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Antiwear properties of lard methyl esters and rapeseed oil with commercial ashless additives

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1. Introduction

Lubricants usually help in prolonging the machine life by providing protection to the moving surfaces against wear. They also cut down on the energy consumption by reducing friction of equipment parts [1]. Historically, vegetable oils used to be a popular lubricant, but their use was minimized with petroleum industry providing cheaper mineral oils for lubrication purposes. Recently, rapidly growing environmental awareness encouraged various research organizations to develop environmentally friendly lubricants [1-3]. Due to these concerns along with the more widespread availability of materials, produced from renewable resources, the demand for environmentally friendly lubricants and additives has been increasing among governmental and industrial users [4, 5]. Vegetable oils and animal fats are among leading candidates for lubricant utilization. With broad commercialization of biodiesel, methyl esters of these materials become readily available as well.

High performance machines demand lubricating oils with carefully designed additive packages. Additives increase useful life and provide additional properties to the lubricant, such as improved flow, modified friction, and resistance to oxidation, extending mechanical and thermal stability [4, 6, 7]. In order to formulate a high performance lubricant, effectiveness of its additives must be maximized. In case of new types of lubricating base oils, the ability of a given additive to meet performance expectations in such base oil must be verified experimentally. Lubricity additives are critical in achieving the necessary friction properties and protection against wear. Tribotesters usually evaluate the ability of lubricants to minimize wear of the surfaces. Ashless additives are typically used for environmentally friendly lubricants. A number of reports have screened the performance of lubricity additives through usage of various tribotesters [8-10]. Four Ball Anti Wear tester [11] is a widely recognized tribotester, appropriate for the evaluation of lubricity additives in new types of base oils [12, 13].

The objective of this study was to investigate several commercial additives, used at recommended treat levels in environmentally friendly lubricants, utilizing a Four-Ball type tribotester. Successful additive selection might improve the wear protection properties. This would demonstrate that further optimization of the additive selection and their treat rates can be justified in environmentally friendly lubricants due to the inherent differences between them and mineral oils.

2. Tested materials

The lubricant samples were prepared from low-erucic Rapeseed Oil (RO), corresponding to the food-grade standard LST 1959 requirements [14] and from Lard oil fatty acid Methyl Esters (LME). The latter were selected due to the growing interest in industrial utilization of fatty waste from meat industry. Methyl esters from lard oil are more cost efficient than the rapeseed esters and provide an additional route to the utilization of excess animal fats. The LME were synthesized in the laboratory using conventional procedue for two-stage alkali-catalyzed transesterification with methanol. Produced LME, aka methyl lardates, were purified to meet those B100 biodiesel standard requirements, which dealt with fuel purity. Their properties are listed in Table 1.

Table 1

Properties of lubricant base oils, used in the study

Property	Base oil		Reference
	RO	LME	
Chemical identity	Low erucic rapeseed oil	Methyl esters of lard oil	
Cloud point, ^oC	n.d.	+18	-18
Pour point, ^oC	-19	+13	-38
Kinematic viscosity, 40 ^oC, mm^2/s (cSt)	35.53	5.39	63.02
Kinematic viscosity, 100 ^oC, mm^2/s (cSt)	7.99	1.95	13.93
Viscosity index	208	-	231

Performance of base oils (aka basestocks) without additives was compared to that of additive formulations in these oils. Additive package AW1 is commercially marketed for the use in vegetable oil based chain saw lubricants for lubricity improvement through Sulfur, Nitrogen and Phosphorous containing ingredients. In addition to antiwear additives, AW1 contained corrosion inhibitors, pour point depressants, antioxidants and other ashless functional ingredients. Its recommended treat level was 2.75% wt. Additive package AW2 was represented by 2:1 wt. blend of AW1 and high molecular weight saturated ester, used commercially as a lubricity enhancer. Additive AW3 was also represented by 2:1 blend of AW1 and another commercial ester of high molecular weight, which was, however, based on unsaturated fatty acids.

A commercial vegetable oil lubricant was used as the “Reference” in these experiments. It was purchased in a retail store and at the time of the study was considered one of the most widespread environmentally friendly chain saw lubricants in Northern and Central Europe. Its appearance, viscosity and other generic bulk properties were similar to those of RO (Table 1).

3. Experimental procedures

Four-ball type tribotester, Fig. 1, was custom made at Lithuanian Agricultural University and had been employed for wear and friction measurements previously [Proceedings 4 Ball]. The balls of 12,7 mm diameter were made of 100Cr6 bearing steel (E = 21.98 $\cdot 10^4$ MPa; $\nu = 0.3$). The testing procedure was adapted from the standard DIN 51 350, Part 3 [15].

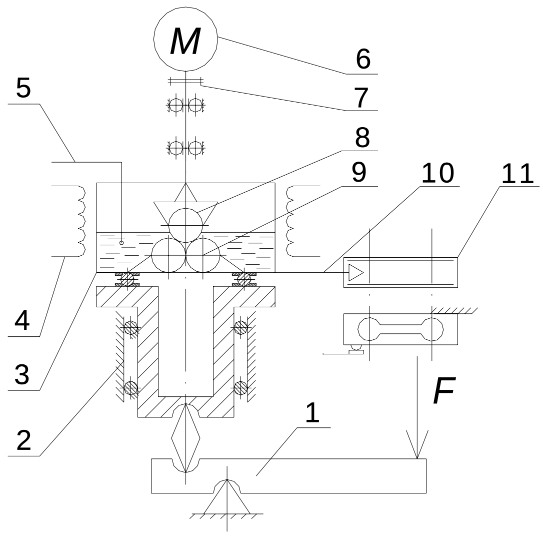

Fig. 1 Schematics of Four-Ball tribotester: *1* – load transfer lever; *2* – vertical center bearing; *3* – oil sample compartment; *4* – oil heater; *5* – thermocouple; *6* – electric motor; *7* – clutch; *8* – upper rotary ball; *9* – lower stationary balls; *10* – torque transfer lever; *11*- force transducer

The test oil sample of 22 cm^3 was poured into the sample compartment, fully submerging the stationary balls. Under the applied load of 150 or 300 N, rotation speed of 1420 rpm, the machine was run for 1 hour. Prior to each experiment, all the appropriate parts of the machine, i.e. bottom and upper ball holders, oil vessel and the test balls were washed in an ultrasonic bath with hydrocarbon solvents, and then dried.

Friction surfaces were analyzed with Scanning Electron Microscope (SEM) JEOL JSM-5600. The diameters of the circular wear tracks (wear scars) on three stationary balls were measured with an optical microscope. For each run the scar measurements were reported as an average of the Wear Scar Diameter (WSD) of the three balls in millimeters. Friction moment between the balls, represented by torque, and temperature change of the liquid sample were also recorded during the test.

Load distribution of the balls in contact is illustrated in Fig. 2. The relationship between the force in the ball contact F_n and the total load F is given [16] as following

$$F_n = \frac{\sqrt{6}}{6} F = 0.408F \qquad (1)$$

where F is total load applied to the tribosystem.

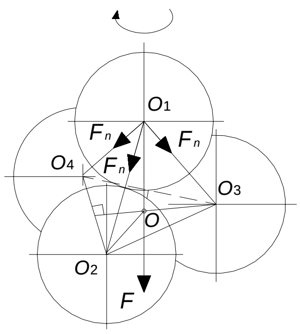

Fig. 2 Scheme of load distribution in the Four-Ball tribotester: F - total load; F_n - force in the ball contact; O – geometric center of the system; O_1, O_2, O_3 and O_4 – centers of the balls

Before actual movement of the balls against each other, while already in contact at full load, the balls deform under the force F_n and produce elastic indentation as shown in Fig. 3. Diameter of the spot, which forms under stationary load between the balls [17] can be calculated

$$d = 2\sqrt[3]{\frac{1.5\left(1-\nu^2\right)F_n r}{E}} \qquad (2)$$

were ν is Poisson ratio; r is the ball radius; E is the modulus of elasticity.

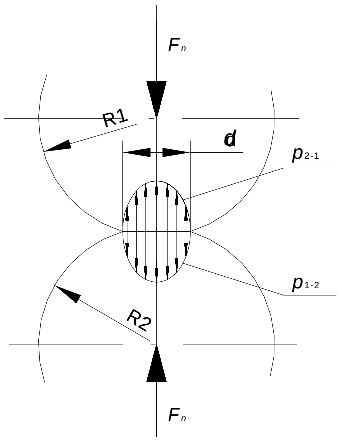

Fig. 3 Scheme of elastic indentation of two balls under stationary contact: F_n – force between two balls; $R1$ and $R2$ – radii of the two balls; d – diameter of elastic indentation; $p_{1\text{-}2}$ and $p_{2\text{-}1}$ – pressures exerted under contact on the upper and lower balls respectively

This also allows to easily calculate average pressures in the contacts.

4. Results and discussion

Initial tests were carried out with AW1 and AW2 (2.75 and 4% wt. treat levels resp.) under 150 N load. See the results in Fig. 4.

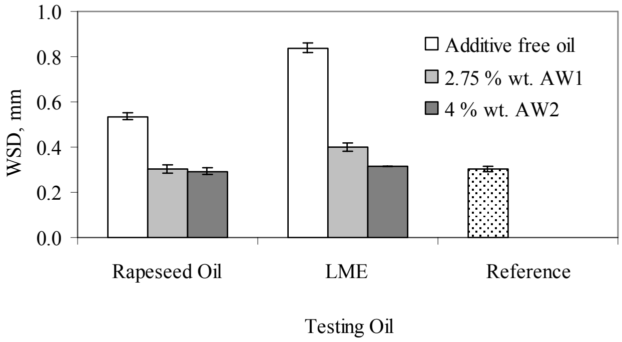

Fig. 4 Comparison of Four-Ball test (load: 150 N) wear scar diameters (WSD) of Rapeseed Oil (RO) and Lard Methyl Esters (LME) with and without antiwear additives. Reference: commercial vegetable oil based chain saw lubricant

Fig. 4 shows that additive-free base oils do not provide nearly as sufficient protection against wear as does the commercial lubricant. However, incorporation of the additive package AW1 dramatically improves the wear protection. RO+AW1 performs similarly to the Reference, while LME+AW1 produces higher scars due to its low viscosity. In absolute numbers (disregarding strains, which occur under stationary conditions without surface movement), addition of 2.75% wt. AW1 reduces the WSD by 1.8 times in RO and 2.1 times in LME. Another additive AW2, which contains the saturated high molecular weight ester, improves the performance even further. The WSD of LME+AW2 is only slightly above that of the much more viscous Reference. Antiwear performance of another formulation RO+AW2 is equal to that of the Reference.

Previous research has shown that a film is formed in the presence of liquid lubricant between the balls in contact [18]. In this study the film formation was observed both in case of the Reference and RO+AW1, see Fig. 5.

As demonstrated by Fig. 5, the mechanisms of antiwear protection seem to be equivalent between the Reference and RO+AW1. The wear scars, including their boundaries with areas outside the surface contact, seem to have similar appearance. However, in case of AW2, microscopy of the wear scars suggests quite different tribology regimes, because the appearance is no longer similar to that of AW1 and Reference, see Fig. 6.

When RO+AW2 was examined under SEM, the appearance of the scar boundary vicinity did not resemble the appearance of a typical wear scar. Although close to the scar perimeter, but clearly within the scar itself large sections of undamaged ball surface could be identified without any visual changes to the original surface roughness.

Although the absolute numeric WSD values are only somewhat lower than those of the Reference, the pronounced appearance differences on the scar surfaces (e.g. Fig 5, c and 6) suggest that the scar formation on the outer portions of the contact area using RO+AW2 as a lubricant does not proceed in a typical manner. Wear-free contact strains, occurring solely due to the exerted pressure without the actual physical damage of the surface asperities seem to constitute a significant portion of the wear scar. Using Eqs. (1) and (2), the stationary strains (elastic indentations) were calculated for both experimental loads of 150 and 300 N, see Table 2.

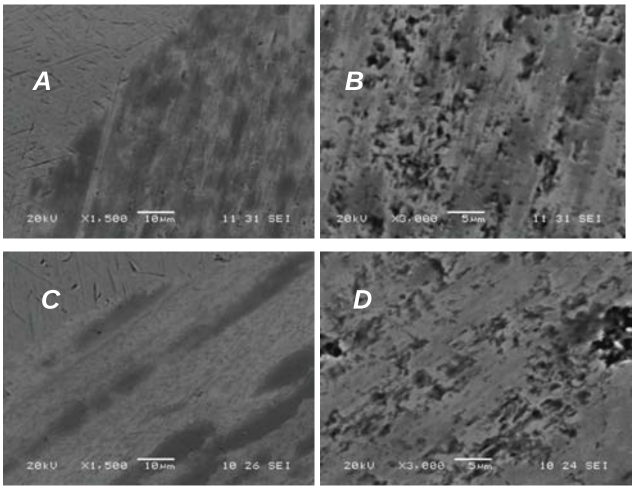

Fig. 5 Film formed after the wear test at 150 N: *A&C:* boundary between wear scar and outer surface, *B&D:* inner portion of wear scar, *A&B:* RO + AW1, *C&D:* Reference oil

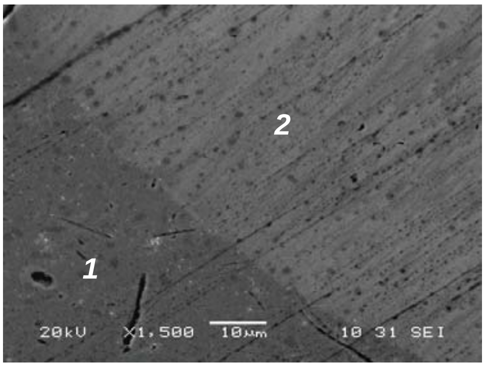

Fig. 6 SEM photomicrographs of stationary ball after testing RO+AW2 at 150 N load: *1* – outside the wear scar; *2* – inside the wear scar

Table 2

Strains between the balls under load

Load, N	Force acting between the balls, N	Diameter of the spot, formed in surface contact, mm	Contact Pressure, MPa
150	61.2	0.272	1053.2
300	122.4	0.343	1324.7

No evidence was found that at 150 N the size of the wear scar after the test could exceed the stationary contact strain. Thus it can be concluded that under this load regime (average normal contact pressure of 1053.2 MPa), incorporation of 4% wt. of AW2 into RO produces wear patterns, which are significantly impacted by pressure distribution within the contact zone. Per Fig. 3, the pressures are lower towards the perimeter of the contact zone than those in its center. Consequently, this testing configuration might not be ideally suitable to differentiate between materials with excellent antiwear properties.

Load of 300 N was selected in an attempt to improve the differentiation among the lubricants under higher loads. The results are provided in Fig. 7.

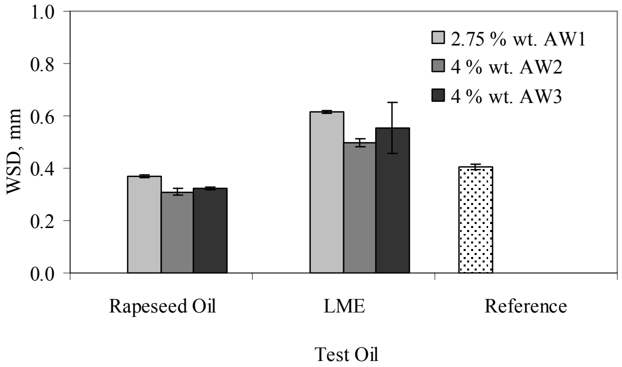

Fig. 7 Comparison of Four-Ball test (load: 300 N) wear scar diameters (WSD) of Rapeseed Oil (RO) and Lard Methyl Esters (LME) with and without antiwear additives. Reference: commercial vegetable oil based chain saw lubricant

Under this load, RO+AW2 addition performs much better than the commercial lubricant (‘Reference’), resulting in 1.3 times smaller WSD than that of the Reference. The effect of this additive in LME is not sufficient to compensate for its lower viscosity, nevertheless, the results show that AW2 is much more effective than AW1. Additive AW3, which contained the unsaturated ester, was tested under this load regime (contact pressure 1324.7 MPa), showing that fully saturated AW2 performed better in both base oils.

The improvement in performance of AW2 over AW1 might have several explanations. One likely reason is that at higher treat levels more additives are available for antiwear film formation. This results in more effective separation of the moving surfaces and better protection against wear. However, this statement could not be confirmed by further data. Additional testing showed that the increase in AW1 concentration from 2.75 to 4% did not quantifiably affect the performance in the test.

Additional reason might be that due to the higher molecular weight ester component, present in AW2, the viscosity of the additive film becomes higher, what also favorably affects the protection against wear.

SEM images of the wear scars at 300 N for the Reference and RO+AW1 are compared in Fig. 8. It can be observed that less wear damage is visible in RO+AW1, meaning that this formulation protects against wear more effectively than the commercial lubricant.

The WSD trends are further confirmed by experimental data from friction force and temperature measurements, see Table 3 and Table 4. This data clearly shows that additives with better lubricity reduce the heat losses and lower the torque.

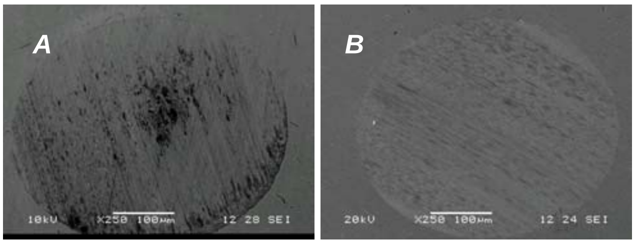

Fig. 8 SEM photomicrographs of the wear scar after testing under 300 N: A – Reference, B – RO+AW1

Table 3

Wear Scar Diameter (*WSD*), torque (*M*) and temperature increase (*ΔT*) during the Four-Ball test at 150 N load

Test Oil		*WSD*, mm	*M*, mNm	*ΔT*, °C
Reference		0.305	51	32
RO	Additive-free	0.535	52	33
	2.75 % wt. AW1	0.302	46	31
	4 % wt. AW2	0.293	38	26
LME	Additive-free	0.838	61	37
	2.75 % wt. AW1	0.400	66	40
	4 % wt. AW2	0.317	33	24

Table 4

Wear Scar Diameter (*WSD*), torque (*M*) and temperature increase (*ΔT*) during the Four-Ball test at 300 N load

Test Oil		*WSD*, mm	*M*, mNm	*ΔT*, °C
Reference		0.406	120	58
RO	2.75 % wt. AW1	0.368	100	56
	4 % wt. AW2	0.309	71	37
	4 % wt. AW3	0.322	73	40
LME	2.75 % wt. AW1	0.615	132	62
	4 % wt. AW2	0.496	112	52
	4 % wt. AW3	0.554	131	60

Additive package AW3 shows some improvement over AW1, but its effectiveness is not as convincing as that of AW2. Since AW3 contains unsaturation, chemical transformations, such as oxidation or polymerization, are more likely than those in AW2. Such degradation reactions might result in a partial loss of synergism between antiwear additives and the ester, producing somewhat poorer performance than in the case of AW2.

Qualitatively, all the samples can be ranked in the same order using all 3 measured parameters: WSD, torque and temperature increase. All the samples produce the same lineup with each parameter: worst performance = LME+AW1 < LME+AW3 < LME+AW2 < Reference < RO+AW1 < RO+AW3 < RO+AW2 = best performance. This indicates that the tribotester runs were consistent with reliable measurements. Friction coefficients could also be calculated from the torque data.

Convincing advantages of these test formulations over the commercially widespread environmentally friendly lubricant show that major improvements can be made in existing vegetable oil lubricant technology. Readily available commercial ashless additives seem to provide sufficient resources. What appears to be lacking is the fundamental approach to studying the lubricity additive effects in the new types of base oils. As a result, potential synergies between base oils and certain additive chemistries remain unidentified. Shortage of such basic investigations seems to impede the rapid technological improvement of environmentally friendly lubricants and needs to be addressed by the appropriate R&D institutions.

5. Conclusions

Antiwear performance of 3 commercial ashless additives in rapeseed oil and methyl lardate was evaluated in Four-Ball tribotester. These conclusions can be drawn:

1. Without additives, due to its higher viscosity Rapeseed Oil (RO) is more effective protecting against wear than Lard Methyl Esters (LME);
2. Successful selection of commercial ashless additives in RO achieved performance, which was clearly better than that of the commercial lubricant; LME with additives can approach the performance of a more viscous commercial lubricant;
3. The improved performance can be confirmed by wear scar diameter, torque and temperature increase.

6. Acknowledgement

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PELENŲ NESUDARANČIAIS PRIEDAIS MODIFIKUOTO METILO ESTERIO IR RAPSŲ ALIEJAUS DILIMO SLOPINIMO SAVYBIŲ TYRIMAS

Reziumė

Tepamųjų medžiagų priedai, naudojami mineraliniams ir biologiniams tepalams modifikuoti, yra nevienodai efektyvūs. Tyrėme mažai eruko rūgšties turintį rapsų aliejų (RA) ir kiaulių riebalų rūgščių metilo esterį (KME), modifikuotus bepeleniais komerciniais priedais. Modifikavimui naudotų priedų sudėtyje buvo S, P, N ir kitų funkcinių elementų bei stambiamolekulių esterių.

Tyrimai atlikti keturių rutulių bandymo mašina. Nusidėvėję paviršiai vertinti optiniu mikroskopu ir SEM. Tyrimais nustatėme, kad tepimas nemodifikuotu RA ir KME yra neefektyvus. Esant 150 N apkrovai priedais modifikuoti RA ir KME pagal dilimo slopinimą prilygo komercinei bioalyvai. Esant 300 N apkrovai, priedais modifikuotas RA buvo gerokai efektyvesnis ne tik už KME, bet ir už komercinę alyvą. Tai patvirtina tiek dilimo pėdsako skersmuo, tiek trinties momentas bei tiriamos tepamosios medžiagos temperatūros pokytis.

Tirtų priedų kompozicijos pagal tepimo savybes yra kur kas efektyvesnės už naudojamus tirtoje komercinėje alyvoje. Taigi šiuo metu taikoma biotepalų gaminimo technologiją galima gerokai pagerinti.

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ANTIWEAR PROPERTIES OF LARD METHYL ESTERS AND RAPESEED OIL WITH COMMERCIAL ASHLESS ADDITIVES

Summary

Effectiveness of lubricity additives in base oils from renewable resources is often different than that in mineral oils. Low erucic Rapeseed Oil (RO) and Lard oil Methyl Esters (LME) were fortified with commercial ashless additives. A fully formulated additive package with S, P and N containing lubricity enhancers and other functional ingredients was evaluated along with two commercial high molecular weight esters in Four Ball tribotester. Without additives, both oils showed poor antiwear properties. However, after selecting the most appropriate additives, performance of LME and RO under 150 N load was similar to that of a more viscous commercial lubricant. Under 300N load the lubricity of RO with these additives was significantly better than that of LME or the commercial lubricant. This is confirmed by wear scar diameters, torque and temperature increase. Antiwear properties of the selected additive formulations were clearly better than those of a commercially widespread vegetable oil based chain saw lubricant, suggesting that current formulation technology of biolubricants can be significanly improved.

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ИССЛЕДОВАНИЕ ПРОТИВОИЗНОСНЫХ СВОЙСТВ РАПСОВОГО МАСЛА И МЕТИЛОВЫХ ЭФИРОВ МОДИФИЦИРОВАННЫХ БЕЗЗОЛЬНЫМИ ПРИСАДКАМИ

Резюме

Присадки смазочных материалов, используемые для модификации минеральных и биологических масел, неодинаково эффективны. Исследовалось рапсовое масло (РМ), содержащее малое количество кислоты эрука, и метиловый эфир свининных жирных кислот (МЭСЖК), модифицированные коммерческими присадками, несодержащими золу образующих веществ. Присадки включали в себе S, P, N и др. функциональные присадки, а также крупномолекулярные эфиры.

Смазывающие свойства масел исследовались на четырехшариковой машине трения согласно требованиям DIN 51 350. Износ поверхностей оценивался оптическим и скенирующим электронным микроскопами. Установлено, что смазывание немодифицированными РМ и МЭСЖК является неэффективным. При нагрузке 150 N модифицированное РМ и МЖЭСК по противоизносным свойствам оказались равными более вязкому коммерческому продукту. При нагрузке 300 N модифицированное РМ было более эффективным, чем МЖЭСК и коммерческое масло. Это подтвердили исследования диаметра пятна износа, момента трения, а также температуры разогрева испытуемых смазочных материалов.

Составы исследуемых присадок смазочных материалов, были явно лучше, чем используемые в контрольном коммерческом масле. На основе исследовании можно полагать, что свойства биологических масел могут быть улучшены.

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