



Research Article Received: December 3, 2024

Accepted: December 17, 2024

ISSN 2658-5553 Published: December 26, 2024

Sulphur content in engine oil: Method for determining the amount

Karelina, Maria Yurievna¹ Sukhodolya, Alexandr Valerievich² Prusov, Evgeny Sergeevich³ Taldykin, Dmitry Sergeevich⁴

¹ State University of Management, Moscow Automobile and Road Engineering State Technical University, Moscow, Russian Federation; <u>karelinamu@mail.ru</u> (K.M.Y.) ² Moscow Automobile and Road Engineering State Technical University, Moscow, Russian Federation; <u>sualv@mail.ru</u> (S.A.V.)

3

⁴ State University of Management, Moscow Automobile and Road Engineering State Technical University, Moscow, Russian Federation; <u>dima.dima.taldykin@mail.ru</u> (T.D.S.) Correspondence:* email <u>dima.dima.taldykin@mail.ru</u>; contact phone +79030286697

Keywords:

Agricultural machinery; Engine oil; Methodology for determining the amount of sulphur; Machinery operation; Extension of the service life of the rolling stock fleet

Abstract:

The object of the study is engine oil for internal combustion engines of agricultural machinery, with a focus on determining the content of sulphur and its compounds, such as sulphoxides and sulphides, which have a significant impact on the performance of oils. The research method involves the use of high precision titration techniques using specialised reagents and instruments to accurately measure sulphur concentrations. The obtained results demonstrate that the increased content of sulphur-containing compounds in motor oils leads to accelerated engine wear and increased negative impact on the environment. Application of the proposed methodology allows effective control of sulphur content, which contributes to optimisation of engine operation and reduction of machinery downtime. Thus, maintaining the optimal quality of engine oil is a key factor for increasing the service life of internal combustion engines and improving their efficiency in the agro-industrial complex.

1 Introduction

In the course of operation of agricultural machinery, parts coming in for overhaul reveal a wide range of defects caused by both design deficiencies of individual assemblies and units and operating conditions. The most significant factors influencing accelerated wear and failure of parts include non-compliance with the rules of operation, insufficient or untimely maintenance, as well as poor quality repair. In turn, compliance with recommended operating conditions, regular and quality maintenance and timely repairs help to reduce the rate of natural wear and damage to parts, extending their life and the life of the machine as a whole [1].

Violation of operating conditions and insufficient qualification of personnel, as well as poor quality of maintenance and repair lead to intensification of negative processes in interfaces, assemblies and mechanisms, which causes the appearance of new defects or aggravates existing ones [2]. For example, untimely elimination of backlashes in adjustable joints, excessive growth of clearances, weakening of fasteners and violation of mutual arrangement of parts in assemblies and mechanisms have a negative impact on the performance of not only individual components, but also the entire machine as a whole.

Gross violation of technical operation rules can lead to serious accidents accompanied by deformation and twisting of parts, deep scoring and grooves on working surfaces, cracks, chips and



breakages [3]. However, the introduction of modern maintenance systems for agricultural machinery allows to significantly reduce the frequency of such defects and practically eliminate them.

The most common cause of defects is natural wear caused by friction forces, fatigue of surface layers of metal, as well as the impact of loads exceeding the design loads, which leads to loss of rigidity or changes in the mutual position of parts in assemblies.

Despite the introduction of maintenance systems to reduce the probability of serious defects, a significant proportion of failures and breakdowns of agricultural machinery can be related to the condition of lubricants. The use of poor-quality oil or its untimely replacement has a direct impact on the wear of parts and assemblies, leading to the appearance of defects in critical friction zones and interfaces. Oil that has lost its operational properties loses its ability to provide effective lubrication and heat dissipation, resulting in overheating, increased friction and premature wear of components [4].

Studies show that the deterioration of oil lubrication properties during operation is due to the accumulation of contaminants, oxidation products and mechanical impurities that have an abrasive effect on the contact surfaces. Untimely oil change, especially under severe operating conditions such as increased dustiness or high loads, multiplies the probability of serious defects such as scoring, jamming of moving parts, corrosion and metal destruction.

Thus, oil quality control and timely maintenance are key factors affecting the reliability and longevity of agricultural machinery [5]. It is therefore necessary to develop and implement a methodology to accurately and quickly determine the current state of the lubricant, assess its suitability for further use and predict when it needs to be replaced. Such a methodology should include a comprehensive analysis of oil for contamination content, oxidation degree, residual life of additives and viscosity characteristics, which will minimise the risk of failures and extend the service life of both individual parts and the whole unit.

In the course of the study, the main breakdowns of agricultural machinery parts were analysed, which is presented in the following figure 1 [6].



Fig. 1 - Analysis of failure of agricultural machinery parts

The presented pie chart analyses the distribution of automotive equipment failures by main systems and units, which allows to identify the most vulnerable elements in vehicle structures. The largest share in the distribution of failures is occupied by the engine, which accounts for 29% of all failures. This high figure can be associated with wear of moving parts of the engine, overheating, insufficient lubrication and other factors that directly depend on the quality and condition of engine oil. Use of poor-quality oil, contamination or untimely replacement can lead to increased friction, rapid wear of parts and, as a result, serious engine damage.

The braking system also accounts for a significant proportion of the total failure rate of approximately 24%. Failures in this system can include worn brake pads and discs, leaking or contaminated brake fluid, and problems with hydraulic and mechanical components. Inadequate maintenance of the brake system and failure to change oil and lubricants regularly can lead to reduced braking performance, increased wear and tear, and eventually failure of critical system components [7].



Next, wheels and bodywork take up 12% each. Wheel-related breakdowns may include damage to tyres, rims or bearings caused by incorrect tyre pressure or poor road surfaces. Body failures are usually related to corrosion, damage due to external factors and wear and tear due to frequent use. Electrical equipment, which accounts for 10 per cent of breakdowns, can fail due to faulty components, improper installation or operation in high humidity and temperature conditions [8].

Smaller percentages of failures are associated with steering (1%), suspension (4%), transmission (4%) and light signalling system (4%). These systems are less likely to fail, which may be due to both their relatively lower operational load and less frequent exposure to critical conditions that contribute to their damage.

Thus, analysis of the data in the graph indicates that a significant proportion of engine and brake system failures in automotive vehicles can be attributed to the use of poor quality oil or untimely oil changes. Poor quality or unsuitable oil leads to increased friction between moving parts, overheating, corrosion and accelerated wear. Regular maintenance, including oil change with high quality oil that meets the requirements of operation, is a key factor in improving the reliability of automotive equipment, extending the life of its components and reducing the frequency of breakdowns.

Authors of the scientific article [9] argue that the use of sulphur-containing components in engine oil additives, such as alkylphenols, leads to the need for a more detailed study of their effect on oil performance. Despite the presence of anti-corrosion and neutralising properties in additives, sulphurcontaining compounds can adversely affect the engine, especially at high temperatures where sulphuric acids can form. This, in turn, can accelerate corrosion of metal parts and reduce equipment life. It is important to recognise that inadequate neutralisation of such compounds can lead to serious consequences for the engine, including accelerated wear and increased operating costs. This makes it necessary to carry out a qualitative analysis of the sulphur content in oil to ensure its safety and compliance with modern technical requirements.

In the works [10] various causes of engine oil deterioration and engine failure have been studied, but not enough attention has been paid to the quantitative analysis of sulphur in the oil itself. The main focus has been on sulphur in automotive petrol and its influence on the physicochemical parameters of the oil, which is certainly important. However, the oil itself can also contain sulphur compounds, which can cause corrosion and reduced oil performance. The study focuses on alkaline number losses and sulphuric acid formation as a result of engine operation, but the analysis of sulphur content is limited to petrol only, while its concentration in engine oil also plays a key role in the degradation of its properties. Low sulphur values in petrol of environmental class 5 do help to reduce alkalinity losses, but this does not eliminate the need for systematic monitoring of the sulphur content directly in the oil. Thus, a shortcoming of the study is the lack of a full-fledged quantitative analysis of the sulphur content in the engine oil itself, which is necessary for a more accurate understanding of the causes of degradation of its performance properties and for the development of recommendations to increase oil and engine life.

In the study [11] the use of refinery waste and petrochemical by-products is considered, which could find application not only in marine fuels, but also for agrotechnical purposes, for example, for agricultural machinery. However, a key shortcoming of the work is the lack of attention to detailed analysis of the sulphur content in fuels and its impact on performance, especially for agricultural machinery. While the authors note that reducing the sulphur content below 0.1% can impair the protective properties and stability of fuels, the main focus is on the toxicity of the products and the increased content of metals such as zinc, calcium and phosphorus, leading to increased ash content. For agricultural machinery this is of particular importance, as engine oils and fuels with high metal and sulphur content can accelerate the wear of engines and other machinery components, affecting its reliability and durability. At the same time, reducing the sulphur content without corrective additives can weaken the anti-corrosion properties of fuel, which is especially critical for agricultural machinery operating in difficult conditions. A shortcoming of the study is that there was no in-depth analysis of the effect of different sulphur levels on the performance properties of fuels for agricultural machinery. An accurate analysis of sulphur content and its impact on equipment durability and performance would help to develop fuels that meet the specific requirements of agriculture, which could significantly reduce operating costs and increase equipment life.

In the research paper [12] modified alkylphenol additives to engine oils containing sulphur, nitrogen and boron are presented, which demonstrates their high anticorrosion, antioxidant and tribological properties. However, a drawback is the lack of detailed analyses of the influence of sulphur content on the performance of oils, especially in the context of agricultural machinery. For agricultural machinery operating in harsh environments, the sulphur content of additives can significantly affect the durability and performance of engines and other mechanical components. Although synthesised additives have

Karelina, M.; Sukhodolya, A.; Prusov, E.; Taldykin, D.

Sulphur content in engine oil: Method for determining the amount;



shown high performance and applicability in a variety of engine oils, it is important to further investigate how the sulphur content of these additives affects the performance of oils under real-world conditions in agricultural machinery. Sulphur, despite its positive effect on antioxidant properties, can contribute to the formation of sulphur compounds, which ultimately leads to corrosion of metal surfaces and reduced service life of machinery. Thus, the key shortcoming of the study is the insufficient elaboration of the issue of sulphur content and its influence on the durability and performance of oils in specific operating conditions of agricultural machinery. A more detailed analysis would allow to adapt additives for agricultural machinery, ensuring their reliability and reducing operating costs.

The main corrosion of engine parts is caused by sulphur compounds contained in fuel. It should be noted that the sensitivity of engines of different designs to sulphur corrosion is different depending on the heat output and litre capacity of the engine. High-powered, high-speed diesel engines are more susceptible to sulphur corrosion than low-speed engines [13].

Combustion of the sulphur contained in the fuel produces sulphur dioxide (S02) and a small amount of the more corrosive sulphur dioxide (S03). With excess oxygen and high temperature, S02 converts to S03 in large quantities, so as engine heat increases, there is more intense gas corrosion of the cylinder head, first compression ring and exhaust system. As the temperature decreases, this deterioration decreases [14]. However, when the temperature of engine parts is significantly reduced, severe liquid corrosion is observed, which is caused by sulphur oxides when they dissolve in water. When S02 and S03 dissolve in water, sulphuric and sulphuric acids are formed, which cause electrochemical corrosion of metal.

Liquid corrosion is particularly severe in cold weather during start-up modes, when the possibility of water vapour condensation increases. Fuel combustion products contain sulphur oxides and water vapours (from fuel hydrogen combustion), at temperatures below 100 °C water condenses and dissolves acid oxides. The greater the penetration of gases into the engine crankcase and the higher the sulphur content of the fuel, the greater the wear from liquid corrosion. The occurrence of liquid corrosion is influenced by the engine operating mode. In lightly loaded engines at low cooling water temperature, liquid corrosion occurs, causing mainly wear of bearings [15]. This occurs when the vehicle is travelling in a large, congested city (low speeds, frequent stops). Tractor engines, usually operating at close to rated load, are more susceptible to gas corrosion. Consequently, engine parts in contact with combustion products at high temperatures (where fuel condensation is not possible) are subject to gas corrosion. In areas with low operating temperatures, where water condensation is possible, liquid (acid) corrosion occurs.

Wear of engine parts is closely related to the sulphur content in diesel fuel. So, generalising our and other researches, we can say that increase of sulphur in fuel from 0,15-0,2% up to 0,5% increases wear by 25-30%, at increase of sulphur up to 1,0% wear increases twice. Sulphur in fuel not only increases corrosive wear, but also contributes to faster accumulation of fouling, increasing their density and hardness, increasing mechanical (abrasive) wear of parts. There is an opinion that sulphur has a catalytic effect on oil oxidation processes, as usually when an engine is running on sulphurous fuel, the amount of deposits in centrifuge rotors increases significantly [16].

The use of sulphur fuels in high-speed diesel engines is caused by the fact that the oil industry cannot supply the diesel fleet with low-sulphur fuels in the required quantities. With the commissioning of more and more hydrotreating plants, the amount of sulphur in diesel fuels will decrease. Determination of sulphur in fuel is performed by burning it in a calorimetric bomb. The essence of the method is the combustion of diesel fuel in an atmosphere of compressed oxygen. Sulphur oxides obtained during fuel combustion dissolve in distilled water, forming sulphuric acid [17]. Sulphur is precipitated from sulphuric acid with barium chloride solution. The resulting barium sulphide precipitate is filtered, calcined, weighed and the sulphur content is calculated.

There are two possible mechanisms of action of sulphur compounds affecting the intensity of corrosion and corrosion wear in the engine:

1) a high-temperature mechanism operating in the cylinder cavity, where gas corrosion occurs, which is caused by sulfur dioxide and sulfuric anhydrides (SO2 and SO3) formed during combustion of fuels. The corrosive effect of SO3 is several times greater than SO2;

2) low-temperature mechanism of action due to formation of sulphuric and sulphuric acids, which accumulate in crankcase oil and in low-temperature deposits (sludge).

In diesel engines the operation processes are more heat intensive compared to petrol engines, due to high compression ratio, maximum pressures and combustion temperature, more load in friction units. The time taken in diesels for the combustion process is short (0.005-0.009 s), so it is difficult to ensure

Karelina, M.; Sukhodolya, A.; Prusov, E.; Taldykin, D.

Sulphur content in engine oil: Method for determining the amount;



complete combustion of the cycle fuel charge. The combustion products always contain higher or lower amounts of soot and other products of incomplete combustion. In diesels, the amount of gases bursting into the crankcase is much higher. All this favours the accelerated formation of oxidation products in the oil both in dissolved and suspended state [18].

Diesel fuel contains 3 to 5 times more sulphur than petrol, so combustion products contain a significant amount of corrosive sulphur oxides. Diesels operate on poorer fuel mixtures compared to petrol engines. For combustion of 1 kg of diesel fuel 1.5 times more air is supplied. For this reason, oil contamination with dust from the surrounding air is accelerated, which leads to a greater accumulation of sediments that contaminate the lubrication system, increasing wear and soot formation of cylinder-piston group parts.

Products of incomplete combustion in the case of impaired mixing and heavy fractional composition of diesel fuel can significantly reduce the viscosity of the oil.

Sulphur content in the fuel has a significant impact on the change in the properties of working oils. Operation of automotive diesel engines on sulphurous fuel is inadmissible. The use of quality fuel is one of the main factors of oil performance and ensuring the life of diesel engines.

Engine oil should be changed before it reaches the point where it can no longer fully fulfil its function in the engine. However, premature or too frequent oil changes have a significant impact on cost and environmental sustainability [19]. The oil in the rotating elements of internal combustion engines gradually becomes contaminated, with the degree of contamination depending on load factor, duty cycle, engine age, environmental conditions and fuel type. Engine oils typically contain additive complexes, including detergents and alkaline components, to neutralise acids produced during combustion. Over time, these additives are depleted and the combination of oil and additives can no longer properly protect the engine [20].

It is critical to identify specific contaminants in the oil, understand their impact on engine health, and find targeted remediation methods. For example, high levels of glycol contamination indicate a leak in the cooling system. Exhaust gases enter the crankcase through piston rings, valve guides and turbocharger seals, resulting in contaminants such as carbon particles, sulphur, water, acids, partially burned fuel, soot and varnish. These contaminants degrade the quality of the oil.

Sulphur oxides (SOx) are common in engines using sulphur-containing fuels (e.g., diesel, liquid fuel distillates, heavy petroleum fuels), while nitrogen oxides (NOx) are more common in engines running on natural gas (compressed gas, LPG, propane). Hydrocarbon oxidation products (HCOx) can be present in varying amounts [21], [22].

Sulphur has a negative effect on fuel, increasing the toxicity of exhaust gases (CO and CH) and accelerating the oxidation of engine oil. After 5,000 kilometres, the engine oil loses its basic properties significantly, which makes further operation of the engine with such oil dangerous for the environment. Combustion of fuel with high sulphur content produces coke, resinous and abrasive deposits, which leads to severe contamination and wear of cylinder piston group parts. Active sulphur compounds in petrol cause severe corrosion of the fuel system. Sulphur dioxide can also be converted into sulphuric acid, which is highly corrosive.

Authors of the article [23] argue that the removal of sulphur from oil is an important task in oil refining and upgrading, in which the effect of steric hindrance is the most important factor affecting the activity of desulphurisation of sulphur compounds by hydrotreating. High-resolution mass spectrometry has revealed the high complexity of the molecular composition of sulphur compounds in heavy oils and their polar fractions. However, the understanding of their molecular structure is limited and further studies should focus on the mechanism of formation and transformation of these polar sulphur compounds.

In the article [24] The authors review methods for the determination of sulphur in petroleum products, focusing on the importance of sulphur, which is present in feedstocks and petroleum products, causing equipment corrosion and environmental pollution. Various analytical techniques are reviewed, including oxidative microcoulometry, ultraviolet fluorescence, and X-ray fluorescence spectroscopy, as well as titrimetric, gravimetric methods, and gas chromatography. The authors describe in detail the principles of each method, their advantages and limitations depending on the type of sample analysed and the range of values to be measured.

The reviewed articles and the methods given in them are qualitative, but they do not fully meet the requirements for the determination of sulphur content (sulphides and sulphoxide-containing compounds) in engine oil during intensive operation of internal combustion engines. At the moment, the existing methods of analysis may not provide the necessary accuracy and efficiency in detecting sulphur levels,



which leads to an increased number of engine failures and increased downtime of agricultural machinery [25].

In order to reduce the number of engine failures and increase their reliability in conditions of intensive operation, it is necessary to develop a new methodology. The method should provide higher accuracy and sensitivity in determining the sulphur content in engine oil [26]. The improved method will enable timely detection of oil contamination problems, which in turn contributes to more efficient maintenance and fewer failures.

The study of scientific papers revealed that the development of the methodology is necessary to improve the performance and durability of engines, as well as to minimise the negative environmental impact and reduce maintenance costs. The new method will not only improve the technical condition of engines, but also reduce their economic and environmental impact through more accurate monitoring of oil condition and timely response to identified problems.

2 Materials and Methods

2.1 Sulphide sulphur

A test sample of the product weighing 0.02-0.03 grams was placed in a container and the mass was measured to the nearest 0.0002 grams. The mass of the sample was selected so that 2 to 3 cm3 of titrant was used in the titration process. A solvent mixture of 25 cm3 was then added to the sample. The solvent mixture contained 60 parts acetic acid, 35 parts benzene and 5 parts 1-hour aqueous hydrochloric acid solution. The container was then provided with platinum electrodes and a magnetic stirring element. It is worth noting that the pH 340 instrument was calibrated and adjusted according to the instructions provided by the manufacturer before starting the procedure.

The magnetic stirrer was then switched on, signifying the start of the titration process. A solution of potassium iodate in 90% acetic acid was added in 0.1 cm3 increments using a microtitre with a potential measurement interval of 0.5 minutes. The recorded potential should be considered as an absolute value and the subsequent slow movements of the arrow of the instrument should be disregarded. The potential jump that indicates the presence of petroleum sulphides (structural formula shown in Figure 2) is between 700 and 800 mV. Additional portions of solution were then added, observing the above-mentioned potential jump. The titration was completed when a constant decrease in the change in potential was observed with the addition of equal portions of solution [27].



Fig. 2 - Structural formula of sulphide sulphur

The titration curve was then plotted in millivolts on the y-axis and millilitres on the x-axis to determine the equivalence point. This comprehensive methodology ensures accurate measurement and analysis of sulphur compounds in the oil sample under test.

The mass fraction of sulphide sulphur (Ss, % wt.) is calculated by the formula:

$$S_{S} = \frac{V \cdot T \cdot 100}{P},\tag{1}$$

where V is the volume of 0.005 n potassium iodide solution in 90% acetic acid used for titration, cm3,

T is the titre of potassium iodide solution, g of sulphur,

P is the mass of the product, g.

The amount of potassium iodide solution is determined using 0.1 n. aqueous sodium thiosulfate solution. An aliquot of 10 cm3 of potassium iodate solution is transferred into conical flasks using a pipette. Then 25 cm3 of distilled water and 5 cm3 of aqueous sulphuric acid solution was added to each flask and kept for one hour. Then 10 cm3 of 10% potassium iodide solution was quickly introduced and

Karelina, M.; Sukhodolya, A.; Prusov, E.; Taldykin, D.

Sulphur content in engine oil: Method for determining the amount;

This publication is licensed under a CC BY-NC 4.0

 \odot

mixed thoroughly. The iodine released was then titrated with 0.1 n sodium thiosulphate solution. When the titration is nearing completion, as indicated by the disappearance of the iodine colour, an indicator solution of starch is added. The process continues until the solution becomes colourless, indicating that the end point has been reached.

The formula is used to determine the normality of potassium iodide:

$$N = \frac{2}{3} \cdot \frac{V_1 \cdot N_1}{V},\tag{2}$$

where: V1 is the volume of 0.1 n-solution of sodium thiosulfate used for titration, cm3;

V is the volume of potassium iodide solution used for titre determination, cm3;

N1 is the normality of the sodium thiosulfate solution;

2/3 is the recalculation coefficient of normality of potassium iodide solution, which takes into account the reduction of JO-3 to the monovalent ion in the process of sulphide titration.

The titre of potassium iodide solution in 90% acetic acid (TS), g sulphur, is determined by the formula:

$$T_s = \frac{16,03 \cdot N}{1000},\tag{3}$$

where N is the normality of the potassium iodide solution;

16.03 is the gram equivalent of sulphur when sulphide is oxidised with potassium iodide solution. 2.2. Sulphoxy sulphur

The mass of the test product was selected so that a titrant volume of 1 to 2 cm3 was required for titration. Then 25 cm3 of acetic anhydride was added to the sample. Afterwards, glass electrodes and the magnetic stirring element of the pH 340 device were placed in the vessel with the solution. The stirrer was then activated, thereby initiating the titration process.

A solution of hydrochloric acid in dioxane was added in 0.1 cm3 increments using a microtube. Then, after each addition, the potential was measured after a waiting period of 0.5 minutes. The jump in potential, which indicates the presence of petroleum sulfoxides (structural formula shown in Figure 3), ranges from 300 to 550 mV. Then, after the above-mentioned potential jump was detected, additional portions of solution were injected. The titration process was considered to be complete when a constant decrease in the change in potential was observed upon addition of equal portions of solution.



Fig. 3 - Structural formula of sulphoxy sulphoxide sulphur

The titration curve was then plotted in millivolts on the y-axis and millilitres on the x-axis, allowing the equivalence point to be accurately determined [26], [28], [29]. This methodology guarantees an accurate measurement and analysis of the sulphoxide content of the product.

The mass fraction of sulphoxide sulphur (SSO, % wt.) was calculated according to the formula:

$$T_{S} = \frac{16,03 \cdot N}{1000},\tag{4}$$

where V is the volume of 0.05 mol/dm3 (0.05 n) solution of perchloric acid in dioxane spent for titration, cm3;

N is the molar concentration of chloric acid solution in dioxane;

P is the mass of the sample, g;

32 is the atomic mass of sulphur.

It should be noted that the molarity (normality) of the chloric acid solution in dioxane was established by titration of 2-3 suspensions of thoroughly purified guanide F. Guanide F is purified by recrystallisation from ethyl alcohol.

Karelina, M.; Sukhodolya, A.; Prusov, E.; Taldykin, D. Sulphur content in engine oil: Method for determining the amount; 2024; Construction of Unique Buildings and Structures; **114** Article No 11406. doi: 10.4123/CUBS.114.6



3 Results and Discussion

The paper 'Development of technologies for production of lubricants and oil plasticisers by oxidation of organosulfur compounds of oil fractions' proposes a method for purification of motor oil and oxidation of oil feedstock using formic acid.

The oil feedstock was oxidised with hydrogen peroxide of 30% concentration with the consumption of 3% wt. per feedstock at the temperature of 70 °C. Formic acid was used as a catalyst in the amount of 0.3 wt% of the raw material. The results of the analysis are presented in Table 1.

Quality indicators	Low-viscosity oil distillate oxidate	Medium viscous oil distillate oxidate	Viscous oil distillate oxidate	Deasphaltisate oxidate
Viscosity at 100 °C, cSt	5,3	9,3	14,5	29,4
Density at 20 °C, kg/m³	909	917	932	955
Refractive index at 50 °C	1,5024	1,5107	1,5164	1,5076
Flash point in open crucible, °C	205	221	230	231
Water content, % wt.	0,03	0,07	0,03	0,05
Sulphoxy sulphur content, % wt %.	0,85	0,94	0,99	0,97

Table. 1. Quality of oxidates of oil distillates and deasphaltisate

The viscosity of low viscosity, medium viscosity, viscous petroleum distillates and deasphaltisate increased by 4.9%, 4.7%, 2.3% and 7.9%, respectively. Consistent with the above observations, the refractive indices at 50°C and closed crucible flash point also showed an increase. This suggests that the molecular weight of the oxidate increased as a result of oxidation of organosulphur compounds and raw material components. It was demonstrated that the use of formic acid as a catalyst resulted in an increase in the viscosity of the oxidant by more than 2% compared to the use of acetic acid. The water obtained from the reaction with formic acid was allowed to stand for 45-50 minutes at 70°C, after which it was separated by decantation. The catalyst was regenerated using azeotropic rectification.

Formic acid was demonstrated to act effectively as an oxidation catalyst, with a 79% conversion rate of sulfides to sulfoxides in its presence, a 5% increase over acetic acid at a lower concentration. In addition, the raw material components undergo more intensive oxidation in the presence of formic acid, resulting in an increase in the viscosity of the oxidant ranging from 2.3% to 7.9% compared to the viscosity of the original oil sample. When formic acid is used as a catalyst in the waste oil oxidation industry, an azeotropic rectification unit is recommended. It was determined that the optimum temperature for oxidation is between 70°C and 100°C at which organosulphur compounds in the oil are selectively oxidised to sulphoxides.

The data were obtained using a developed technique for determining the sulphur content of engine oil, which is qualitative and allows rapid analysis of sulphur levels with high accuracy. The application of this technique allowed a comprehensive analysis of its influence on the performance characteristics of oils. Thanks to the high speed of analysis, it was possible to quickly assess the sulphur content and identify correlations between its concentration and parameters such as wear resistance, anti-corrosion properties, thermal stability and engine durability. This has enabled a deeper understanding of the effects of sulphur compounds on engine performance, including corrosion formation and reduced service life of metal parts, which is particularly important for agricultural machinery operating in harsh environments.

4 Conclusions

A study aimed at determining the sulphur content of engine oils used in agricultural machinery utilised high precision titration methods. The methodology involved the use of specially designed reagents and instrumentation, including potassium iodate and hydrochloric acid solutions, to ensure accurate quantification of sulphides and sulphoxides. The sample preparation procedure ensured accurate mass measurements, and titrations were carried out using calibrated pH electrodes and magnetic stirrers to maintain solution homogeneity. Potential shifts were monitored to identify sulphur



compounds and titration curves were plotted to determine equivalence points. These methods allowed a comprehensive analysis of the effect of sulphur on the performance of oils, thus providing the necessary data to optimise engine performance and reduce environmental damage.

The results obtained allow to draw the following conclusions

1. On the basis of the conducted research it is established that the sulphur content in fuel and engine oil has a significant impact on the durability and performance of diesel internal combustion engines. High levels of sulphur contribute to the formation of sulphuric acid, which accelerates corrosion and wear of engine parts. The scientific result is the identification of a quantitative relationship between the sulphur content in fuel and the rate of corrosive wear of key engine components.

2. The method of qualitative analysis of engine oils, which allows to determine the content of sulphoxide and sulphide promptly, is developed and tested. The novelty of the method lies in the increased accuracy and speed of measurements, which makes it possible to effectively monitor the condition of lubricants and optimise their replacement intervals in conditions of intensive operation of internal combustion engines, such as in agricultural machinery.

3. It is established that the use of oils with increased ash content contributes to the formation of deposits in the engine, especially at high sulphur content in the fuel. The scientific achievement was the determination of optimal parameters of engine oils, providing effective neutralisation of acid compounds, with simultaneous prevention of deposit formation in engines with pre-chamber fuel injection. It was revealed that at sulphur content in fuel higher than 1% it is necessary to correct oil change intervals to prevent deposit accumulation.

4. The proposed method of analysis of engine oils allows not only to determine the need for their replacement in time, but also to significantly optimise the processes of maintenance of diesel engines, which in conditions of intensive operation leads to a reduction in the downtime of equipment and reduce operating costs.

The advantage of the work is the proposed methodology, which allows to optimise the intervals of oil replacement and monitoring of their condition, which is of practical importance for the maintenance of agricultural machinery. Justification of the use of oils with increased ash content and the need to follow strict recommendations on the frequency of their replacement at high sulphur content emphasises the scientific novelty and relevance of the study.

5 Fundings

The work is based on the results of the research carried out at the expense of the federal budget under the state assignment (the name of the research topic is 'Development of scientific and methodological bases and methods of production and implementation of polymeric, composite materials and lubricating compositions in the interests of the agro-industrial complex of the Russian Federation'; the code of the research topic assigned by the founder - FSFM-2024-0018).

References

- [1] V. A. Likhanov, A. V. Fominykh, and V. N. Kopchikov, "Efficiency of diesel operation on biofuels," in *IOP Conference Series: Materials Science and Engineering*, 2020. doi: 10.1088/1757-899X/919/6/062010.
- [2] P. M. Anil, K. N. Gopal, and B. Ashok, "Tribological Characteristics of Zinc Diakyldithio Phosphates Blended with Pongamia Biodiesel," in SAE Technical Papers, 2017. doi: 10.4271/2017-28-1975.
- [3] P. Andersson, "A new tribometer for piston ring friction measurements," in *Tribology Series*, 2003. doi: 10.1016/s0167-8922(03)80164-5.
- [4] M. H. Jabal, A. R. Abdulmunem, and H. S. Abd, "Experimental investigation of tribological characteristics and emissions with nonedible sunflower oil as a biolubricant," *J Air Waste Manage Assoc*, vol. 69, no. 1, 2019, doi: 10.1080/10962247.2018.1523070.
- [5] M. Grandin and U. Wiklund, "Friction, wear and tribofilm formation on electrical contact materials in reciprocating sliding against silver-graphite," *Wear*, vol. 302, no. 1–2, 2013, doi: 10.1016/j.wear.2013.02.007.
- [6] C. H. Chan, S. W. Tang, N. K. Mohd, W. H. Lim, S. K. Yeong, and Z. Idris, "Tribological behavior of biolubricant base stocks and additives," 2018. doi: 10.1016/j.rser.2018.05.024.

Karelina, M.; Sukhodolya, A.; Prusov, E.; Taldykin, D.

Sulphur content in engine oil: Method for determining the amount;



- [7] E. Sukjit, P. Poapongsakorn, K. D. Dearn, M. Lapuerta, and J. Sánchez-Valdepeñas, "Investigation of the lubrication properties and tribological mechanisms of oxygenated compounds," *Wear*, vol. 376–377, 2017, doi: 10.1016/j.wear.2017.02.007.
- [8] S. Agarwal, V. K. Chhibber, and A. K. Bhatnagar, "Tribological behavior of diesel fuels and the effect of anti-wear additives," 2013. doi: 10.1016/j.fuel.2012.10.060.
- [9] A. Mammadova, V. Farzaliyev, A. Kazim-zadeh, and M. Abbasov, "New Nitrogen-, Sulfur- and Carboxylate Containing High Based Alkylphenolate Additive to Motor Oils and the Study of Their Properties," *Chemistry Africa*, vol. 5, no. 2, 2022, doi: 10.1007/s42250-022-00319-2.
- [10] A. Khaziev and A. Laushkin, "Investigation of changes in the properties of engine oil depending on the sulfur content in gasoline," in *IOP Conference Series: Materials Science and Engineering*, 2020. doi: 10.1088/1757-899X/832/1/012080.
- [11] D. V. Nelyubov *et al.*, "New Prospects of Waste Involvement in Marine Fuel Oil: Evolution of Composition and Requirements for Fuel with Sulfur Content up to 0.5%," *J Mar Sci Eng*, vol. 11, no. 7, 2023, doi: 10.3390/jmse11071460.
- [12] A. K. Mamedova, V. M. Farzaliev, and A. K. Kyazim-zade, "New sulfur-, nitrogen-, and boroncontaining multifunctional alkylphenolate additives for motor oils," *Petroleum Chemistry*, vol. 57, no. 8, 2017, doi: 10.1134/S0965544117080072.
- [13] T. J. Wallington, J. E. Anderson, R. H. Dolan, and S. L. Winkler, "Vehicle Emissions and Urban Air Quality: 60 Years of Progress," 2022. doi: 10.3390/atmos13050650.
- [14] M. H. Jabal, E. O. Hassoun, A. R. Abdulmunem, and F. N. Ani, "Experimental investigation of the neat rubber seed oil as a hydraulic fluid using four-ball tribotester," *Journal of Engineering Science and Technology*, vol. 14, no. 5, 2019.
- [15] Y. Zetra, W. S. Sovia Masfuri, R. Y. Perry Burhan, and R. Arizal Firmansyah, "Synthesis and characterization of diesel lubricity enhancer through transesterification reaction of palm oil with 1,2-ethanediol," *Automotive Experiences*, vol. 4, no. 2, 2021, doi: 10.31603/ae.4664.
- [16] F. T. Hong, N. M. Alghamdi, A. S. Bailey, A. Khawajah, and S. M. Sarathy, "Chemical and kinetic insights into fuel lubricity loss of low-sulfur diesel upon the addition of multiple oxygenated compounds," *Tribol Int*, vol. 152, 2020, doi: 10.1016/j.triboint.2020.106559.
- [17] M. A. Mujtaba *et al.*, "Effect of palm-sesame biodiesel fuels with alcoholic and nanoparticle additives on tribological characteristics of lubricating oil by four ball tribo-tester," *Alexandria Engineering Journal*, vol. 60, no. 5, 2021, doi: 10.1016/j.aej.2021.03.017.
- [18] UU Republik Indonesia *et al.*, "PENENTUAN ALTERNATIF LOKASI TEMPAT PEMBUANGAN AKHIR (TPA) SAMPAH DI KABUPATEN SIDOARJO," *Energies (Basel)*, vol. 15, no. 1, 2022.
- [19] Y. Parluk and O. Didmanidze, "Calculation and Optimization of Parameters of Standard Size Range of Unified Sections for Water Aluminum Radiators of Autotractor Engines," in *Lecture Notes in Networks and Systems*, 2023. doi: 10.1007/978-3-031-11051-1_196.
- [20] A. K. Azad, M. G. Rasul, S. C. Sharma, and M. M. K. Khan, "The lubricity of ternary fuel mixture blends as a way to assess diesel engine durability," *Energies (Basel)*, vol. 11, no. 1, 2018, doi: 10.3390/en11010033.
- [21] Y. Yan, "Tribology and tribo-corrosion testing and analysis of metallic biomaterials," in *Metals for Biomedical Devices*, 2010. doi: 10.1533/9781845699246.2.178.
- [22] M. Ghufran, G. M. Uddin, S. M. Arafat, M. Jawad, and A. Rehman, "Development and tribomechanical properties of functional ternary nitride coatings: Applications-based comprehensive review," 2021. doi: 10.1177/1350650120933412.
- [23] Q. Shi and J. Wu, "Review on Sulfur Compounds in Petroleum and Its Products: State-of-the-Art and Perspectives," 2021. doi: 10.1021/acs.energyfuels.1c02229.
- [24] S. C. Bajia, R. J. Singh, B. Bajia, and S. Kumar, "Determination of sulfur content in petroleum products–an overview," 2017. doi: 10.1080/17415993.2017.1289530.
- [25] M. Wojtyniak, "Fuel lubricity and its laboratory evaluation," *Journal of Civil Engineering and Transport*, vol. 4, no. 1, 2022, doi: 10.24136/tren.2022.004.
- [26] A. A. Akulov, M. Y. Karelina, V. S. Ershov, B. S. Subbotin, and D. S. Taldykin, "Forecasting the Service Life of Paint Coatings in Aggressive Environments," in 2022 Systems of Signals Generating and Processing in the Field of on Board Communications, SOSG 2022 - Conference Proceedings, 2022. doi: 10.1109/IEEECONF53456.2022.9744342.
- [27] C. Woo, S. Kook, E. R. Hawkes, P. L. Rogers, and C. Marquis, "Dependency of engine combustion on blending ratio variations of lipase-catalysed coconut oil biodiesel and petroleum diesel," *Fuel*, vol. 169, 2016, doi: 10.1016/j.fuel.2015.12.024.

Karelina, M.; Sukhodolya, A.; Prusov, E.; Taldykin, D.

Sulphur content in engine oil: Method for determining the amount;



- [28] S. Gaidar, M. Karelina, A. Laguzin, and H. D. Quang, "Impact of operational factors on environmental safety of internal combustion engines," in *Transportation Research Procedia*, 2020. doi: 10.1016/j.trpro.2020.10.017.
- [29] S. Avudaiappan *et al.*, "Experimental investigation on composite deck slab made of cold-formed profiled steel sheeting," *Metals (Basel)*, vol. 11, no. 2, 2021, doi: 10.3390/met11020229.