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BIOSTABLE LUBRICANT COMPOSITION FOR MARINE, LOCOMOTIVE AND STATIONARY DIESELS

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Abstract: The paper presents the results of research into the biostability of M-10 base oil samples with addition of protective additives for various purposes which are a part of the earlier composition of M-14B₂ lubricating oil developed by us. It was established that despite the different nature of these additives (alkyl phenolates, dithiophosphates, sulfonates), all these samples are affected by microorganisms. It found that the introduction of 0,25% α-phenyl-β-nitroethene into the composition of these samples provides their long-term protection from microbiological damage. Based on the results obtained, a new biostable lubricating oil composition for marine, locomotive and stationary diesel engines was developed which does not lose its performance properties for a long time.

Keywords: lubricating composition, bacteria, fungi, biocides, additives, biostability, engine oil, corrosion.

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Introduction

One of the reasons for the aging of lubricating oils is their microbiological damage. This process is one of the problems of the oil industry and the exploitation of petroleum products. The activity of microorganisms causes the decomposition of petroleum products and the destruction of metal containers in contact with petroleum products, since lubricating oils affected by microorganisms cause corrosion of metals after a certain time [1].

Hydrocarbons contained in lubricating oils undergo bio-oxidation, decomposition and a number of chemical changes under the effect of microbial enzymes. As a result, the composition of lubricating oils changes due to the formation of oxygen compounds and slags, and their performance properties deteriorate. Numerous studies show that nearly all mineral oils are affected by microorganisms in terms of high temperature and humidity.

The impact of bacteria and fungi of various nature on motor oils is explained by the

fact that the hydrocarbons of base oils, being a source of nutrition for microbes, undergo biodegradation. It should be noted that the process of hydrocarbon biodegradation in base oils differing in the content of hydrocarbons (paraffinic, naphthenic, aromatic, saturated and unsaturated various aliphatic chains) is very different, thus paraffinic hydrocarbons are very susceptible to microbiological damage, while aromatic and naphthenic hydrocarbons are stable [2, 3, 4]. To study these factors, it is necessary to explore additives for various purposes that ensure the performance properties of compositions of technical lubricating oils. Bio-damage of technical lubricating oils, which is one of the environmental problems, has been poorly studied in our country.

Previously, on the basis of M-10 base oil with additives for various purposes, we developed a new lubricating composition for M-14B₂ oil with the following compositions (mass, %) [5]:

- multifunctional, detergent-dispersing, neutralizing, antioxidant and anti-corrosion additives AKI-150 – carbonylated calcium salt of the condensation product of alkylphenol with formaldehyde and amino acetic acid – 3.5;
- Viscoplex 2-670 – polymetacrylate type viscous additive – 0.7;
- antioxidant, anticorrosion additive ДФ-11 – 50% solution of zinc dialkyldithiophosphate in mineral oil – 1.2;
- detergent-dispersant additive - C-150 – colloidal dispersion of carbonate and calcium hydroxide, stabilized by calcium sulfonate in И-20А oil – 1.3;
- depressor Viscoplex 5-309 – 0.6;
- antifoam additive ПМС – 200А – 0.003

Since the additives introduced into the designed composition of the additive oil were organic compounds of various classes, it'd be of interest to investigate the bio resistance of these compounds as a part of the base oil M-10 separately.

The purpose of this work is to study the bio-resistance of the samples of the basic oil of the M-10 with addition of additives for various purposes, which are part of the composition of the M-14B2 oil; in the selection and testing of biocide to protect these samples; creating on the basis of the results obtained by the bio-resistant lubricant M-14B2; study of the effect of biocide on the main operational properties of lubricants.

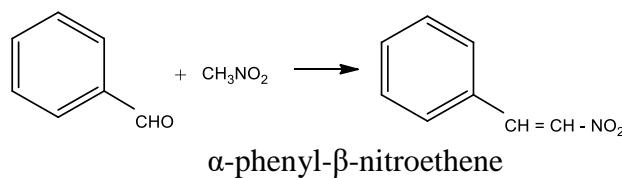
We have collected information about compounds called "biocides" and used for protection of petroleum products [6, 7, 8].

A number of widely used commercial

biocides are insoluble in oil which is associated with their very different composition and structure.

In the periodical literature, there are few examples of oil -soluble biocide compounds. Earlier, at the Institute of Chemistry of Additives of the National Academy of Sciences of Azerbaijan M.A. Shakhgeldiev with employees [6], the antimicrobial properties of α -phenyl- β -nitroethene and its derivatives replaced in the gasoline ring were investigated.

It was established that they have high antimicrobial properties and protect oil distillation fuels from bio-damage for a long time. Since these compounds are oil-soluble compounds, in our studies we used α -phenyl- β -nitroethene, which was obtained by condensation of benzaldehyde with nitromethane [9]:



Experimental part

Based on the base oil M-10 samples of oils were prepared containing in their composition detergent-dispersing, neutralizing, antioxidant, anticorrosive additives in the amount contained in the M-14B2 lubricating oil developed by us. The bio resistance of these samples in relation to microorganisms was studied according to ГОСТ 9.082-77 and ГОСТ

9.052-88 [10, 11]. For testing, *Pseudomonas Aeruginosa* bacteria and *Cladosporium Resinae* fungi were used. The same samples containing additional 0.25% α -phenyl- β -nitroethene were prepared with them. The tribological characteristics of the new lubricant composition were determined on a four-ball friction machine ChMT-1.

Results and discussion

Following results of microbiological tests, it was found that despite the fact that the samples contained additives of sulfonate, alkyl phenolate, dithiophosphate, and other additives,

on the second day of testing, all of them were subjected to continuous damage by both bacteria and fungi (samples 1, 3, 5, 7, 9), (Table 1).

Table 1. Microbiological characteristics of samples

Samples	Biocides 0,25%	Microbial growth inhibition zone diameter, cm	
		bacterium	fungus
1. M-10 +3.7% AKI-150	—	+*	+
2. + —" —"	α-phenyl-β-nitroethene	3.0-2.5	1.3-1.3
3. + 1.2% ΔΦ-11	—	+	+
4. + —" —"	α- phenyl -β- nitroethene	2.5-2.5	—
5. + 1.3% C-150	—	+	+
6. + —" —"	α- phenyl -β- nitroethene	3.0-3.0	—
7. + 0.7% Viscoplex 2-670	—	+	+
8. + —" —"	α- phenyl -β- nitroethene	2.5-2.5	4.0
9. + 0.6% Viscoplex 5-309	—	—**	+
10. + —" —"	α- phenyl -β- nitroethene	1.1-1.2	—

*(+) Complete microorganism growth., **(–) lack of microorganism growth

As can be seen from Table 1, the introduction of 0.25% α-phenyl-β-nitroethene into the composition of these samples protects them from damage by both bacteria and fungi, while in samples with the addition of 1.2% ΔΦ-11, 1.3% C-150, 0.6% Viscoplex 5-309 there is absolutely no fungal growth (samples 4, 6, 10).

Tests of the lubricating composition M-14B₂, in which the above protective additives are introduced, have shown that on the second day of testing it is completely affected by microorganisms.

Our derived results on the high antimicrobial effectiveness of α-phenyl-β-nitroethene in the composition of M-10 oil samples with protective additives contained in the M-14B₂ composition allowed us to use this biocide to protect this lubricant composition. The results of the M-14B₂ composition testing without biocide and with the addition of 0.25% α-

phenyl-β-nitroethene are given in Table 2.

As can be seen from the above data, the lubricant composition M-14B₂ is not biostable and on the second day of the test it is completely affected by bacteria and fungi. The introduction of 0.25% α-phenyl-β-nitroethene into this composition ensures its protection from microbiological damage even under conditions of forced infection by microorganisms.

The use of lubricating oils and the creation of their new analogues make it necessary to study the antioxidant, anticorrosive, detergent properties and a number of other quality indicators through qualification tests.

We have studied the effect of the inclusion of α-phenyl-β-nitroethene in the lubricant composition M-14B₂ in line with the above properties required by ГОСТ.

Table 2. Results of microbiological tests of lubricant composition M-14B₂

Composition	Without biocide	0.25% α-phenyl-β-
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			nitroethen, diameter zone, cm	
	bacterium	fungus	bacterium	Fungus
M-10 + 3.5% AKİ-150 + 0.7% Viscoplex 2-670 +1.2% ДФ-11+1.3% С-150+0.6% Viscoplex-5-309 +0.003% ПМС-200А	+	+	1.6-1.8	2.3-2.5

The main physical-chemical parameters of the new lubricant composition are shown in Table 3 in comparison with the properties of the known prototype motor oil for an identical purpose. Also, the Table indicates the requirements in accordance with ГОСТ 12337-84 for engine oil M-14B₂.

Kinematic viscosity at 50°C, mm²/s:

before testing – 51.16%

after testing – 74.3%

change in viscosity – 45.2%

The antioxidant properties of the biostable oil composition were evaluated by the change in oil viscosity at 50°C after 40 hours of testing, cСт, on an ИКМ unit in accordance with ГОСТ 20457-75.

Table 3. Test results for antioxidant properties

Index	Norm for oil group B ₂	New lubricating oil of M-14B ₂ brand with biocide α-phenyl-β-nitroethene
Evaluation of the antioxidant property on the ИКМ unit in accordance with ГОСТ 20457-75, increase in kinematic viscosity at 50°C mm ² /s	The increase in oil viscosity, no more than, 100	45.2

The anti-corrosion property of the new lubricant composition with the α-phenyl-β-nitroethene biocide was determined in the ДК-НАМИ-М1 instrument in accordance with ГОСТ 11063-77. The amount of sediment

formed when testing the composition without the biocide is 0.3%. The amount of sediment in a sample containing 0.25% biocide is nearly the same 0.25%.

Table 4. Characteristics of M-14B₂ motor oil

Index	ГОСТ 12337-84	M-10	
		AKİ-150 С-150 ДФ-11 V-2-670 V-5-309 ПМС-200А	AKİ-150 С-150 ДФ-11 V-2-670 V-5-309 α-phenyl-β nitroethen ПМС-200А
Kinematic viscosity, mm ² /c, 100°C	13.5-14.5	14.28	14.32
Viscosity index, no more than	85	90	92

Alkaline number, mgKOH/g, no less than	4.8	6.5	7.2
Sulfate ash, %, no more than	1.2	0.84	0.78
The content of mechanical impurities, %, no more than	0.02	0.014	0.013
Flash point °C no less than, in open crucible	210	220	230
Pour point, °C, no higher than	minus 12	minus 15	minus 17
Corrosivity on lead plates, g/m ² , no more than	—	Absent	Absent
Detergent properties according to ПЗВ, points, no more than	—	0	0
Density at 20°C kg/m ³ no more than	910	893	897
Detergent potential 250°C, %	80	95	93
Determination of color on the CNT colorimeter, CNT unit (with dilution 15:85)	4.0	4.0	3.5
Mass fraction of active elements, %, no less than			
Calcium	0.15	0.51	0.14
Zinc	0.045	0.44	0.062
Phosphorus	0.04	0.037	0.041
Degree of purity, mg/100g of oil, no more than	600	500	510

The combination of α -phenyl- β -nitroethene biocide with additives AKI-150, C-150, Viscoplex-2-670, DФ-11, Viscoplex-5-309 does not affect the physicochemical and

operational properties of the created new lubricant composition M-14B₂ [12].

The tribological characteristic is also established in accordance with ГОСТ 9490-75.

Table 5. Lubricating properties of commercial engine oil and new experimental M-14B₂ oil

Indicators	Lubricating properties			
	Load wear index, N	Critical load, N	Welding load, N	Wear scar diameter, mm,
M-14B ₂ commercial engine oil: ЦИАТИМ-339 ПМС «А» ДФ-11 ПМС-200A	363	548	1960	0.45
M-14B ₂ experimental oil in new composition: Viscoplex-2-670 AKI-150 C-150 ДФ-11 Viscoplex-5-309 α -phenyl- β -nitroethene ПМС-200A	353	548	1960	0.48

Tests results given in Tables 3, 4, 5 show that the introduction of 0,25% biocide α -phenyl- β -nitroethene into the M-14B₂ lubricant composition does not impair its main quality

indicators (antioxidant, anticorrosion, detergent, lubricating), and they are on the level of appropriate indicators of commercial oil M-14B₂.

Conclusion

1. It was established that the M-14B₂ lubricating oil composition containing additives for various purposes and chemical structure was not biostable and could be completely affected by microorganisms during storage and transportation.
2. It revealed that despite the different chemical nature and structure of additives for various purposes which are a part of the M-14B₂ lubricant composition, all these additives do not have antimicrobial properties.
3. The efficiency of the α -phenyl- β -nitroethene biocide developed at the Institute of Chemical Problems of the National Academy of Sciences of Azerbaijan in the compositions of M-10 oil containing functional additives of the M-14V2 lubricating oil composition was studied. It

has been established that all these compositions containing the indicated functional additives acquire biostability when 0.25% is added to their composition. α -phenyl- β -nitroethene.

4. By including α -phenyl- β -nitroethene at a concentration of 0.25% in the M-14B₂ lubricating oil composition, a new biostable M-14B₂ composition was developed that meets modern requirements for motor oils used in marine, diesel locomotive and stationary diesel engines.
5. Through qualification tests, it was established that the introduction of α -phenyl- β -nitroethene into the compound of the lubricant composition does not affect the main quality indicators of the lubricant composition M-14B₂.

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GƏMİ, TEPLIVOZ VƏ STASİONAR DİZEL MÜHƏRRİKLƏRİ ÜÇÜN BİODAVAMLI SÜRTKÜ KOMPOZİSİYASI

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Xülasə: Məqalədə M-10 baza yağı və müxtəlif təyinatlı aşqarlarla tərəfimizdən işlənib hazırlanmış M-14B₂ sürtkü yağının bioloji davamlığının tədqiqat nəticələri verilmişdir. Müəyyən edilmişdir ki, müxtəlif təbiətli aşqarlar (alkilfenolyatlar, ditiofosfatlar, sulfonatlar) mikroorganizmlərin təsirinə məruz qalır. Bu sürtkü kompozisiyاسının tərkibinə 0.25% α -fenil- β -nitroeten biosidinin daxil edilməsi onların uzun müddət mikrobioloji zədələnmədən qorunmasını təmin edir. Alınan nəticələr əsasında gəmi, teplovoz və stasionar dizel mühərrikləri üçün istismar xassələrini uzun müddət itirməyən yeni sürtkü yağı işlənib hazırlanmışdır.

Açar sözlər: sürtkü kompozisiyası, bakteriyalar, göbələklər, biosidlər, aşqarlar, biodavamlılıq, motor yağı, korroziya

БИОУСТОЙЧИВАЯ СМАЗОЧНАЯ КОМПОЗИЦИЯ ДЛЯ СУДОВЫХ, ТЕПЛОВОЗНЫХ И СТАЦИОНАРНЫХ ДИЗЕЛЕЙ

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Аннотация: В работе приведены результаты исследования биостойкости образцов базового масла М-10 с добавками защитных присадок различного назначения, входящих в состав разработанной нами ранее композиции смазочного масла М-14B₂. Установлено, что, несмотря на различную природу этих присадок (алкилфеноляты, дитиофосфаты, сульфонаты), все эти образцы поражаются микроорганизмами. Показано, что введение в состав этих образцов 0.25% α -фенил- β -нитроэтина обеспечивает их длительную защиту от микробиологического поражения. На основании полученных результатов разработана новая биостойкая композиция смазочного масла для судовых, тепловозных и стационарных дизелей, не теряющая свои эксплуатационные свойства в течение длительного времени.

Ключевые слова: смазочная композиция, бактерии, грибы, биоциды, присадки, биостойкость, моторное масло, коррозия.