Elżbieta ROGOŚ[*], **Andrzej URBAŃSKI**[*]

THE ANTIWEAR AND EXTREME-PRESSURE PROPERTIES, AND VISCOSITY-TEMPERATURE CHARACTERISTICS OF THE LUBRICANTS CONTAINING VEGETABLE OIL AND AW/EP ADDITIVES

WŁAŚCIWOŚCI PRZECIWZUŻYCIOWE I PRZECIWZATARCIOWE ORAZ CHARAKTERYSTYKI LEPKOŚCIOWO-TEMPERATUROWE KOMPOZYCJI OLEJ ROŚLINNY-DODATKI AW/EP

Key words:

vegetable oils, antiwear properties, antiscuffing properties, rheological properties

Słowa kluczowe:

oleje roślinne, właściwości przeciwzużyciowe, właściwości przeciwzatarciowe, właściwości reologiczne

Abstract

The lubricating and rheological properties of compositions based on vegetable oil mixtures and selected additives were examined. The additives were dedicated both to vegetable oils as well as to petroleum products. The additives varied in chemical structure and the content of active elements. It was

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[*] Institute for Substainable Technologies – NRI, ul. Pułaskiego 6/10, 26-600 Radom, Poland.

concluded that the nature of particular additives as well as their concentration in the composition significantly altered the initial lubricating and rheological properties of the base oil. The differences were diverse and highly dependent on the composition. The most beneficial effects were obtained when the additives containing phosphorus and nitrogen were added to the base oil.

INTRODUCTION

The widely used group of industrial oils are products based on crude oil. The petroleum derivatives constitute about 90% of annual base oil production **[L. 1]**. In general, the Polish market reflects this relation as well **[L. 2]**. Almost 85% of base oil production belongs to the I API group, regarded as (according to the origin and chemical composition) hardly biodegradable and harmful to the natural environment **[L. 3]**. During operation thereof, the negative ecological impact of petroleum oil bases rises due to the emerging thermo-oxidation by-products **[L. 4]**. Spent petroleum oils are regarded as highly harmful to the environment and therefore treated as hazardous waste **[L. 5, 6]**.

The social awareness of the risks resulting from the use of petroleum industrial oils implies the need for more reasonable substitutes – readily biodegradable and non-toxic. In particular, the applications where: a lubricant may get into contact with the environment are the most desirable targets. The most potential alternative oil bases are vegetable oils – renewable, characterized by minimal ecological impact, and readily biodegradable **[L. 7–9]**.

The use of vegetable oils as a biodegradable industrial base oils require their modification in order to make them more suitable for a particular application. With the reference to such requirements, vegetable oils reveal high viscosity-thermal properties, high ignition temperature, and good antiwear activity **[L. 10, 11]**. However, the fulfilment of even more restrictive expectations for the load resistance (i.e. for bearings, pneumatic machinery, hydraulics) entails the modification of lubricating properties **[L. 12]**. The adequate properties of the lubricating composition shape the long-term operation of the machine. The lubricating properties of vegetable oils may be altered with additives. Due to the ecological aspect, the additives used for this purpose must not contain metals **[L. 13, 14]**. Readily biodegradable lubricants are predominantly used in machines operating outdoors. Thus, the adequate rheological properties are also desirable. In this paper, the authors present the results on modification of vegetable base oil with different additives and their impact to rheological properties of the base.

MATERIALS AND METHODS

During the experiments, the compositions based on vegetable oil and additives were investigated. The base oil consisted of rapeseed oil ($85\%_{m/m}$) and castor oil

(15%$_{m/m}$). The basic physiochemical properties of the base oil are listed below (**Table 1**).

Table 1. Physiochemical properties of vegetable oil base used in experiments
Tabela 1. Właściwości fizykochemiczne roślinnej bazy olejowej

Feature:	Analytical method	Base oil
Viscosity class	PN-ISO 3448:2009	VG 46
Kinematic viscosity at 40°C, mm^2/s	PN-EN ISO 3104:2004	43,04
Viscosity index	PN ISO 2909:2009	191
Corrosivity, Cu, 120°C, 3 h, corrosion degree	PN-EN ISO 2160:2004	1
Thermal stability, Cu, 135°C, 96 h	PN C-96057-6	1

The AW/EP lubricating additives were selected to carry out the experiments. The mentioned additives are dedicated for vegetable base oils and do not contain metals. For comparison purposes, one typical petroleum additive containing zinc was used. The additives chosen for the experiments are regarded as non-impeding the corrosively of base oil, which is essential for final application. The oil compositions to be tested are listed below (**Table 2**).

Table 2. The investigated oil compositions
Tabela 2. Badane kompozycje olejowe

Additive	Purpose	Active element content [%]	Additive content [%$_{m/m}$]	Designation
R-1 (the mixture of ammonium phosphates)	Vegetable oils	P: 4.8; N: 2.7	1	R-1-1
			0.5	R-1-0.5
			0.2	R-1-0.2
R-5 (the mixture of ammonium phosphates, di-t-buthyl-p-kresol and alkulcarboxyl acid)	Vegetable oils	P: 0.25; N:0.34	10	R-5-10
			7	R-5-7
			5	R-5-5
R-6 (triphenyl phosphate)	Vegetable oils	P: 3.15	3	R-6-3
			2.5	R-6-2.5
			1.5	R-6-1.5
N-11 (alkyl derivatives of zinc dithiophosphates)	Vegetable oils	P: 3.04; Zn: 3.63; S: 6.29	3	N-11-3
			2	N-11-2
			1	N-11-1

The antiwear and antiscuffing properties of oil compositions were examined. The experiments were carried out according to PN-C-04147:1976 as well as the method developed in ITeE – PIB, based on a modified T-02 tester under constantly growing load **[L. 15]**. In both methods, the components of the friction pair were ½” steel balls, made of bearing steel 100Cr6. The normative method was used for the estimation of friction trace diameter on the test balls (constant load of 392.1 N, speed 1450 rpm, 1 h) and the load of welding. Using the T-02, the scuffing load and the limiting load of scuffing were assessed under the following conditions: speed of 500 rpm, load amp of 409 N/s, initial load of 0 N, and temperature of 20°C. The final result was an arithmetic average of three tests. The components of tested friction pairs were examined using a scanning electron microscope coupled with X-ray energy-dispersive spectroscopy (SEM/EDS).

The experiments on rheological properties were carried out on a rotation rheometer, equipped with external thermostat, allowing the runs under -30–200°C. The viscosity vs. temperature curves were determined under–30–80°C, by constant cutting speed of 100 s^{-1}. The measurements were performed using cone-plate set up. For each lubricating composition, three separate curves (viscosity vs. temperature) were determined and the changes in dynamic viscosity were calculated as an arithmetic average of three separate measurements.

Results and discussion

The experiments revealed the beneficial impact of each additive on antiwear and antiscuffing properties of tested oil compositions. The majority of compositions had more profitable parameters of trace diameter, scuffing load, and limiting load of scuffing in comparison to the unmodified base oil. **Figure 1** depicts the values of mentioned parameters.

Each of the rested additive revealed a beneficial influence on the antiwear properties of the oil base. Apart from composition N-11-1, the traces of wear measured onto the test balls were much smaller. The lowest wear of the friction pair was observed for the compositions containing R-5 and R-6 additives, in the concentration of 10 and 3%, respectively. The wear traces measured for these samples were smaller by more than 95% in comparison to the base oil without additives. The remaining oil compositions revealed about 40-50% less wear of the friction pair when compared to the control.

The assessment of antiwear and antiscuffing properties of the compositions were performed under scuffing conditions indicating the most beneficial influence of R-1 and N-11 additives. Compositions containing mentioned additives revealed the highest scuffing load as well as the limiting load of scuffing. These compositions were characterized by the highest resistance of lubricating film and by the smoothest course of scuffing and its consequences. For the most beneficial concentrations of mentioned compositions, the similar values of scuffing load were measured, which were about 36-38% higher in comparison to the control (oil base). On the other hand, the addition of R-1 or N-1 provided a higher limiting load of scuffing of about 115% and 95%, respectively. The other additives had considerably lower impact on the mentioned parameters. The scuffing load values, apart from the R-5-5 composition, increased by 5-10%, and the limiting load of scuffing increased by about 10-15%.

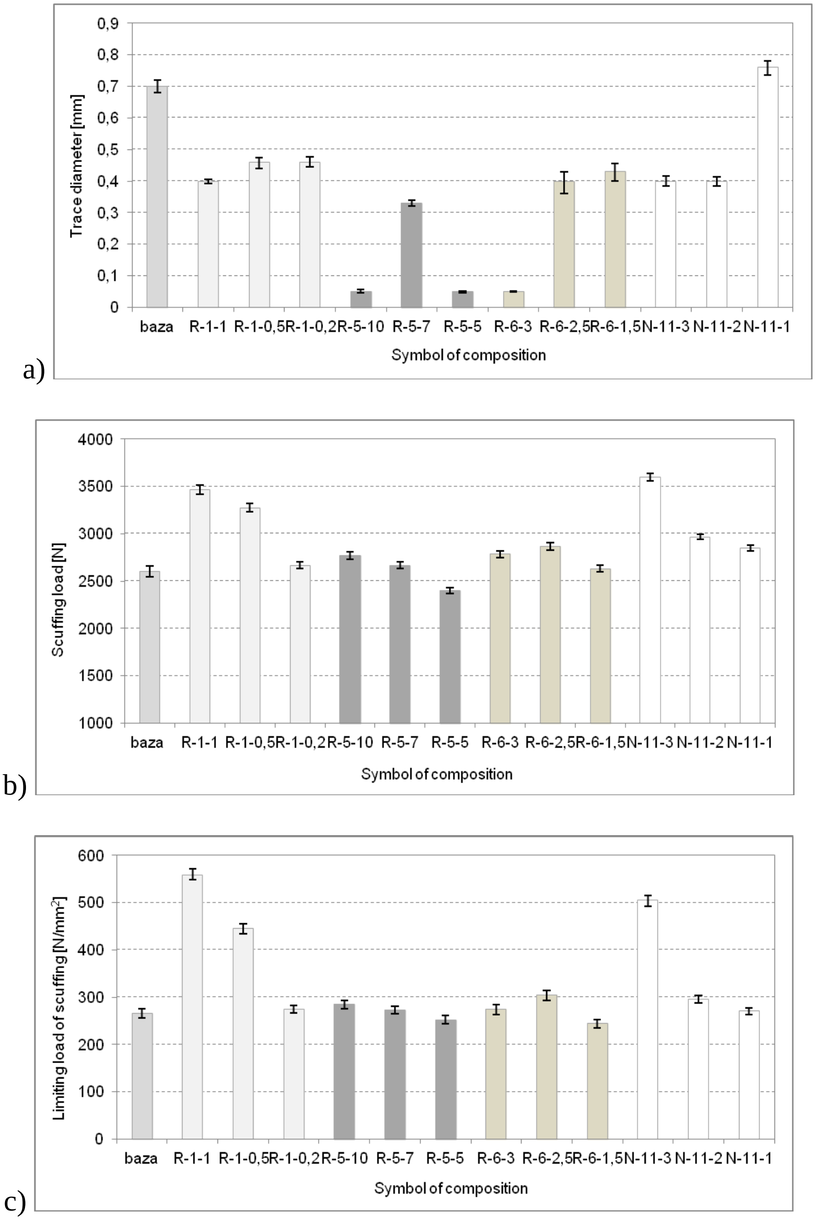


Fig. 1. The values of: a) trace diameter, b) scuffing load and c) limiting load of scuffing for tested compositions

Rys. 1. Wartości: a) średnicy skazy, b) obciążenia zacierającego, c) granicznego nacisku zatarcia kompozycji olejowych z dodatkami smarnymi

In order to analyse the results of friction, the friction pairs after each test run under linearly increasing load were examined. The measured parameters were trace appearance and the presence of particular elements, which were expected upon chemical composition of the additive. **Figure 2** depicts the images and mappings of elements present in friction traces on the ball surfaces lubricated with the most beneficial compositions.

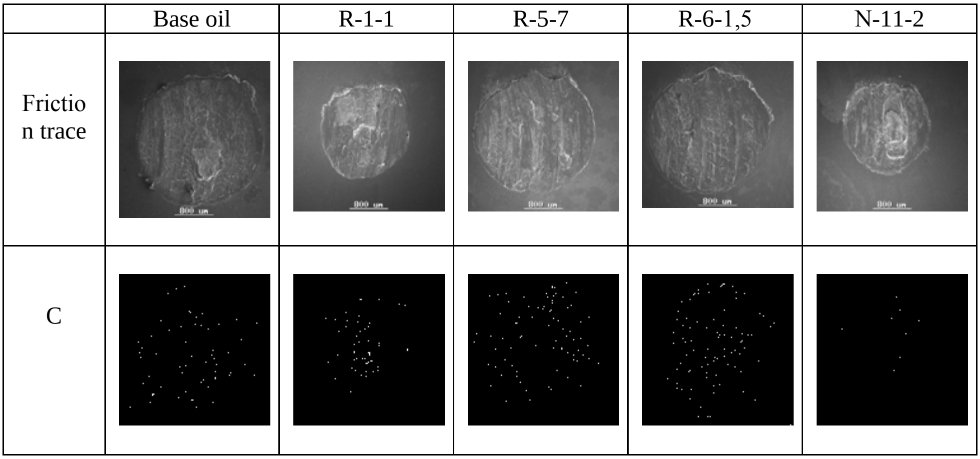


Fig. 2. SEM images and element mappings on the friction traces
Rys. 2. Obrazy skaningowe i mapy rozmieszczenia pierwiastków na powierzchniach śladów tarcia powstałych na kulkach testowych po badaniu kompozycji olejowych z dodatkami smarnymi

The friction trace surfaces were uneven, with distinct accretion surrounded with a few furrows – the effect of adhesive wear. Only the addition of R-1 and N-11 resulted in considerable smaller friction traces. However, the mentioned additives do not alter the appearance of the traces themselves. Their sizes were similar and, apart from the sample containing R-6 additive, the analysis revealed considerable accretions, indicating the adhesive nature of the wear.

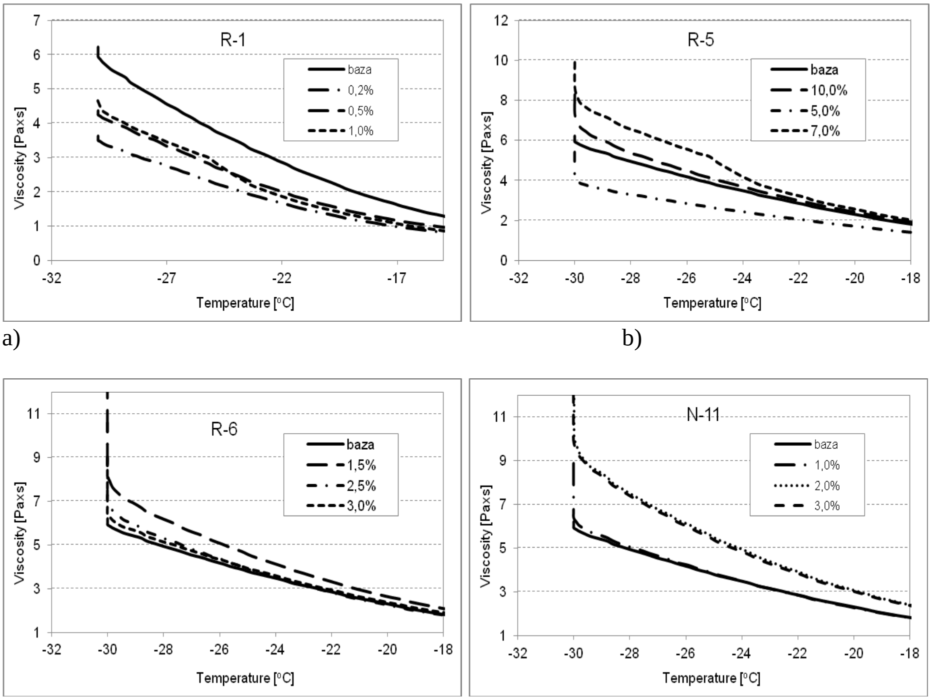
Table 3 lists the content of elements found in friction traces arisen in friction pairs lubricated with selected oil compositions.

Table 3. The element content found in the friction traces after selected test runs
Tabela 3. Zawartość pierwiastków w warstwie wierzchniej śladów zużycia po badaniach kompozycji olejowych z dodatkami smarnymi

Element	Additive content [%]				
	R-1	R-5	R-6	N-11	Base
carbon	25.06	19.38	27.47	17.03	22.87
iron	72.87	78.68	69.59	80.41	74.37
phosphorus	0.05	0.17	0.07	0.09	not detected

The outer surface of friction traces contained phosphorus, carbon, and iron. Due to the detection limit of EDS mapping technique (1%), the map for phosphorus did not reveal the presence of this element. For the test balls, the carbon and phosphorus content was greater and the iron content lower than the initial values prior to the test (C: 0.95–1.1%, P: max 0.025%, Fe: 95–97%). The higher carbon content may be a result of tribochemical reactions leading to the by-products "covering" the active elements (heteroatoms). The reduction in iron content may be assumed as the effect of the deposition of the by-products on the friction traces.

Figure 3 depicts the correlation between additive content on the rheological properties of vegetable oil base. Because the most visible changes of viscosity occurred within temperatures of 30–20°C, the results include a narrower temperature range than actually investigated.



a) b)

c) d)

Fig. 3. The correlation between temperature and dynamic viscosity for oil compositions containing various additives

Rys. 3. Wpływ temperatury na zmianę lepkości dynamicznej kompozycji olejowych przy różnych stężeniach dodatków smarnych

The temperature-viscosity characteristics depended on the nature and content of the particular additive. The additives revealed profitable (R-1) or diverse (others) influence on the rheological properties of base oil. Amongst other additives, only R-5 in a concentration of 5% improved the susceptibility of the base oil to changes of viscosity under the influence of temperature. In contrast to the composition containing R-6 additive, those containing R-1, R-5, and N-11 revealed deterioration of the overall rheological properties.

Figure 4 depicts the temperature-viscosity characteristics of the lubricating compositions containing additives in concentrations providing the best antiwear and antiscuffing properties.

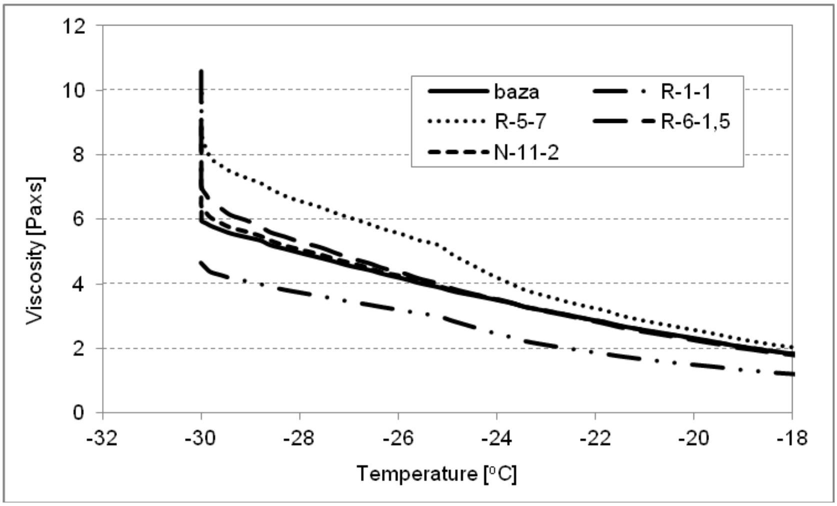


Fig. 4. The dependency of dynamic viscosity on the temperature, determined for oil compositions revealing the best antiwear and antiscuffing properties

Rys. 4. Zależności lepkości dynamicznej od temperatury wyznaczone dla kompozycji olejowych charakteryzujących się najwyższymi właściwościami przeciwzużyciowymi i przeciwzatarciowymi

Depending on the particular additive, some of them improved (R-1), deteriorated (R-5), or had no significant influence on the rheological properties of vegetable oil base (R-6 and N-11). The oil compositions containing additives were characterized by various alterations of viscosity in connection with the temperature.

Table 4 lists the values of dynamic viscosity (in reference to the viscosity at 20°C) of the base oil and oil compositions revealing the best lubricating properties. The arrows indicate trends of the parameter change.

Only the R-1 additive (phosphorus and nitrogen content of 4.8% and 2.7%, respectively) had a beneficial influence on the dynamic viscosity of the oil base at all temperatures. The changes of dynamic viscosity observed for compositions containing this additive were slighter than the oil base. In the temperature range of 20–80°C, other compositions revealed slightly better (R-5), worse (R-6), or similar rheological parameters (N-11), when compared to the unmodified base oil. At the temperatures between 20– -30°C the observed changes were more considerable. The composition containing R-6 additive (phosphorus content of 3.15%) revealed a greater increase in viscosity than base oil. Instead, the compositions with R-5 (0.25% P, 0.34% N) and N-11 (3.04% P, 6.29% S, 3.63% Zn) were characterized by little change in dynamic viscosity at 10 and 0°C. The temperatures below 0°C caused more considerable changes in the mentioned parameters. Chemical analysis of the additives revealed a beneficial role of phosphorus on the rheological properties of the oil compositions.

Table 4. The changes of dynamic viscosity (in reference to the viscosity at 20°C) measured for the unmodified vegetable base oil and its compositions with the most profitable additives

Tabela 4. Zakres zmian lepkości dynamicznej bazy oraz kompozycji olejowych charakteryzujących się najwyższymi właściwościami smarnymi w odniesieniu do lepkości w temperaturze 20°C

	Change of the dynamic viscosity [%]				
Temperature [°C]	Base oil	R-1-1	R-5-7	R-6-1,5	N-11-2
-30	↑ 7522.5	↑ 7387.9	↑ 10697.0	↑ 9666.2	↑ 8955.0
-20	↑ 2816.7	↑ 2267.1	↑ 3063.5	↑ 2987.6	↑ 3101.7
-10	↑ 805.6	↑ 695.6	↑ 850.2	↑ 845.7	↑ 853.5
0	↑ 270.1	↑ 242.9	↑ 260.3	↑ 281.1	↑ 262.5
10	↑ 86.3	↑ 76.6	↑ 84.3	↑ 89.2	↑ 83.4
Dynamic viscosity at 20°C [Pas]	0.0816	0.0621	0.0803	0.0719	0.0709
30	↓ 40.4	↓ 38.9	↓ 39.6	↓ 41.6	↓ 41.3
40	↓ 61.6	↓ 59.5	↓ 60.2	↓ 62.7	↓ 61.6
50	↓ 73.8	↓ 72.6	↓ 70.7	↓ 75.2	↓ 73.8
60	↓ 81.5	↓ 79.8	↓ 79.9	↓ 82.8	↓ 81.4
70	↓ 86.1	↓ 85.1	↓ 85.7	↓ 87.4	↓ 86.3
80	↓ 88.9	↓ 87.9	↓ 88.8	↓ 90.2	↓ 88.7

CONCLUSIONS

The role of lubricant additives is the improvement of rheological characteristics of base oils. Appropriately selected additives should not impede any crucial properties of the base. The antiwear and antiscuffing additives containing heteroatoms in their molecules (S, P, and N) may be corrosive to metals and their alloys but may also have a beneficial influence on the base oils as lubricants – AW/EP additives.

Based on experiments described in this paper, it may be concluded that ashless additives containing phosphorus and/or nitrogen provide very good antiwear and antiscuffing properties when added to the rapeseed/castor base oil. Some additives of this type were more effective than those containing sulphur and zinc. The modification of the boundary phase of vegetable oil composition occurs not only through heteroatom reaction with the material but also through organic derivatives. The advantageous feature of the mentioned additives was also no corrosive activity to copper under normal as well as restrictive conditions. A slight influence on the rheological properties of the base oil is also worth mentioning. Among the examined additives, the most profitable antiwear, antiscuffing, as well as rheological properties revealed the R-1 (amine group containing phosphorus). Its presence in the base oil resulted in a more resistant lubricating film and ensured the high quality of friction zone that was clearly seen in lower wear of the friction pair. The overall effectiveness of the composition containing R-1 was similar or even better than the composition containing petroleum N-11 additive. When taking into consideration the chemical composition of the additives, it may be concluded that there is no need for sulphur and zinc to ensure good antiwear and antiscuffing properties of vegetable base oils. These elements may be replaced with organic compounds containing phosphorus.

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Streszczenie

Przedstawiono wyniki badań właściwości smarnych i reologicznych kompozycji olejowych wytworzonych na bazie mieszaniny olejów roślinnych z dodatkami smarnymi. Były to dodatki dedykowane olejom roślinnym oraz produktom naftowym. Dodatki różniły się strukturą chemiczną oraz zawartością pierwiastków aktywnych.

Stwierdzono, że zarówno rodzaj, jak i stężenie dodatków zmieniły właściwości smarne i reologiczne oleju bazowego, przy czym zakres zmian jest zróżnicowany. Najkorzystniejsze działanie smarne i reologiczne wykazywał dodatek do olejów roślinnych zawierający fosfor i azot.