mie 1908).

The intensity of the light scattered by the sample depends on the size and refractive index of the particles, as well as on the angle at which the scattering is detected. This means that not all particles of different sizes in the same sample are detected with the same sensitivity. Traditional single angle DLS measurement can give different particle size distributions for a mixture depending on the angle at which the measurement is made. In MADLS measurements, correlation data for multiple detection angles are combined using Mie theory to obtain a higher resolution particle size distribution.

To calculate the particle size distribution in used engine oil from the measured correlation function, we used the RILT program (Marino 2004) based on the CONTIN algorithm. The program has been modified to determine the correlation functions.

The samples for the study were M-20G2SD marine oil, Mobil 5w50 synthetic oil, and AUP (MG-22-B) marine hydraulic oil. AUP oil is used as a hydraulic fluid in marine engineering. The measurements were carried out without using a solvent and with a solvent. Liquid CsL.4 paraffin was used as a solvent. Waste oils are not transparent; therefore almost all measurements were carried out using a solvent. Concentrations of solutions: AUP oil (spent within 500 hours) - 6.25%, Mobil oil (spent within 100 hours) - 1.6%, marine oil M-20G2SD (spent within 300 hours) - 0.5%.
3. Experimental research results and their analysis

An important characteristic of the interaction of radiation with a medium is a scattering indicatrix - a curve that graphically displays the dependence of the scattered light intensity on the scattering angle. The form of this dependence is determined by the size and shape of the scattering particles. In general, the scattering indicatrix is not expressed in an explicit function and is described in the table. When solving many applied problems, simplified approximations of the scattering indicatrix are used. The most common of such approximations is Henyey-Greenstein (Henyey and Greenstein 1941) function:

\[
\Phi(\theta) = \frac{1-g^2}{4\pi} \frac{1}{(1+g^2-2g\cos\theta)^{3/2}},
\]

(6)

where \( \theta \) – scattering angle, \( g \) – parameter determining the main characteristic of the indicatrix – its elongation. The parameter \( g \) is determined by the size of the scattering particles, the radiation wavelength, and the particle size distribution. When constructing the indicatrix to take into account the correction for the value of the scattering volume, the intensity was multiplied by \( \sin \theta \).

In order to exclude the influence of the solvent on the measurement results, the experiment was carried out, inter alia, according to the angular and backscattering scheme. The scattering indicatrix for fresh and used AUP oil (without solvent), approximated using formula (6), is shown in Fig. 1. Due to the opacity of the used oil, there is a considerably intense backscattering of light.

![Figure 1. Scattering indicatrixes of fresh (red) and used (blue) hydraulic oil AUP (MG-22-B).](image)

Figure 2 and Figure 3 show correlation functions for fresh and used AUP marine hydraulic oil without solvent at different scattering angles. As can be seen from the figure, the correlation times are practically independent of the scattering angle for both fresh and used oil. For used AUP oil, the correlation time is shorter than for fresh oil. The results of studying the distribution of the hydrodynamic radii of particles for different scattering angles for fresh and used AUP hydraulic oil are illustrated in Figure 4. It can be seen that distributions for used and clean oils differ from each other. For used oil, the values of hydrodynamic radii are significantly less than for fresh oil. As the scattering angle increases, the \( R_h \) distributions change from monomodal to bimodal. \( R_h \) values are determined by the ratio of the average molecular weights of different hydrocarbons, the viscosity of the oil, the presence of additives and viscosity modifiers, metal particles, soot, water, etc.
Changes in the particle size distribution in used oil are associated with a change at the molecular level (thermal polymerization, oxidation, evaporation, thermal cracking) and with changes caused by contamination (formation of soot, ingress of water and air, metal particles of rubbing parts).

Figure 5 and Figure 6 show distributions of hydrodynamic radii for different scattering angles for fresh (a) and used (b) M-20G2SD marine oil and Mobil 5w50 oil. In both cases, with an increase in the scattering angle $\theta$, the hydrodynamic distribution of radius of oil particles increases and $R_h$ of used oils is bigger than $R_h$ of fresh oils.

![Figure 2. Correlation functions for different scattering angles for used hydraulic AUP oil.](image)

![Figure 3. Correlation functions for different scattering angles for fresh hydraulic AUP oil.](image)

Comparison of the distributions of the hydrodynamic radii of fresh and used AUP, Mobil, and M-20G2SD oils (in solvent) obtained at $\theta=\pi/2$ is shown in Figure 7. All distributions are not unimodal. The used AUP and M-20G2SD oils have an increase in the hydrodynamic radii $R_h$ in comparison with fresh oils, in contrast to Mobil oil, where the opposite is true, the $R_h$ values of the used oil are lower.

![Figure 4. Distributions of hydrodynamic radii for different scattering angles for fresh (a) and used (b) AUP hydraulic oil.](image)

When analyzing the distribution of the hydrodynamic radii of particles, it is important to take into account their dependence on the viscosity of oils. During operation, engine oil degrades and in most cases its viscosity increases. The reasons for the increase in oil viscosity are: violation of the combustion efficiency of the fuel-air mixture, thermal polymerization of the oil, oxidation, evaporation, sludge
formation, water entering the oil, mixing with air. The oil viscosity can increase due to the formation of dissolved coke and oxides, contamination with soot. This leads to frictional brake, to insufficient lubricant supply to the bearings, to a drop in engine power, to a violation of the smoothness of the speed set, the appearance of a cavitation process, etc. However, the oil viscosity can also decrease, this is due to thermal cracking (thermal destruction of oil molecules), i.e. the opposite polymerization process. Polymer macromolecules can be destroyed by shear forces, and this leads to a loss of viscosity. Finally, the viscosity of the engine oil drops due to fuel contamination. Low viscosity results in a too thin oil film, which, as a result, causes severe wear at the friction points, excessive heat generation, loss of oil cooling efficiency and an increase in the oxidation process.

As can be seen from Table 1, the average hydrodynamic radii of particles of used oils M-20G2SD and AUP in the solvent Csl.4 (liquid paraffin) are significantly larger than for fresh oils. Due to the bimodality (multimodality) of the distributions of the correlation times, all values in Table 1 have two (three) values.

But for Mobil oil, the opposite is true: in used oil, the average hydrodynamic radius of particles is smaller than that of fresh oil. The particle diffusion coefficient depends on the correlation time and the scattering vector. The smallest diffusion coefficients were found for fresh Mobil oil and used M-20G2SD oil.

| Substance                               | Correlation time $\tau$, ms | Diffusion coefficient $D$, cm$^2$/s·$10^{-10}$ | Hydrodynamic radius $R_h$, nm |
|-----------------------------------------|----------------------------|-----------------------------------------------|-------------------------------|
| Marine engine oil M-20G2SD (fresh)      | 12; 250                    | 19; 0.9                                       | 25; 562                       |
| M-20G2SD oil (used)                     | 40; 425                    | 5.6; 0.5                                       | 79; 794                       |
| Mobil 5w50 oil (fresh)                  | 40; 520                    | 5.6; 0.4                                       | 63; 1259                      |
| Mobil 5w50 oil (used)                   | 10; 60; 620                | 22; 3.7; 0.4                                   | 25; 158; 1585                 |
| Marine hydraulic AUP oil (fresh)        | 10; 900                    | 22; 0.2                                       | 32; 1995                      |
| AUP oil (used)                          | 25; 200                    | 9; 1.1                                        | 63; 398                       |
| Liquid paraffin Csl.4 (solvent)         | 5; 540                     | 45; 0.4                                       | 20; 1200                      |

Figure 5. Distributions of hydrodynamic radii for different scattering angles for fresh (a) and used (b) M-20G2SD marine oil.

Figure 6. Distributions of hydrodynamic radii for different scattering angles for fresh (a) and used (b) Mobil 5w50 oil.
Even fresh engine oil is a complex system of many substances: base oil containing a mixture of different hydrocarbons, a viscosity modifier, additives (detergents, anti-corrosion, etc.). Large particles scatter light better, and the intensities of the peaks associated with them in the distributions are bigger. As a result, even a small amount of large particles in the oil can mask the detection of small particles, even if they are large. Large particles in oil are usually micelles of the viscosity modifier polymer and dust.

As seen from Figure 7, the size distributions for fresh and used oils have different polydispersities. The nature of the distributions of the hydrodynamic radii of particles in the studied samples is predominantly bimodal. The distribution peaks are located in two main domains: from 10 nm to 100 nm and above 100 nm, respectively. The presence of viscous-thickening additives in fresh oils leads to the appearance of large particles (micelles) in the oils, and on the distributions of the hydrodynamic radii of the peaks in the second domain. In used oils, these peaks either decrease in magnitude (Mobil, AUP oils), or disappear altogether, which corresponds to a state of low aggregation or micelle formation of the viscosity modifier polymer. The level of aggregation of the viscous-thickening polymer (viscosity modifier) changes in used oils.

Figure 7. Distributions of hydrodynamic radii for the studied oils in solvent: a – fresh, b – used.

4. Conclusion
The in this work, some fresh and used marine oils have been investigated by the method of photon correlation spectroscopy, which made it possible to obtain the distributions of correlation times, diffusion coefficients and hydrodynamic radii of particles of these substances. The reasons leading to changes in these distributions in used oils have been analyzed. The effect on particle size distribution of viscosity is shown, which, depending on the reasons (engine malfunctions), can change both upward and downward. By the nature of the distribution of large particles, it has been established that the level of aggregation or micelle formation of the polymer of the viscosity modifier can decrease in used oils. Compared to fresh oil, used oil has an increase in the content of aromatic hydrocarbons; in addition, due to the oxidation of naphthenic and alkane hydrocarbons, as a rule, the average molecular weight of the oil changes, which manifests itself in the distributions of diffusion coefficients and hydrodynamic radii. The results of the study performed show that the method of dynamic light scattering makes it possible to obtain parameters suitable for analysing the condition of engine oil and for obtaining diagnostic data.
on the condition of the engine for used oil. The development of new diagnostic methods for ship engines is the basis for creating a method for detecting defects at an early stage of their formation, thereby improving the efficiency of preventing malfunctions and ensuring navigation safety.

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