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EVALUATION OF SOME ORGANIC DISULFIDES AS ANTIMICROBIAL ADDITIVES FOR LUBRICATING OIL M-8

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Abstract. The use of additives is increased by environmental issues and applications that require lubricants operating under severe conditions. The paper studies the antimicrobial properties of some organic disulfides of the interaction between motor-oil additives for lubricating oil M-8. The compounds are tested as antimicrobial additives for lubricating oils. The antimicrobial activity of compounds in oil is estimated on value of repression zone diameter of the growth of microorganisms. The results of tests revealed that the compounds in certain concentration (0.25%) efficiently suppress the growth of microorganisms. Their antimicrobial activity is higher than the industrial additive 8-hydroxyquinoline used as a standard.

Keywords: *organic compounds, disulfides, lubricating oil, environmental, biodegradation, antimicrobial additives.*

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1. Introduction

Importance of environmental issues has increased over the past two decades, so that lubricants are considered part of these issues.

One of the reasons for pollution of environmental pollution is petroleum-based lubricants. It's serious due to inherent toxicity and non-biodegradability (Boshui *et al.*, 2012; Haus *et al.*, 2001; Bartz, 1998). Public attention and awareness of the need to protect the environment over the past decades has stimulated the development of lubricants that are more or less compatible with the environment.

Therefore, environmental compliance of lubricants has become the subject for researches (Erhan *et al.*, 2000; Rebeccal & Rogere, 1998). Eco-friendly lubricant technology and design aims to meet both operational and environmental requirements to harmonize performance and environmental requirements (Madanhire *et al.*, 2016).

A lubricant is a substance used to reduce friction, especially in an engine or other moving components (Salman, 2014). Most liquid lubricants are petroleum-based ones. Typically, petroleum-based lubricants are derived from fossil oils or petroleum. All over the world, all kind of oil-based lubricants are used in commercial vessels, agriculture, forest, cars and trucks equipment as well as manufacturing industry. Oceans and environment are polluted by million liters of petroleum-based lubricants from operational discharges and leaks. The main cause of pollution and contamination is

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discharging or leaking of lubricant, going immediately in the ground. It has hazardous effects on life on earth. Generally, oil-based lubricants and oil don't possess biodegradability property. Bio-degradable lubricants and fluids manifest chemical dissolution by bacteria or other biological means. For the purpose of protecting the environment and make it sustainable life, some countries apply environmental regulations and labels such as Blue angel (Germany), Eco mark (Japan), Ten circle mark (China), The Thai Green Label Scheme (Thailand), Eco Logo (Canada), Environmental Choice New Zealand (New Zealand), Green mark (Taiwan), Green label (Singapore). These labels focus on health, climate, water and resources. Labels and some governmental regulations encourage the use of eco-friendly or biodegradable lubricants, oils and fluids.

Lubrication fluids are used for lubrication of various engines or other moving components. The main function is to reduce wear on moving parts; it also cleans, inhibits corrosion, improves sealing, and cools the engine by carrying heat away from moving parts.

Increasingly, there is awareness that lubricants contacting with soil, water, wetlands, and other sensitive areas can negatively impact the environment. This has both manufacturers and users of lubricating systems switching to more environmentally acceptable alternatives, such as those that are biodegradable and non-toxic. These biodegradable and non-toxic lubricants possess the properties comparable to mineral oil-based fluids in some applications.

Biodegradation is one of three processes that transform or break down materials that enter the environment (the other two being physical (or weathering) and chemical (sometimes referred to as photoxidation). Biodegradability is the most important aspect with regard to the environment of a substance. Biodegradation is the chemical breakdown of materials by living organisms (or their enzymes) in the environment. The organisms include bacteria, yeast, protozoans, and fungi, which break down molecules for sustenance, typically yielding carbon dioxide and water. Certain chemical structures are more susceptible to microbial breakdown than others; vegetable oils and synthetic esters, for example, will in general biodegrade more rapidly than mineral oils under the same conditions.

Biodegradation refers to biological activities resulting in the breakdown of a compound (Ismail, 2008; Stephen *et al.*, 2013). Biodegradation of complex molecules usually involves the interactive effort of mixed populations of microorganisms and relies on the metabolic versatility of bacteria and fungi and the rate of degradation depends on the composition of the molecules (George & Metting, 1993). Lubricant biodegradability is the extent to which the material can be broken down by microorganisms into innocuous products such as carbon dioxide and water.

According to Hawrot and Nowak (2006), biological degradation of hydrocarbons in the environment is linked to a number of physical and chemical factors including the concentration and chemical structure of contaminant, moisture, oxygen, temperature and pH. The rate and efficiency of biodegradation depends on the occurrence of adequately numerous and active microflora in the contaminated environment (Moneke & Nwangwu, 2011). The organisms capable of degrading hydrocarbons include *Pseudomonas aeruginosa, Bacillus subtilis, Alcaligenes, Acinetobacter iwoffi, Flavobacterium spp, Micrococcus roseus, Cornybacterium, Trichoderma spp, Candida spp, Aspergillus spp (A. niger and A. flavus), Rhizopus spp* (Ramadan *et al.*, 2012).

As it's known, petroleum-based lubricants, which consist predominantly of hydrocarbons and subsidiary of additives which are often environmentally hazardous, for many reasons still dominate in the lubricant market and will presumably continue to play an important role in the future applications of lubricants. Even though mineral base oils choice has far never been recommended in biodegradable lubricant formulations, improvement of their environmental safety such as better biodegradability and development of greener additives are indeed indispensable.

Lubricant oil behavior in environment along with its properties is considered a source for the development of new fluids (Tamada *et al*., 2012). Thus, the studies on the lubricants possessing lower environmental impact and faster biodegradation capacity are considered a useful alternative. Therefore, synthetic and semi-synthetic lubricant oils have been developed.

Similar to all lubricants, after several months of operation loses its operational properties, ages and requires replacement. All types of lubricants become contaminated and lose their performance due to changes in some of their properties (Shakirullah *et al.,* 2006). Hertzman et al. (1985) reported that 600,000 tons of lubricant is lost to the environment annually. This may constitute serious environmental hazard to the environment and also a potential hazard to the long-term health status of the population (Wright *et al.,* 1993). Some compounds in hydrocarbons may not be degraded by organisms (Atlas & Bragg, 2009). Others may be degraded and broken down into carbon dioxide, water and cell mass (fatty acids) (Moneke, & Nwangwu, 2011) while others may be transformed into other compounds.

One of the reasons for lubricant ageing is its defeat by microorganisms. Lubricating oils used during storage and transportation in harsh environments cause formation of toxic substances due infection by microorganisms. In this regard, it is important to study biological stability of waste oils for high-speed engines with additives of different functional purposes along with the development of their regeneration.

The key issue in lubricants against biodegradation is selection of reliable base oils and additives with suitable properties. The studies reveal that the most effective method for protecting lubricants against microbial destruction is a chemical method, i.e. the use of chemicals - biocides (Fuchs *et al.,* 1993). Solving the problem of microbial destruction of waste lubricating oils is one of the urgent challenges of modern microbiology and petrochemistry (Farzaliyev *et al.,* 2014). Simultaneously, development of alternatives for conventional lubricant additives such as organic disulfides was also a subject of interest.

Biocides were developed for protecting oil against microbial destruction. It was found that the use of biocides in the recommended concentration has no negative effect on the main properties of the lubricating oil.

Purpose of the study

The paper presents the results of the studies on the biological stability of the lubricating oil M-8 as well as the study of the biological stability of used samples of lubricating oil and their protection with the use of antimicrobial additives of various compositions.

2. Materials and methods

The previous work disclosed the synthesis of benzylalkanoyldisulfides (Aliyev & Azizova, 2014). In this article, we set ourselves the goal of studying the duration of action of disulfides.

For evaluating the effect of unsymmetrical organic disulfides on biodegradation of oils, 0.25% mass percent of disulfides was incorporated into lubricating oil.

The studies were conducted with spent lubricating oil M-8 (75 days) in conditions of forced infection by bacteria and fungi. The results of microbiological tests are set into Table 1.

Table 1. The results of microbiological tests

Biocide	**The total number of microorganisms**, cells / ml, after the test duration, days.						
	1	**7**	**14**	**30**	**45**	**60**	**75**
Benzilmetanoildisulfid	0	0	0	0	0	0	0
Benziletanoildisulfid	0	0	0	0	0	0	0
Benzilpropanoildisulfid	0	0	0	0	0	0	0
Benzilbutanoildisulfid	0	0	0	0	0	0	0
Benzilpentanoildisulfid	0	0	0	0	0	0	0
Benzilmetanoildisulfid	0	0	0	0	0	0	0
Benzilheksanoildisulfid	0	0	0	0	0	0	0
8-hydroxyquinoline	0	0	0	10^3	10^6	10^7	Complete defeat
Without additive	10^2	10^5	10^6	10^{11}	emulsion stratified		

The tests were carried out using lubricant oil for various biodegradation periods. The samples were analyzed at 1, 7, 14, 30, 45, 60 and 75 days of biodegradation. The pH, turbidity analysis of the medium was carried out.

Biological stability of oil was determined by the test methods for resistance to bacteria and fungi. In each case, the lubricating oil was infected by microorganisms. The infection manifested itself and resulted in excessive damages in 60 days or less. The toxicological levels during the biodegradation period were observed through the tests using the following organisms: *Mycobacterium lacticolum*, *Aspergillus niger*, and *Candida tropicals.* Cultures of fungi and bacteria were obtained from the Institute of Chemistry of Additives of ANAS, and were supported by periodic reseeding and cultivation immediately before testing.

The tests procedure was as follows. The nutrient medium (20-25ml) was poured into a Peri dish (meat-peptone agar for bacteria, wort agar for fungi), and after hardening of the medium, 5 mm-deep pits were made on its surface with a sterile drill pits (diametr 10 mm), into which 0.25 ml of oil sample was added with the additive. The Petri dishes were placed in a thermostat and kept at 29±2°C, over 3 (samples with bacteria) and 7 days for (samples with fungi).

Biostability of the studied oils was determined by the diameter of microbial growth inhibition.

3. Results and discussion

As a result, microbiological tests revealed that all studied oils used for 75 days and regenerated lubricating oil M-8 (without additive) – are not biological stable, and are completely affected by microorganisms on the first week - bacteria and fungi.

Organic compounds containing disulfide group (–S–S–) structure are the most effective among synthesized and previously studied sulfides biocides for oil (Aliyev & Azizova, 2015; Berberova *et al.*, 2019; Aliyev *et al.*, 2021; Aliyev, 2012; Aghayev *et al.*, 2012; Akperov, 2016). The derived compounds were added to oil samples M-8 at a concentration of 0.25%. 8-hydroxyquinoline was used a reference biocide. The tests found that both unsymmetrical organic disulfides exhibit high antimicrobial properties in all the samples of lubricating oil M-8 at a concentration of 0.25% and provide complete long lasting protection against destruction by bacteria and fungi.

4. Conclusion

The antimicrobial properties of some organic disulfides of the interaction between motor-oil additives for lubricating oil M-8 are studied. The compounds are tested as antimicrobial additives for lubricating oils. Microbiological tests revealed high efficiency and broad spectrum of antimicrobial activity of the additives on the microorganisms affecting petroleum products.

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