



BIO-RESILIENCE IN LUBRICANT TECHNOLOGY: INVESTIGATING AND ENHANCING FUEL LUBRICANT MATERIAL STABILITY AGAINST BIOSUSCEPTIBILITY

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Abstract: *The ever-increasing reliance on synthetic lubricants in automotive and industrial applications has raised concerns regarding their environmental impact. Microbial degradation of these lubricants contributes to oil pollution, ecosystem disruption, and greenhouse gas emissions. This scientific article delves into the realm of bio-resilience in lubricant technology, focusing on the investigation and enhancement of fuel lubricant material stability against biodegradation. The growing demand for sustainable energy solutions underscores the need for robust lubricants that can withstand environmental challenges. This study explores the intricate interplay between fuel lubricant materials and biodegradation processes, aiming to uncover key mechanisms and develop strategies for bolstering bio-resilience.*

Keywords: *FLM, additives, biosusceptibility, microbial attack, climatic conditions*

Аннотация: *Постоянно растущая зависимость от синтетических смазочных материалов в автомобильной и промышленной сфере вызывает беспокойство по поводу их воздействия на окружающую среду. Микробиологическое разложение этих смазочных материалов способствует загрязнению нефтью, нарушению экосистемы и выбросам парниковых газов. Эта научная статья углубляется в область биоустойчивости в технологии смазочных материалов, уделяя особое внимание исследованию и повышению устойчивости материалов топливно-смазочных материалов против биоразложения. Растущий спрос на устойчивые энергетические решения подчеркивает потребность в надежных смазочных материалах, способных противостоять экологическим проблемам. В этом исследовании изучается сложная взаимосвязь между материалами топливных смазок и процессами биоразложения с целью раскрыть ключевые механизмы и разработать стратегии повышения биоустойчивости.*

Ключевые слова: *FLM, присадки, биопоражаемость, микробное воздействие, климатические условия*

Introduction

Due to the annual increase in the production of cars and tractors in Central Asia, where special climatic conditions prevail, the need for a constant increase in oil production and refining becomes integral. This includes the introduction of new deposits of raw materials located in remote and inaccessible areas of this region, taking into account specific climatic features. In this regard, saving oil products is becoming one of the promising solutions

to the problem in the field of the fuel and energy complex and is considered as a task of national importance in the context of harsh climatic conditions.

Cars and tractors in Central Asia, as in other regions, consume significant amounts of liquid fuel, lubricants and special technical fluids. According to the International Energy Agency (IEA) [1], in 2021, Central Asia consumed 2.9 million tons of diesel fuel, 1.7 million tons of gasoline and 0.4 million tons of liquefied petroleum gas (LPG). This represents about 1% of global liquid fuel consumption. The

main consumers of liquid fuel in Central Asia are road transport, agriculture and industry. Road transport consumes about 60% of all liquid fuels, agriculture - about 20%, industry - about 20%. In recent years, Central Asia has seen an increase in liquid fuel consumption. This is due to the growth of the region's economy, population growth and transport development. Based on the forecasts of IEA, liquid fuel consumption in Central Asia will grow in the coming years. In 2030 it could be about 4.2 million tons.

Uzbekistan, a significant participant in the automotive sector of Central Asia, has established ambitious objectives. As outlined in the recently endorsed Strategy Uzbekistan 2030 program, the country strives to achieve an annual production of 1 million vehicles by the year 2030 [2].

According to data from the Statistics agency [3], as of January 1, 2023, the Republic of Uzbekistan had a total of 3,396.5 thousand light vehicles owned by individuals, signifying a growth of 629.4 thousand units compared to January 1, 2022. This indicates a percentage increase of approximately 23%.

With the increase in the production of more economical diesel power plants and the improvement of the technical level of gasoline engines adapted to the climatic conditions of Central Asia, it becomes important to study the possibilities of replacing expensive types of fuel with more affordable ones, switching to gas fuel, as well as improving the quality of operating materials and saving them through rational use in the process of operating vehicles in this unique climatic context.

Fuels and lubricants (FLMs) are key components required for the reliable operation of ground-based equipment such as cars, tractors, aircraft, etc. The quality of fuel and materials, as well as their correct use and consumption, directly affect the service life and efficiency of equipment.

Lubricants play a crucial role in reducing friction and wear in machinery, thereby enhancing lifespan and efficiency. Traditionally, lubricants have been derived from petroleum, offering robust performance but presenting significant environmental drawbacks. Their persistence in the environment and susceptibility to biodegradation by diverse microorganisms lead to soil and water contamination, impacting ecosystems and human health.

Understanding Biodegradation Mechanisms:

The first observations and descriptions of microorganisms belonged to Anthony Leeuwenhoek (1695), who not only described, but also gave sketches of many microorganisms [4]. However, the underdeveloped industry and agriculture of that time hampered the development of natural sciences, including the application of Leeuwenhoek's discovery and the science of microbiology in general.

At the beginning of the 20th century, scientists noticed the ability of microorganisms to absorb hydrocarbons from solid, liquid and gaseous petroleum products. This led to the formation of an independent branch of microbiology—petroleum microbiology [5].

In 1976, the British Corrosion Center published a report [6] indicating that microbiological contamination of fuels and lubricants was a serious problem that could lead to sudden failures and accidents of components and systems of ship and aircraft power equipment. The report indicated that microorganisms may be present in FLM in the form of spores, which can germinate and multiply in the engine fuel system.

Modern fuels and lubricants must meet all these requirements. To do this, they contain various additives that improve their properties. Under operating conditions of engines, corrosion damage to the working surfaces of parts (friction pairs) is caused by chemical and microbiological processes occurring simultaneously in the fuel [7].

The main microbiological problem in the oil refining industry is contamination of stored petroleum products (accumulation of water, colonies of microorganisms, etc.) [7], which can lead to loss of product quality, formation and wear of sludge, corrosion of pipelines and storage tanks both at the refinery and at the end consumer.

This phenomenon was first discovered in Central Asia [7], when using FLM in hot climates, then similar phenomena were discovered in regions with temperate climates. The ability of microorganisms to use FLM hydrocarbons in the process of life is not only of independent interest as a subject of physiology and biochemistry, but also causes significant problems in the field of oil production, oil refining, petrochemistry, and especially in the exploitation of petroleum products.

In Fig. Figure 1 shows photographs of a colony of microorganisms grown in samples of diesel fuel during tests of the performance of fuel filters installed in the fuel systems of A-01M diesel engines of the T-4A "Altai" tractor (Tashkent region, state farm Pskent-1), this shows that increased temperature has a large importance for the growth of microorganisms [7].

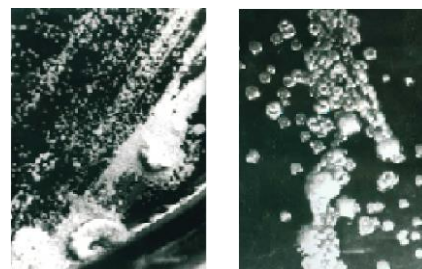


Fig. 1. Colonies of microorganisms, diesel fuel samples taken from the fuel system of the T-4A tractor.

Changes in the basic properties (physical, chemical and operational) of fuel lubricants under the influence of a colony of microorganisms can lead to an increase or decrease in oil pressure in oil systems. This leads to clogging of pipelines and filters, wear of oil pump parts, and jamming of the pressure relief valve. These faults, in turn, lead to loss of tightness of components and systems. With long-term operation of an internal combustion engine in such oil and untimely replacement of filter elements, the concentration of harmful impurities leads to a critical concentration.

As a result of this, microbiological damage to FLM remains a serious problem that can lead to emergency situations.

Microorganisms act in groups. For microbial attacks to be successful, their army (colony) in petroleum products must be large enough. As a result, large colonies of bacteria-microorganisms are formed that can cause serious damage to equipment, machine components, etc.

Colonies of microorganisms (biomass) in petroleum products can clog vents, coils, filters, and any number of other sensitive areas. Clogged filters can increase maintenance costs because they need to be replaced more frequently.

More serious problems can arise from low pressure oil systems, and blocked oil supply points can starve components of essential lubricating fluid, which can lead to serious undesirable consequences. Needless to say, the damage caused by insufficient lubrication can be enormous [8].

Investigating Bio-Resilience Factors:

The life activity of all living beings depends on the environment in which they live. Microorganisms, like other living beings, need food, water, oxygen and other conditions to live. Each type of microorganism has its own metabolic characteristics, and therefore imposes certain requirements on the environment.

Microorganisms are living organisms, so they are influenced by environmental factors. The most important factors affecting the life of microorganisms are temperature, humidity, the availability of food and oxygen. Changes in these factors can lead to the following consequences:

- *Change in the rate of growth and reproduction of microorganisms*
- *Changes in the properties of microorganisms*
- *Death of microorganisms*

In tropical and subtropical climates, microorganisms tend to multiply faster than in temperate or cold climates.

There is a certain parallelism between the life activity of microorganisms and environmental factors. The more favorable the conditions for a given microorganism, the more intensively it

develops, the higher the rate of its life activity in water, soil, FLM, etc.

To study the processes of destruction of petroleum products by microorganisms, it is necessary to take into account the following factors:

physical factors (environmental humidity, environmental temperature, radiation); chemical factors (composition and reaction of the environment); and biological factors.

Research has shown that temperature is the most important environmental factor affecting the life of microorganisms [9]. This is due to the fact that the rate of chemical reactions, including biochemical ones, increases as the temperature rises.

When the temperature rises, the metabolic rate of microorganisms also increases, which leads to their more active growth and reproduction. The dependence of the reaction rate on temperature is usually expressed by the Arrhenius equation [10]:

$$k = A \cdot e^{\left(\frac{-E_a}{R \cdot T}\right)}$$

where:

- k* is the reaction rate constant;
- A* - pre-exponential factor;
- E_a* - activation energy;
- R* - universal gas constant;
- T* - temperature.

From this equation it can be seen that the reaction rate constant increases with increasing temperature. The temperature coefficient for many biological processes, including the growth of microorganisms, usually lies in the range of 3.0 - 4.0 at room temperature (18 ÷ 22 ° C). This means that when the temperature increases by 10 degrees, the growth rate of microorganisms increases by 3 to 4 times.

Microorganisms are classified in a system that includes several levels, from broad groups to narrower categories. The main levels of classification of microorganisms include domain, kingdom, phylum, class, order, family, genus and species [7].

Various types of microorganisms are known: bacteria, molds and yeasts, algae, actinomycetes, etc. Bacteria (genus *Micrococcus*, *Bacillus*, *Nocardia*, *Brevibacterium*, *Pseudomonas*, *Mycobacterium*, *Corinebacterium*, *Achromobacter*), fungi (genus *Aspergillus*, *Rhizopus*, *Trichoderma*, *Cladosporium*, *Penicillium*, *Candida*, *Hansenula*, *Richia*), actinomycetes (genus *Streptomyces*, *Actinomyces*) [11].

Temperature regimes largely determine the existence and development of microorganisms. Their values vary depending on the chemical composition and depth of FLM cleaning. These temperature regimes are called cardinal, and they are different for different microorganisms.

The maximum temperature for the growth of microorganisms is called the temperature maximum.

For most microorganisms, the temperature maximum lies in the range from 45 to 60°C. However, some microorganisms, such as thermophiles, can grow at temperatures above 100°C.

The minimum temperature for the growth of microorganisms is called the temperature minimum. For most microorganisms, the temperature minimum lies in the range from 0 to 10°C. However, some microorganisms, such as psychrophiles, can grow at temperatures below 0°C.

Analytical Techniques for Assessing Biodegradation

There is always some air present in vehicle fuel tanks. This is due to the fact that the valves in the fuel tank caps communicate with the atmosphere. While the vehicle is moving, a vacuum is created in the area where the fuel tank is located. This is due to the fact that the air in the tank remains under pressure, and the tank constantly changes its volume depending on fuel consumption.

The vacuum in the area where the fuel tank is located causes dust, which may contain microorganisms, to be sucked into the tank. Microorganisms entering the fuel tank begin to multiply. Microorganisms enter FLM from the air and can remain in them for a long time. They begin to multiply intensively under favorable conditions, especially in the presence of water [12]. At the same time, they consume hydrocarbons contained in the fuel or act on them with the products of their metabolism. Microbiological contamination of fuel leads to deterioration of its performance indicators. As a result, the fuel may become more viscous and sediment and other impurities may form. This can lead to problems starting the engine, reduced engine power, and other problems.

In addition to microbiological contamination, sedimentation often occurs in FLM in the form of a sludge of a stable water-oil emulsion, which includes organic and inorganic insoluble contamination products. Sedimentation occurs as a result of the deposition of water, inorganic and organic impurities in FLM. Water can get into the FLM as a result of precipitation, condensation or other factors.

Water makes up 50% of the sediment in FLM. The water content in petroleum products is regulated by regulatory documents. For example, the water content in gasoline should not exceed 0.02%, and in diesel fuel - 0.05% [7]. Inorganic impurities make up 30-67% of the sediment in FLM. Organic impurities make up 2-33% of sediment in FLM. They can form as a result of oxidation or thermal decomposition of fuel.

Research by scientists [9] has shown that various microorganisms, including bacteria, fungi and yeast, may be present in fuel and lubricants.

The most common types of microorganisms in FLM are:

- Bacteria: *Pseudomonas* (80% of all microorganisms in FLM), *Micrococcus* (10%), *Mycobacterium* (5%), *Desulfaviria* (5%);
- Fungi: *Aspergillus* (30%), *Penicillium* (20%), *Chadosporium* (20%);
- Yeasts: *Candida* (10%), *Torula* (10%).

Microorganisms are highly active organisms that can consume hydrocarbons as an energy source. They are able to quickly adapt to new conditions and reproduce in a wide range of temperatures and pH.

Case Studies: Successful Implementation of Bio-Resilience Strategies:

In the 1960s, Soviet scientists I.T.Nette, N.N.Grechushkina and others conducted research on the isolation and identification of microorganisms that can grow and develop on fuel and lubricants [13]. The authors examined soil samples from the oil regions of Ukraine, Tatarstan, as well as soil near Moscow taken from gas stations. R.W.Stone, M.Fenske and A.White from the USA also studied the ability of microorganisms to destroy FLM hydrocarbons [14]. In their studies, they used different fractions of FLM, differing in molecular weight and molecular structure. L.Bushneil and N.Haas isolated various species of *Pseudomonas* and *Corynebacterium*, which made good use of FLMS, especially lubricating oils.

During the oxidation of hydrocarbons by microorganisms, the following changes were observed:

- Change in pH: the environment becomes more acidic.
- Increased emulsification of FLM: FLM becomes more viscous and difficult to mix with water.
- Shift in fraction boiling points: FLM fractions shift towards heavier hydrocarbons.
- Formation of organic acids: organic acids are formed in FLM, which reduce pH and impair the performance properties of FLM.

S.E. Zobell et al. established a number of patterns in the destruction of hydrocarbons by microorganisms [15]:

- Hydrocarbons with long chain structures are destroyed faster than those with short chains.
- Aliphatic hydrocarbons are oxidized more easily than aromatic and polymethylene hydrocarbons.
- Unsaturated compounds are used by microorganisms preferentially to saturated ones.
- Isocompounds are less absorbed than straight chain compounds.

A major aviation company introduced a novel aviation lubricant with advanced bio-resilience additives [7]. The lubricant incorporated antimicrobial agents and oxidation inhibitors to combat microbial contamination and extend lubricant life. After implementation, the company observed a 15%

reduction in lubricant degradation, leading to increased engine efficiency, lower maintenance costs, and an extended interval between oil changes.

The process of oxidation of hydrocarbons to carbon dioxide and water is accompanied by the accumulation of bacterial protoplasm. Methane, organic acids, ketones, aldehydes and alcohols are formed as intermediate products. Of the many different types of microorganisms existing in nature, about two hundred are capable of oxidizing FLM hydrocarbons.

Microorganisms, using FLM hydrocarbons as an energy source, are capable of oxidizing not only paraffin and naphthenic hydrocarbons, but also aromatic hydrocarbons. This is facilitated by their diverse adaptation to various substrates.

The results of studies of the growth characteristics of bacterial cultures depending on the temperature and concentration of samples of diesel fuels and gas condensates in a mineral environment gave the following results [7]:

- biomass content (g/l) in a mineral medium with diesel fuel DL: culture - *Ps. fluorescens* at 28°C - 3.9 and 45°C - 5.0, respectively - gas condensates of the fields - Achak - 2.5 and 2.7, Shatlyk - 2.7 and 3.1;
- accumulation of biomass (g/l) in a mineral environment with different concentrations of diesel fuel DL: culture - *Ps. fluorescens*: at 2% - 2.8; 10% - 4.1 and at 20% - 5.9.

For the cultivation (growing) of microorganisms in diesel fuel and gas condensates in laboratory conditions, the following medium was used:

- DL grade diesel fuel - a sample taken from the tractor fuel tank during operation in hot climates;
- gas condensates - samples taken from the Achak and Shatlyk fields as a source of carbon (at different concentrations in the environment 2,10,20%);
- ammonium phosphate - 4 g (NH₄) HPO₄ and NH₄HPO₄;
- potassium chloride - 0.2 g (KCL);
- sodium chloride - 0.1 g (NaCl);
- magnesium sulfate - 0.2 g (MgSO₄) and other microelements.

The cultivation of microorganisms was carried out on a rocking chair, in Erlenmeyer flasks (500 ml) with 100 ml of culture liquid for up to 4 days, at different temperatures (28 and 45°C) with the addition of DL diesel fuel and gas condensates from the Achak and Shatlyk fields.

The accumulation of biomass was determined by the gravimetric method on membrane filters No. 3, 5 after removal of salts (5% solution of hydrochloric acid HCl) and residual hydrocarbons (hexane - C₆H₁₄).

From the results of laboratory studies, it is clear that the greatest accumulation of biomass (up to 5 g/l of dry biomass) was observed in a medium with DL

diesel fuel at a temperature of 45°C (5.0 g/l) and a concentration of 20% diesel fuel (5.9 g/l).

Improving the properties of FLM

Improving the properties of fuels and lubricants is an important area in the fuel and energy complex and the automotive industry. The development and introduction of more efficient fuels and oils can help improve the energy efficiency of engines.

Developing lubricants that provide effective protection against engine wear, corrosion and oxidation improves the longevity of engines and other mechanical parts. Research into additives and inhibitors that ensure fuel stability over long periods of storage, as well as resistance to chemical processes, can improve fuel quality. Additives perform various functions such as increasing lubricity, reducing wear, protecting against corrosion, increasing service life, etc. Anti-biodegradation additives play an important role in maintaining the quality of fuels and lubricants.

Additives are an integral part of fuel and lubricants. Every year the range and scope of additives expands. Additives must meet certain requirements to ensure high quality fuel materials and their reliable operation. These requirements include:

- High performance: additives must provide the desired effect, such as reduced wear or increased lubricity.
- Stability: Additives must retain their properties over long periods of time and at different temperatures.
- Miscibility: additives must mix well with FLM and not linger in the filters.
- Insolubility in water: additives should not be mixed with water to avoid the formation of emulsions.
- Harmlessness: additives should not have a harmful effect on materials, the power and lubrication system, as well as on human health.

Microorganisms can directly destroy the metal surface, but more often they stimulate damage processes. As mentioned earlier, biocorrosion processes occur under the influence of microorganisms and, under favorable conditions, this process is stimulated.

As practice has shown, bacterial corrosion can occur at 6-40°C, pH=1÷10.5 in the presence of organic and inorganic materials that are by-products of the synthesis of microorganisms.

To create a product that functions as an antimicrobial additive for FLM, it is necessary to select substances that have the property of inhibiting the development of microbial cells, i.e., living organism, and not affect FLM and its hydrocarbons. The mechanism of action of individual functional groups on the cell is, in principle, known to biochemistry, since phenols and their derivatives form

compounds with the protein structures of the microbial cell, causing their denaturation.

In our search for antimicrobial additives for FLM, we proceeded from the experience gained in the synthesis and study of pesticide drugs in various industries, medicine and agriculture.

With the goal of choosing a drug to protect FLM, we first of all studied the range of microorganisms that infect FLM operated in tropical and subtropical conditions.

When selecting antimicrobial compounds, it is necessary to ensure their good compatibility with the FLM for which they are intended. In addition, the drug should not be toxic to humans or impair the physicochemical and operational properties of FLM.

It should be noted that compounds that are insoluble in the FLM under study and that pose a danger to humans when used (explosive or flammable material, substances with increased toxicity) cannot be used.

The methodology for testing the effect of pesticides on fungal and bacterial cultures does not differ from traditional methods.

During initial testing, drugs are added to the FLM in an amount of 1% of its mass. If the additive exhibits bactericidal-fungicidal properties, it is necessary to reduce this dosage; if the compounds are not active enough, the concentration can be increased only if compatible with FLM. In the overwhelming majority of cases, the concentration of substances is taken no higher than 1%, trying to introduce the smallest possible amount of a foreign drug into the FLM, and also taking into account in the future the cost of the product with such an additive.

It turned out that certain additives to FLM can serve as protective antiseptic additives that prevent microbiological decomposition of FLM.

Among these additives, in our opinion, the most promising are the following groups of compounds: 8-hydroxyquinoline and its derivatives, barium and calcium sulfonates, esters of alkylxanthogenic acids, esters of anthranilic acid, pyrazolidone derivatives, the minimum effective concentration of which is 1 wt.% and below has been tested in composition of oils for various purposes (aviation, transformer, diesel, motor, etc.) [16]. These oils were susceptible to damage by fungi and bacteria.

Alpha-naphthoquinone and ortho-hydroxyquinoline are organic compounds that have bactericidal and fungicidal properties. They are used as an additive in fuel and oil to prevent biodegradation. In small additives in FLM, these additives dissolve almost completely and have a certain effect on microorganisms, namely, they transfer microorganisms to an anabiotic state ("resting" state), i.e., influence the reaction rate of protein formation.

The mechanism of action of alpha-naphthoquinone and ortho-hydroxyquinoline is that they disrupt the cell membrane of microorganisms,

which leads to their death. Adding these additives to fuel and oil can help prevent the following problems caused by biodamage:

Corrosion: Microorganisms can produce acids and other substances that corrode metal.

Clogging: Microorganisms can form deposits that can clog fuel filters, oil filters and other vehicle systems.

Odor: Microorganisms can produce unpleasant odors that may be unpleasant to passengers and the driver.

Alpha-naphthoquinone and ortho-hydroxyquinoline are typically added to fuels and oils at levels ranging from 0.01 to 0.05%. This amount is sufficient to provide effective protection against biological damage.

When using the additive dichloro-naphthoquinone, the effect of the additive was very large. To explain this effect, it is important to repeat known studies of biopolymer synthesis. Proteins are formed from 20 types of amino acids, and nucleic acids from 4 types of nucleotides. That is, there must be a special genetic code connecting both sequences of links. This code is a triplet of adjacent nucleotides that forms a codon corresponding to one amino acid residue of the protein chain. The number of possible codons is $4^3 = 64$, i.e., it is redundant to encode 20 amino acids.

Conclusion:

The analytical findings indicate that the storage of FLM under conditions characterized by a significant temperature differential (up to 20 °C between day and night) induces air condensation, resulting in an elevation of water content within the crankcase, escalating from 0.5% to 4% by oil volume. Concurrently, in environments marked by dusty air conditions ($42.8 \mu\text{g}/\text{m}^3$), the analysis reveals an augmentation in biomass, manifested as a rise in microbial colonies from an initial absence to a level of 4.5 points (5-point scale). This combined impact has discernible consequences on the physicochemical attributes of the oils, potentially compromising their operational efficacy. Furthermore, the reliability of filter elements within the oil systems of internal combustion engines is susceptible to deterioration.

The cumulative implications of these environmental factors necessitate strategic interventions. Optimization of storage conditions to mitigate temperature differentials, implementation of advanced filtration systems resilient to heightened biomass contamination, and the establishment of a regular monitoring regimen are recommended measures. These actions are imperative for preemptively addressing the observed challenges, sustaining optimal oil performance, ensuring the longevity of engine functionality, and upholding the

efficacy of associated filtration systems in internal combustion engines.

Preserving engine FLM from the deleterious effects of microorganisms necessitates the incorporation of antimicrobial additives such as dichloro-naphthoquinone, alpha-naphthoquinone, and ortho-oxyquinoline. The recommended concentration for these additives is up to 0.01-0.1 % by weight. This judicious inclusion serves to safeguard the physicochemical and operational attributes of the engine oil, thereby enhancing its overall service life. By leveraging these antimicrobial agents, the formulation of engine oils can effectively counteract microbial contamination, mitigating potential

degradation and ensuring sustained performance throughout their extended service lifespan.

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