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RESEARCH OF N,N-DIALLYL (3-ARYLISOXASOL-5-YL)-METHYLENESULFONYLAMIDES AS ADDITIVES FOR INCREASING THE LOAD CARRYNG CAPACITY OF SYNTETIC OIL BASED ON THE PENTAERYTHRITOL ESTHER AND BUTYRIC ACID

Об'єктом дослідження є N,N-діаліл-(3-арилізооксазол-5-іл)-метиленсульфоніламіди (Ar: C_6H_5 (1); $C_6H_4–4–CH_3$ (2); $C_6H_4–4–OC_2H_5$ (3)) в якості протизношувальних присадок до олив, які одержано з відповідних сульфонілхлоридів та діаліламіну. Як еталон за дією використано промислову присадку ДФ-11 (діалкілдитіофосфат цинку) (4), а еталон за будовою – аліловий естер 2-меркаптобензтіазолу (5). Як синтетичну оливу використано естер пентаеритриту та н-масляної кислоти, який одержано реакцією естерифікації.

Досліджено деякі фізичні характеристики (відносну в'язкість та показник заломлення) одержаної оливи при додаванні сульфоніламідів (1)–(3) та без них.

Вплив додавання N,N-діаліл-(3-арилізооксазол-5-іл)-метиленсульфоніламідів (Ar: C_6H_5 (1); $C_6H_4–4–CH_3$ (2); $C_6H_4–4–OC_2H_5$ (3)) на динамічну міцність досліджуваної оливи оцінювали за методикою ASTM D2783 (ГОСТ 9490-75) на чотирикульковій машині тертя за показником критичного навантаження. Випробовування проводили при терті у відповідних рідинах стандартизованих металевих кульок, що виготовлені зі сталі ШХ15 (мікротвердість – 64–66 HRC, параметр жорсткості – $Ra < 0,25$ мкм). Частота обертання верхньої навантаженої кульки відносно трьох нерухомих кульок – 1500 хв$^{-1}$, температура оливи – 20 °С. Час випробувань при кожному навантаженні – 10 с, повторюваність експерименту – три випробування для кожного навантаження.

Дослідження зміни діаметру плями зношення $D_з$ металевих кульок при терті в вихідній оливі без додавання сполуки (3) та відповідно з додаванням здійснено при обертах 1500 хв$^{-1}$, початковій температурі 25 °С, навантаженні 98 Н, часу дослідження – 1 година. Одержані результати свідчать, що $D_з$ оливи без внесення зазначеної сполуки склав 0,75 мм, а при її внесенні (0,1 мас. %) – 0,67 мм, тобто, зниження зношування складає 10,67 %.

Знайдено, що присутність досліджуваних присадок (1)–(3) у малих концентраціях у синтетичній оливі на основі естеру пентаеритриту та н-масляної кислоти може суттєво підвищувати її несучу здатність. Найбільш ефективною є сполука (3), яка в концентрації 0,1 % мас. перевищує несучу здатність, порівняно з (4), у 1,38 рази, а з (5) – у 1,37 рази. Зазначена сполука є більш ефективною у концентрації, що в 10–20 разів є меншою, порівняно з відомими присадками.

Таким чином, застосування N,N-діаліл-(3-арилізооксазол-5-іл)-метиленсульфоніламідів, як присадок для підвищення несучої здатності синтетичних олив на основі естеру пентаеритриту та синтетичних жирних кислот, дозволяє підвищити протизношувальну активність мастильних матеріалів. Тому вони можуть бути використані для створення нових ефективних композицій до олив і нафтопродуктів.

Ключові слова: *N,N-діаліл-(3-арилізооксазол-5-іл)-метиленсульфоніламіди, синтетична олива, відносна в'язкість, показник заломлення, пляма зношення, несуча здатність.*

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1. Introduction

Today, the global production of lubricants is approximately 41 million tons/year, the lion's share of which is oil [1]. Refined petroleum products are toxic and can accumulate in the environment, creating incorrigible environmental problems. Therefore, in Western Europe in recent decades there has been a question of improving the

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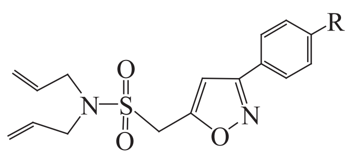
environment in the framework of the Kyoto Protocol and subsequent directives [2, 3]. So, modern oils should have a wide range of operational properties that take into account the needs of both environmentalists and consumers and equipment manufacturers. The use of additives solves this problem [4].

The development of new anti-wear additives of Ukrainian production to improve the operational properties of oils is an urgent problem of modern petrochemicals. Isoxazole derivatives may be interesting in this regard due to their wide range of practically useful properties. Thus, the isoxazole heterocycle is part of certain drugs, for example, Leflunomide [5], Valdecoxib [6], Sulfisoxazole [7], and others. The use of isoxazole derivatives as anticancer agents [8], antioxidants [9], and complexing agents [4] has also been reported [10].

Therefore, the object of research is N,N-diallyl (3-arylisoxasol-5-yl)-methylenesulfonylamides (Ar: C_6H_5 (1); C_6H_4–4–CH_3 (2); C_6H_4–4–OC_2H_5 (3)) as antiwear additives to oils that are derived from the corresponding sulfonyl chloride and dialylamine. And the aim of research is the use of N,N-diallyl (3-arylisoxasol-5-yl)-methylenesulfonylamides as additives to increase the bearing capacity of synthetic oils based on pentaerythritol and synthetic fatty acids (SFA).

2. Methods of research

The search for new substances as additives to increase the bearing capacity of oils and lubricants is of not only scientific, but also practical interest. The specified research objective is solved by the use of N,N-diallyl (3-arylisoxasol-5-yl)-methylenesulfonylamides in the general formula:



, (1)–(3)

where R: H (1); CH_3 (2); OC_2H_5 (3), as additives to increase the bearing capacity of synthetic oils based on pentaerythritol and SFA.

Compounds (1)–(3) are prepared according to a known procedure [11] from the corresponding sulfonyl chloride and dialylamine.

As a reference, to compare the effect of the studied compounds on the tribological properties of oils, the industrial additive DF-11 (zinc dialkyldithiophosphate (4)) was used [12]. The disadvantages of using this additive in oils are the increased ability to form deposits on machine parts and high ash content. This, in fact, is the reason for the abrasive wear of the cylinder-piston group, deposition of soot in the combustion chamber, candles and other parts of the engine, reducing its service life and reliability [13].

The closest in structure to compounds (1–3) is allyl ether 2-mercaptobenzthiazole (5) in a concentration of 1–2 wt. %. It has been previously stated [14] as an ashless antiwear additive for lubricants.

The oil based on pentaerythritol ester and *n*-butyric acid was obtained according to the procedure [15].

Some physical characteristics of the obtained oil were studied with the addition of N,N-diallyl (3-arylisoxasol-5-yl)-methylenesulfonylamides (1)–(3) (relative viscosity – with a VU viscometer (GOST 1532-54) according to [16], and the refractive index on the IRF-22 device (USSR) in accordance with [17]) (Table 1).

The relative viscosity is calculated according to the well-known formula, namely:

$$\eta = t/t_0,$$

where η is the relative viscosity; t is the expiration time of the oil with the additive; t_0 is oil outflow time without additive.

Three measurements of the oil outflow time with an additive (t) for various concentrations and three measurements of the oil outflow time without an additive were carried out. The arithmetic mean of the results of three determinations is taken as the result of determining the expiration time.

The refractive index was measured first at a temperature of 25 °C, and then recalculated n_D^{20} according to the formula:

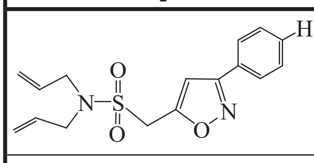
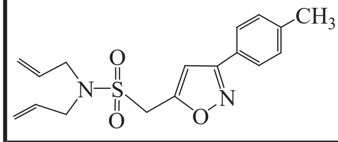
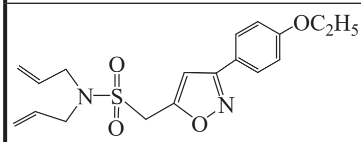
$$n_D^{20} = n_D^{25} + (t-20)\cdot 0.00035,$$

where $n_D{}^{25}$ is the refractive index at the temperature of the experiment; n_D^{20} is the refractive index at a temperature of 20 °C; t is the temperature of the experiment, °C; 0.00035 is the change in refractive index when the temperature changes by 1 °C.

To assess the tribological properties of oils, indicators such as the load wear index U_l, the bearing capacity (or maximum load) R_{cr}, and the welding load R_w and the diameter of the wear spot D_w are used. The bearing capacity of liquid lubricant provides a hydrodynamic friction regime in precision friction units of automobile and aircraft engines. The bearing capacity of lubricants increases due to additives that form microheterogeneous associates [18]. So, the additive can affect the structure of the oil with an increase in its bearing capacity.

Table 1

Relative viscosity (η), expiration time (t, t_0) and refractive index n_D^{25} of an oil based on ester of pentaerythritol and *n*-butyric acid with the addition of N,N-diallyl (3-arylisoxasol-5-yl)-methylenesulfonylamides) (1)–(3)

Investigated substances		*C*, wt. %.	η	*t*	$n_D{}^{25}$	$n_D{}^{20}$
	(1)	0.1	0.993	5.483	1.4460	1.4478
	(2)	0.1	0.950	5.243	1.4450	1.4468
	(3)	0.5 0.1 0.01	0.959 0.999 0.945	5.294 5.515 5.215	1.4458 1.4458 1.4450	1.4476 1.4476 1.4468
Pentaerythritol tetrabutyrate		–	–	t_0=5.52	1.4444	1.4462

In practical terms, the studied compounds (1)–(3) can be used as additives to existing oils and lubricants.

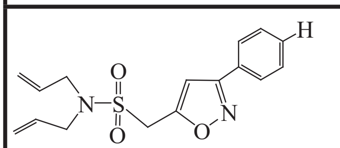
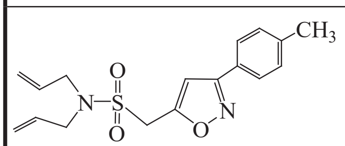
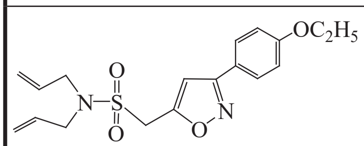
Thus, aviation oils for gas turbine engines, helicopter gearboxes and other equipment of brands B-3V (TU 38.101295-85), LS-240 (TU 301-04-010-92) and PTS-225 (TU 38.401-58-1-90) are synthetic oils based on pentaerythritol esters and fatty acids with a complex of additives. They differ in viscosity, lubricating properties, pour points and other operational properties [19].

The dynamic strength of the test oil was evaluated according to the method of ASTM D2783 (GOST 9490-75) on a four ball friction machine according to the critical load index. This indicator represents the maximum load at which metal contact (scoring) does not yet occur during friction in the test liquid of standardized metal balls made of ShKh15 steel (microhardness – 64–66 HRC; stiffness parameter – Ra<0.25 μm) [20].

Experimental conditions: rotation speed of the upper loaded balls in relation to three stationary balls – 1500 min^{-1}; oil temperature – 20 °C; test time at each load – 10 s; experiment repeatability – three tests for each load (Table 2) [21].

Table 2

Maximum oil loading based on ester of pentaerythritol and butyric acid in the presence of additives [21]

Investigated substances	C, wt. %.	P_{cr}, H
 (1)	0.1	800
 (2)	0.1	710
 (3)	0.5 0.1 0.01	750 1000 800
DF-11 (4)	1.0 0.1 0.01	875 725 705
Allyl ester of 2-mercaptobenzthiazole (5)	2.0 1.0 0.1	875 880 730

After analyzing the data obtained, it is possible to talk about the effectiveness of the addition of isoxazole-containing additives to oil based on ester of pentaerythritol and butyric acid.

3. Research results and discussion

In the study of the relative viscosity of the oil without the addition of compounds (1)–(3) and with their participation it was found that these additives do not carry out the thickening action of the oil, but only improve the flow rate. This can contribute to lowering the pour point of said oil in winter (Table 1).

According to the Table 1, the refractive index of oil with and without additives is close to the refractive index of glass, n_D^{20} of which is from 1.485 to 1.925.

The study of the diameter of the wear spot D_w of compound (3) was carried out at revolutions of 1500 rpm, an initial temperature of 25 °C, a load of 98 N, and a study time of 1:00. The results obtained indicate that D_w of the oil without making the specified compound was 0.75 mm, and when it was added (0.1 wt. %) – 0.67 mm. Therefore, the reduction in wear is 10.67 %.

Table 2 shows the maximum load of oil based on ester of pentaerythritol and butyric acid in the presence of the proposed compounds and known antiwear additives.

According to Table 2, additives (1)–(3) in low concentrations can significantly increase the bearing capacity of synthetic oils based on pentaerythritol and SFA. The most effective is compound (3), which at a concentration of 0.1 % of the mass significantly increases the bearing capacity of the oil. Moreover, the value for increasing this characteristic is 1.38 times greater in comparison with the industrial additive DF-11, and 1.37 times greater in comparison with allyl ester of 2-mercaptobenzthiazole, respectively. In addition, this compound is more effective in concentration, 10–20 times less compared with known additives.

4. Conclusions

Thus, the use of N,N-diallyl (3-arylisoxasol-5-yl)-methylenesulfonylamides as additives to increase the bearing capacity of synthetic oils based on ester of pentaerythritol and synthetic fatty acids, allows to increase the antiwear activity of lubricants. So, this indicates the prospects of their use for creating new effective compositions for oils and petroleum products.

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