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

Pavliuk O., Sukhoveev V., Pyliavskyi V., Kashkovsky V.

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...
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-arylisoxazol-5-yl)-methylenesulfonylamides (Ar: C₆H₅ (1); C₆H₄–4–CH₃ (2); C₆H₄–4–OC₂H₅ (3)) as antiwear additives to oils that are derived from the corresponding sulfonyl chloride and diallylamide. And the aim of research is the use of N,N-diallyl (3-arylisoxazol-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 not only scientific, but also practical interest. The specified research objective is solved by the use of N,N-diallyl (3-arylisoxazol-5-yl)-methylenesulfonylamides in the general formula:

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{R} & \quad \text{O} \\
\end{align*}
\]

where R: H (1); CH₃ (2); OC₂H₅ (3), as additives to increase the bearing capacity of synthetic oils based on pentaerythritol and synthetic fatty acids (SFA).

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

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-arylisoxazol-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 oil based on pentaerythritol ester and n-butyric acid with the addition of N,N-diallyl (3-arylisoxazol-5-yl)-methylenesulfonylamides (1)–(3) 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-arylisoxazol-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 \(\eta\) 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 \(U_i\), the bearing capacity (or maximum load) \(R_{on}\), 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.

| Investigated substances | \(C\) wt. % | \(n\) | \(t\) | \(n_D^{25}\) | \(n_D^{20}\) |
|-------------------------|-------------|-------|-------|-------------|-------------|
| DF-11 (4)               | –           | –     | \(t_0\) | –           | \(n_D^{20}\) |
| Pentaerythritol tetrabutyrate | –       | –     | 5.52  | 1.4444      | 1.4462      |

Table 1: Relative viscosity \(\eta\), 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-arylisoxazol-5-yl)-methylenesulfonylamides (1)–(3)
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

| Investigated substances | ξ wt. % | P_cr. H |
|-------------------------|--------|---------|
| (1)                     | 0.1    | 800     |
| (2)                     | 0.1    | 710     |
| (3)                     | 0.5    | 750     |
|                         | 0.1    | 1000    |
|                         | 0.01   | 800     |
| DF-11 (4)               | 1.0    | 875     |
|                         | 0.1    | 725     |
|                         | 0.01   | 705     |
| Allyl ester of 2-mercaptobenzthiazole (5) | 2.0 | 875 |
|                         | 1.0    | 880     |
|                         | 0.1    | 730     |

According to the Table 1, the refractive index of oil with and without additives is close to the refractive index of glass, nD20 of which is from 1.485 to 1.925.

The study of the diameter of the wear spot Dw 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 Dw of the oil without making the specified compound was 0.75 mm, and when it was added (0.1 wt. %) it was 0.67 mm. Therefore, the reduction in wear is 10.67%.

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 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 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.

4. Conclusions

Thus, the use of N,N-diallyl (3-arylisoxazol-5-yl)-methylenesulfonamides 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.

References

1. Korneev, S. V., Kornienko, A. A., Iarmovich, I. V. (2013). Oboznovernons veshchovih dlja prihotovleniia plastichnykh smazok. Shbornik nauchnykh trudov “Sword”, 12 (3), 34–37.
2. Dyrektyva 2009/30/YeS. Yevropeiskoho Parlamentu ta Rady pro spryjannia vikorystanniu biolohichnoho palyva abo inshykh vydiv ponovliuvanoho palyva dlia transpota (08.05.2003).
3. Dyrektyva 2009/28/YS. Pro stymuliuvannia vikorystanniu enerhii z vidnosliuvanykh dzherel (23.04.2009).
4. Rudnik, L. R.; Danilov, A. M. (Ed.) (2013). Prisaliki k smazochnym materialam. Svoistva i primenenie. Saint Petersburg: COP «Professia», 928.
5. Solaniki, P. V., Uppelli, S. B., Padaki, S. A., Anekal, D., Dohale, S. B., Bembulkar, S. R., Mathad, V. T. (2015). A Facile Approach for the Synthesis of Highly Pure Immunomodulator Drugs – Leflunomide and Teriflunomide: A Robust Strategy to Control Impurities. World Journal of Pharmaceutical Sciences, 13 (11), 2265–2272.
6. Talley, J. J., Brown, D. L., Carter, J. S., Grano, M. J., Koboldt, C. M., Masferrer, J. L. et al. (2000). 4-[5-Methyl-3-pelylenesulfonamido-[benzaldehyde]-benzenesulfonamide, Valdecoxib: A Potent and Selective Inhibitor of COX-2. Journal of Medicinal Chemistry, 43 (5), 773–777. doi: http://doi.org/10.1021/jm990677v
7. Nasr, T., Bondock, S., Eid, S. (2015). Design, synthesis, antimicrobial evaluation and molecular docking studies of some new 2,3-dihydrothiazoles and 4-thiazolidinones containing sulfonylcarbazole. Journal of Enzyme Inhibition and Medicinal Chemistry, 31 (2), 236–246. doi: http://doi.org/10.3109/14756366.2015.1016514
19. Pyvoyara, V. P. (2010). Metodychni rekomendatsii po khimmo-
tolohii No. 62. Klassifikatsia zmashechnykh olyv za viazkosti
i ekspluatatsiyh kharkhurystykumy po HOST ta mizhnarodnym
standartam. Vykorystannia klassifikatsiyh kharkhurystyk
dlya vyznachennya rasvymozamnosti zahislhnykh ta vitchugianyh
olyv. Kyiv, 28. Available at: http://10xcentr.com.ua/1/193/310/

20. Bozhko, O. O., Yeslyevskyi, S. O., Cherniavskyi, Ye. K. (2015).
Pat. No. 113695 UA. Zastosuvannia 4-(N-hliukozyliden)amino-
benzynoї kysloty yakh prysadok dla pidvyshchennia neschoi zdat-
nosti etanida — komponenta alternatyvnyho paliv. MPK: C10L
1/182 C101 1/189. No. u 2019 07784. Declared: 04.12.2015,
published: 27.02.2017, Bul. No. 4.

21. Pavliuk, O. V., Pyiavskyi, V. S., Sukhovieiev, V. V., Kash-
kovskyi, V. I. (2019). Zastosuvannia N,N-dialil-(3-arylizooksazol-
5-il)-metylisulfonilamidov — yak prysadok dla pidvyshchennia
neschoi zdatnosti aviatichnykh olyv na osnovi esteru penterytrytu
ta syntetychnykh zhyrnykh kyslot. No. w 2019 07784.

Pavlik Oleksandr, Engineer, Department of Organic and Petrochemi-
cal Synthesis, V. P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine, e-mail: pavlukksasha@gmail.com, ORCID: https://orcid.org/0000-0002-1590-1675

Sukhovieiev Volodymyr, Doctor of Chemical Sciences, Leading Re-
searcher, Head of Department of Chemistry, Nizhyn Mykola Gogol State University, Cherniivska Oblast, Ukraine, V. P. Kukhar Insti-
tute of Bioorganic Chemistry and Petrochemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine, ORCID: https://orcid.org/0000-0002-1590-1675

Pyiavskyi Volodymyr, Senior Researcher, Department of Homoge-
neous Catalysis and Petroleum Additives, V. P. Kukhar Institute of Bioorganic Chemistry and Petrochemistry of the National Academy of Sciences of Ukraine, Kyiv, Ukraine, e-mail: Pyiavskyi@nas.gov.ua, ORCID: https://orcid.org/0000-0001-7422-0311

Kashkovsky Volodymyr, Senior Researcher, Deputy Director for
Research, Head of Department of Organic and Petrochemical Syn-
thesis, V. P. Kukhar Institute of Bioorganic Chemistry and Petro-
chemistry of the National Academy of Sciences of Ukraine, Kyiv,
Ukraine, e-mail: kashkovsky@bpci.kiev.ua, ORCID: https://orcid.org/
0000-0001-8413-7132