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1-Aryl-2-Nitroethens as Antimikrobial Additives for Lubricating Materials

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Abstract: *The article presents the investigation results of 1-Aryl-2-Nitroethens as antimicrobial additive to protect lubricating materials from microbial destruction. It is established that addition of 1-aryl-nitroethanol in the composition of lubricating compositions in concentrated 0,05-0,2% for bacteria and 0.01-0.1% for fungi completely inhibits the growth of bacteria and fungi respectively and thus it provides lasting protection of lubricating oils from microbial destruction, also was determined that addition of the above mentioned concentrates of 1-aryl-2-nitroethens do not impair the physico-chemical properties and performance of lubricants.*

Keywords: *lubricating oils, biodamage, microbiological defeat, biocides, antimicrobial additives.*

1. INTRODUCTION

The literature data and research conducted at the Institute of Chemistry of Additives Azerbaijan National Academy of Sciences, indicate that the majority of lubricating oils produced at the present time , during storage , transportation and operation in high humidity and temperature are affected by micro-organisms [1]. Various species of microorganisms (bacteria fungi and protozoa), getting in the lubricant oil composition, use oil as the sole carbon source. As a breeding ground for microorganisms, lubricants change their hydrocarbon composition, physico-chemical properties and performance, and are almost unusable for its intended purpose. Products microbial metabolism increase the acidity of the oil, thereby causing corrosion of equipment, form a slag and sludge, which lead to clogging of the filter, which creates a number of ecological and technical problems. Lubricants lesion intensity depends on their composition. The most effective of the existing methods of protection against biological damage is a chemical method, ie use of antimicrobial additives - biocides [2]. Generally as biocides are recommended those compounds which possess a minimum concentration high antimicrobial efficacy while not degrade main physico-chemical and performance properties of lubricating oils. Extending the life of lubricating oils with biocides several times equivalent to an increase of oil production by the same factor. Biodegradation problem is the subject of detailed research of scientists in most developed countries.

2. MATERIALS AND METHODS

The Institute of Chemistry of Additives of ANAS also for decades maintained a purposeful synthesis of organic compounds of different structure and composition, and the study of their antimicrobial properties against microorganisms, damaging oil and cutting fluids [3-6]. Developed methods of synthesis and investigated the amino methyl derivatives hydroxy benzoic acid esters, N-organyloxymethyl derivatives of heterocyclic amines (morpholine, piperidine, hexamethyleneimine**,** piperazine, 1, 3-oxazine, 1, 3-oxazolidine, 1, 3-imidazolidine, primary hydropirimidine et al.), methylene-bis-oksazine- and methylene- bis-diazatsikloalkanes. These studies have allowed us to develop and put into production a number of highly effective biocides for oil products, and to develop scientific bases of purposeful synthesis of antimicrobial additives for petroleum products and lubricant-liquid coolants. However, naturally occurrence of micro-organisms to adapt to prolonged employ of biocides makes the synthesis of new chemical compounds as antimicrobial additives the pressing question.

As our continued research on the development of new biocide with benzaldehydes condensation with nitromethane 1-aryl-2-nitroethene were recieved [7]:

$$RC_6H_4CHO + CH_3NO_2 + NaOH \longrightarrow$$

$$RC_6H_4CH(OH)CH = NO_2Na \xrightarrow{HCl}$$

$$RC_6H_4CHO = CHNO_2 + NaCl + H_2O$$

Condensation of benzaldehyde (or substituted derivatives) was carried out with nitromethane in methanol solution at 5-10^{0}C adding aqueous NaOH followed by neutralization with aqueous sodium salt solution of HCl. The resulting 1-aryl-2-nitroethene, after recrystallisation from methanol, are tinted yellow crystalline substance with a faint characteristic odor, soluble in common organic solvents. The melting point of the 1-aryl-2-nitroethene is shown in Table 1.

Table1.

$RC_6H_4CH=CHNO_2$, R	Melting point, ^{0}C	
	literary	experimental
H	57-58	57
p-CH_3	109-110	107-109
p-CH_3O	83-84	86-87
p-F	96-99	95-96
o-F	93-94	92-93
p-Cl	115	115-116
o-Cl	105-107	110
p-OH	168-169	168-170
o-OH	150-153	155

1-aryl-2-nitroethene were investigated as antimicrobial additives in a lubricant composition.

Determination of biological stability of lubricants with biocides were conducted by ГОСТ 9.052-75 and ГОСТ 9.082-77. For the tests used oil М-11 (Baku).(ТУ 3820140-76), М-11 (East.) (ТУ 38.101523-80). Tests were carried out on the following three methods:

Method 1: The main point of this method is in maintaining specimens infected with an aqueous spore suspension of fungi and bacteria, in conditions optimal for the development of fungi, without an additional source of organic and mineral nutrition.

Method 2: The main point of this method is in maintaining the samples contaminated with a spore suspension of fungi and bacteria in an aqueous solution of mineral salts, under conditions optimal for the development of fungi on a medium with an additional source of mineral nutrition.

Method 3: The main point of this method is in maintaining specimens infected with a spore suspension of fungi in an aqueous solution of mineral salts in the conditions that are optimal for the development of fungi in a medium with an additional source of organic and mineral nutrition.

Also was tested the sample of known biocide - 1, 3-bis (2-hydroxyethyl) -1, 3-diazacyclobutan (USSR Authors communication 1,181,306..).

Data on comparative efficacy of 1-aryl-2-nitroethenyls RC6H4CH = CHNO2 shown in Table 2.

Table2.

Biocide, R	The effective concentration of biocide in the composition of lubricants, %			
	M-11(Baku.)		M-11(eastern.)	
	bacteria	fungi	bacteria	fungi
H	0,1	0,05	0,1	0,05
п-CH_3	0,2	0,1	0,2	0,1
п-CH_3O	0,2	0,1	0,2	0,1
o-F	0,05	0,01	0,05	0,01
п-F	0,05	0,01	0,05	0,01
o-Cl	0,05	0,025	0,05	0,025
п-Cl	0,05	0,025	0,1	0,025
o-OH	0,1	0,025	0,1	0,025
п-OH	0,1	0,025	0,1	0,025
1, 3-Bis-(2-hydroxyethyl) -1, 3-diazacyclobutan	0,25	0,5	–	–

3. RESULTS AND DISCUSSION

The research results shown in the table testify that administration of 1-aryl-2-nitroethene a lubricant composition at a concentration of 0.05-0.2% and 0.01-0.1% of bacteria and fungi to completely inhibit the growth of bacteria and fungi, respectively. Regardless of the position of the substituent on the benzene ring and the F-Cl-substituted derivatives are more effective than their other analogs.

Adding 1-aryl-2-nitroethene in lubricating materials in concentrations above helps to preserve their physico-chemical properties and performance (Table 3).

Table3.

Index	Testing method	Testing results		
		M-11	M-11 + 0,05% 1-aryl-2-nitroethene (R – H)	M-11+0,05% 1-aryl-2-nitroethene (R – P – F)
Kinematic viscosity, mm^2/s with 100^0C	ГОСТ 33-82	11,46	11,36	11,44
Viscosity index	ГОСТ 25371-82	63	65	63
Congelation point, ^0C	ГОСТ 20287-74	minus 4	minus 8	minus 9
Corrodity on lead plates, g/m^2	ГОСТ 20502-72	210	175	177
Thermooxidative stability with 250^0C, min	ГОСТ 23175-78	14	19	19
acid number, mg KOH/g	ГОСТ 11362-76	0,07	0	0
Cleaning capacity	ГОСТ 10734-64	0	3	3

Throughout the period of the test lubricants with additives of 1-aryl-2-nitroethene in above mentioned concentrations acquire micro stable properties that are maintained even in conditions of toughened experiment - forced infestation by microorganisms.

The antimicrobial properties of the 1-aryl-2-nitroethene were studied in long-term storage conditions (table4and5).

Table4.

Biocide, R	Biocide concentration in oil M-11, масс. %	The number of colonies of microorganisms in 1 ml M11 oil after 450 day tests			
		bacteria		fungi	
		without	with	without	with
1–Aryl-2– nitroethene					
H	0,1	4	6	2	4
p-CH_3	0,2	20-25	25-30	15	20
p-CH_3O	0.2	20-25	25-30	15	20
p-F	0,05	–	–	1-2	1-2
p-Cl	0,05	–		–	–
p-OH	0,1	–	5	–	–
o-OH	0,1	–	–	–	–
M-11 oil (control)	–	cont.	cont.	cont.	cont.

Note: *"– " - absence of microbial growth; Cont. - continuous growth of microorganisms, the amount of which corresponds to 6-7 thousand colonies; without - without entering test-microorganisms; with - with entering test-microorganisms.*

Table5.

Index	M-11 oil		Results after 450 day storage	
	Before test	After 30 days	M-11 + 0,05% 1-aryl-2-nitrorthene (R – H)	M-11 + 0,05% 1-aryl-2-nitroethene (R – P – F)
Kinematic viscosity, mm^2/s with 100^0C	11,46	16,2	11,3	11,1
Viscosity index	63	50	60	61
Congelation point, ^0C	Minus 4	10	Minus 3	Minus 3
Corrodity on lead plates, g/m^2	210	300	200	200
Thermooxidative stability with 250^0C, min	14	5	14	14
Cleaning capacity	0,07	1,7	0,1	0,1

4. CONCLUSIONS

M-11 oil with anti-microbial additives and without them were kept in conventional metal containers under conditions similar to tropical. In the container was added a mixture of microorganisms, damaging lubricants (according to ГОСТ 9.052-75 and ГОСТ 9.082-77), and salts, that serve as mineral and nitrogen nutrition for microorganisms. Oil analysis showed that in the absence of antimicrobial additive the M-11 oil is in full lesion by microorganisms, causing deteriorating performance and its physicochemical properties. In M-11 oil with additives microorganisms were not detected and their properties after 450-day storage change compared to with control.

Thus, the 1-aryl-2-nitroethene possess high antimicrobial properties, will provide complete and lasting protection of lubricants against microbial destruction, have a broad spectrum of antimicrobial action (suppressing the growth of bacteria and fungi), do not impair the physico-chemical properties and performance of lubricants.

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