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Clean technologies

NON-TOXIC ANTIWEAR ADDITIVE FOR FOOD AND BIODEGRADABLE LUBRICANTS

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Abstract. The possibility of using esters of citric and aconitic acids as antiwear (AW) and extreme pressure (EP) additives to vegetable oils has been investigated. The aim of the study is to develop completely non-toxic AW/EP additives for a number of lubricants. Such materials include both biodegradable lubricants based on vegetable oils and lubricants based on synthetic hydrocarbons for food processing equipment. It has been established that esters of polybasic acids and aliphatic alcohols can exhibit antiwear properties at a level comparable to zinc dialkyldithiophosphates. The possibility of increasing the solubility of such additives in vegetable oils at low temperatures when using a mixture of different alcohols for the esterification has also been clarified.

Keywords: citric acid esters, aconitic esters, biodegradable lubricants, food equipment lubricants, non-toxic AW/EP additives.

AIMS AND BACKGROUND

In connection with the constant increase in environmental requirements for vehicles and industrial facilities, one of the priority areas of tribology is the development of environmentally friendly lubricants. Vegetable oils and synthetic esters are most often used as biodegradable base oils. Both types of oils have fundamental limitations on the scope. The greatest problems are caused by two parameters: resistance to oxidation and antiwear properties. The reduced resistance to oxidation of vegetable oils is caused by their chemical composition[1]. As a rule, to improve this parameter, oils with a low content of unsaturated acids are used, for example, castor oil. However, antiwear properties of castor oil are inferior to rapeseed and other oils. For long-term operation at high temperatures, resistant synthetic esters are more suitable. However, the ability of synthetic esters to biodegradation in the natural environment decreases with increasing thermal stability. The same dependence

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is observed for antiwear properties. For applications such as the engines of ships used in inland waters (rivers and lakes), vegetable oils are the preferred lubricants.

Antiwear, extreme pressure and anti-friction properties of lubricants based on vegetable oils can be significantly enhanced by the introduction of additives. It is known that the tribological parameters of vegetable oils are significantly higher than those of pure hydrocarbon oils without additives[2–6]. The use of conventional antiwear additives developed for hydrocarbon oils, such as Zinc dialkyldithiophosphate (ZDDP) or alkyl-salicylates, is either impossible or impractical. The effectiveness of additives varies significantly in base oils of different chemical composition. In addition, ZDDP can be destroyed by chemical interaction with the molecules of vegetable oils. The search for special additives for vegetable oils began only recently.

Three areas can be distinguished among these works: introduction of solid lubricant components into the lubricating oil, for example[7–11], chemical modification of vegetable oils[12,13], and introduction of oil-soluble antiwear components[14–20]. The use of solid lubricant components is limited by greases. The use of nano-suspensions of metals and other inorganic components that are resistant to sedimentation affects the filterability of oils. This is an important parameter of oils for hydraulic systems and engines. In addition, operational impacts lead to a change in the oils composition. The oxidation of the oil and the presence of water can significantly affect the stability of the nano-suspensions. Chemical modification of vegetable oils, for example, the formation of thioesters, reduces the ability to biodegrade and can lead to the formation of corrosive products during operation.

The authors consider the increase in tribological parameters by adding completely soluble functional additives to be most promising in terms of preserving such advantages of vegetable oils and synthetic esters as non-toxicity, absence of smell, ease of production. This method has given excellent results for hydrocarbon-based lubricants. Some examples of such studies are given in Refs 14–20. Despite the successful use of some AW/EP components developed for hydrocarbon oils[16–18], it is noted in a number of papers that the effectiveness of additives is different in hydrocarbon oils and vegetable oils. The increased adsorption of molecules of vegetable oils and esters on the metal surface impedes the adsorption of molecules of traditional AW/EP components. In this regard, more polar substances are most effective than those used in hydrocarbon oils.

In this paper, we consider the possibility of using as AW additives of esters that have chemical and ecological properties that are as close as possible to vegetable and animal fats, but that are characterised by an increased tendency to adsorb on metal surfaces. Vegetable oils are esters of monobasic organic acids and glycerin triatomic alcohol. In this work, the ester of a tribasic organic acid and a monohydric alcohol was tested as an additive. The presence of tribasic acid, forming stable complexes with metals, suggests an increased ability to adsorb. The similarity of the chemical nature of additives and fats, as well as the choice of non-toxic components suggest a good compatibility of additives with vegetable oil and the absence of a negative impact on biodegradability and toxicity.

EXPERIMENTAL

Synthesis of additives. Citric acid was used as tribasic acid. Hexadecanol-1 was used to ensure the solubility in the oils of ether and the products of its partial decomposition. A mixture of acid and alcohol, taken in a molar ratio of 1:3, was heated to 160–190°C. The reaction was carried out for 2–3 h with occasional stirring. Under these conditions, the esterification takes place completely and does not require a catalyst. As a result of heating, citric acid separates water and turns into aconitic acid. The final product is a full ester of hexadecanol and aconitic acid. The injected additive was called AAE-additive. The structural formula is presented in Fig. 1. The resulting product has a wax consistency, the melting point is 60–65°C. It is soluble in hydrocarbons, but insoluble in water.

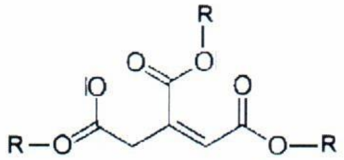

Fig. 1. Formula aconitic acid trihexadecyl ester, where R is the residue of alcohol C_{16}

Determination of the presence of antiwear properties. Refined sunflower oil was used as the base oil. This is one of the most common vegetable oils. Sunflower oil is selected because it contains a large amount of unsaturated fatty acids and has higher antiwear properties than technical oils. The AAE-additive was administered in an amount of 4% by weight.

Antiwear properties were determined by the four ball method on a standard ChMT-1 friction machine complying with the requirements of ASTM D 4172 (Ref. 21), according to the ASTM D 4172 method at a rotation speed of 1200 rpm (0.46 m/s). The normal load is 392 N, the temperature of the oil bath is 40 ± 5°C. The balls were made of steel, the hardness is HRC 64–66, the diameter is 12.7 mm. An optical microscope with an accuracy of 0.01 mm was used to measure wear spots. A general view of the friction machine is presented in Fig. 2.

For the original oil and for the oil with an AAE-additive, three measurements were taken. The measurement results were averaged. The type of wear marks is shown in Fig. 3.

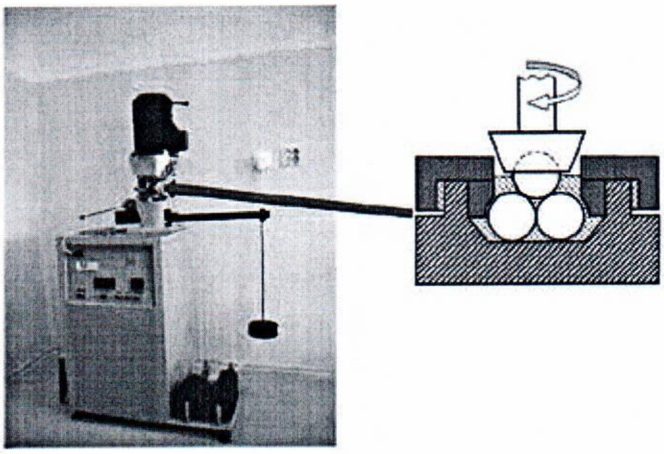

Fig. 2. General view of the four-ball friction machine and the scheme of the friction unit

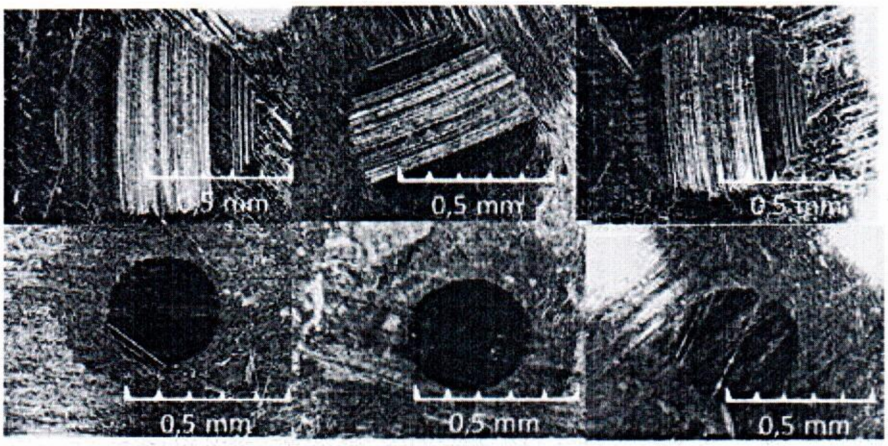

Fig. 3. Typical type of wear marks: the top row is the original vegetable oil; bottom row – oil with 4% aconitic acid trihexadecyl ester (AAE- additive)

The average diameter of wear marks for the original oil was 0.54 mm; for oil with 4% aconitic acid trihexadecyl ester, the diameter was 0.39 mm.

Determining the presence of anti-friction properties. Fluid bearing model testing. The tests were carried out on the machine friction II-5018 in contact 'roller-block'. The diameter of the roller was 90 mm, the material was steel. The block was made of the liner of the tractor bearing, the material was bronze, the dimensions of the working surface were 24 × 2 mm. Test conditions: roller rotation speed 500 min^{-1}, load range 0–2000 N. The oil supply was drip at the entrance to the contact friction of 0.2 ml/s.

The values of the friction coefficient μ were calculated based on the measured friction torque M at each load value F. The contact pressure P was calculated based on the load value and the contact area. The temperature T was measured by a thermoelectric transducer inserted into the side opening of the block.

A general view of machine II-5018, image block and contact assembly is shown in Fig. 4.

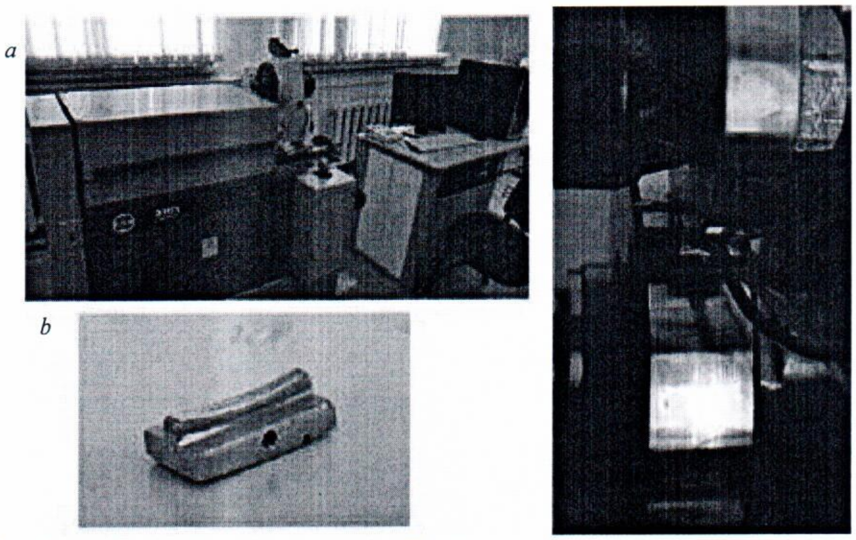

Fig. 4. General view of the friction machine II 5018 – *a*; block – *b*, and friction unit – *c*

The measurement results are presented in Table 1 and Fig. 5.

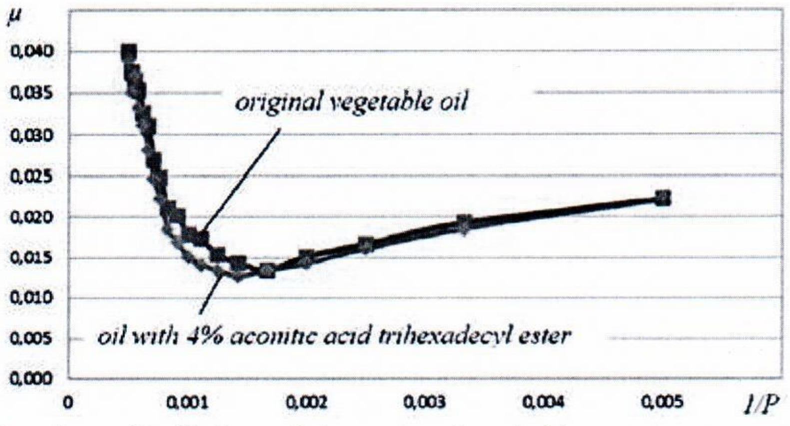

Fig. 5. Dependence of the friction coefficient on the reciprocal of the contact pressure

Table 1. Results of friction torque measurement and calculation of friction coefficient for lubrication with vegetable oil and oil with 4% aconitic acid trihexadecyl ester (AAE-additive)

Common parameters		Base vegetable oil			Oil with an additive		
F (N)	P (MPa)	M (N m)	T (°C)	μ	M (N m)	T (°C)	μ
200	4.78	0.2	57.9	0.0222	0.2	52	0.0222
300	7.18	0.26	56	0.0193	0.25	51.4	0.0185
400	9.57	0.3	55.4	0.0167	0.29	50.4	0.0161
500	11.96	0.34	54.5	0.0151	0.32	50	0.0142
600	14.35	0.36	54.3	0.0133	0.36	50.2	0.0133
700	16.74	0.45	54.5	0.0143	0.4	50.7	0.0127
800	19.14	0.55	54.7	0.0153	0.48	50.7	0.0133
900	21.53	0.7	54.5	0.0173	0.57	51.4	0.0141
1000	23.92	0.8	55.4	0.0178	0.68	52.3	0.0151
1100	26.32	1	57	0.0202	0.84	53.9	0.0170
1200	28.71	1.14	59	0.0211	1	56.3	0.0185
1300	31.10	1.45	63	0.0248	1.3	59	0.0222
1400	33.49	1.7	68	0.0270	1.55	63.3	0.0246
1500	35.88	2.1	75	0.0311	1.9	67	0.0281
1600	38.28	2.35	80	0.0326	2.25	70	0.0313
1700	40.67	2.7	86	0.0353	2.55	79	0.0333
1800	43.06	2.95	91	0.0364	3	89	0.0370
1900	45.45	3.2	100	0.0374	3	100	0.0351
2000	47.85	3.6	107	0.0400	3.5	110	0.0389

The introduction of 4% aconitic acid trihexadecyl ester into vegetable oil, under experimental conditions, did not lead to a change in the antifriction properties of the oil in the steel-bronze contact.

Tests under conditions of boundary friction in a flat sliding contact. Technical rapeseed oil was used to determine the presence of antifriction effect of aconitic acid trihexadecyl ester in plane contact. The AAE-additive was added in an amount of 4% by weight. The measurements were performed on a laboratory device 'Fixed Pin – Rotating Disk'. The device is shown in Fig. 6.

A pin is a cylindrical specimen made of BrO10F1 tin bronze. The diameter is 19 mm. The rotating disk is made of alloy steel with a hardness of HRC56,9. The pin is fixed in the device, which can move freely in a plane parallel to the disk plane and along the normal to the surface. The pressing force F to the disk is created by placing weights on the device for the pin fastening. A tensometric sensor attached to the fastening of the pin.

Using the device shown in Fig. 6, the friction force Ft acting on the pin from the disk was measured. The friction force was measured with an accuracy of 0.1 N. Each experiment at each load value was performed at the same values of time (friction path), disk rotation speed, and ambient temperature. The lubricant was applied to the contact by drip method (drip lubrication) at a rate of 30 drops/min. The experiment parameters are shown in Table 2.

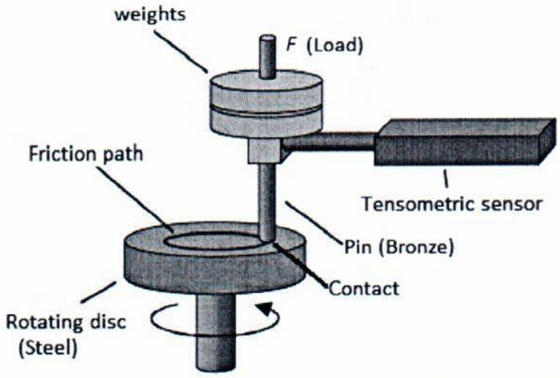

Fig. 6. Diagram of the device for measuring the friction coefficient when lubricated with rapeseed oil with or without additive

Table 2. Experiment parameters

No	Parameters	Value
1	load	$F_1 = 60$ N, $F_2 = 100$ N, $F_3 = 140$ N, $F_4 = 220$ N
2	nominal contact area	$A_a = 283.3$ mm^2
3	nominal contact pressure	$P_{a1} = 21.2$ N/cm^2, $P_{a2} = 35.3$ N/cm^2, $P_{a3} = 49.5$ N/cm^2, $P_{a4} = 77.7$ N/cm^2
4	speed of rotation	$n = 95$ min^{-1}
5	sliding speed of the centre contact	$V_C = 0.89$ m/s
6	initial rape oil temperature	$T = 21^\circ$ C
7	ambient temperature	$T = 21^\circ$ C

The friction coefficient was calculated as the ratio of the friction force to the normal load (the force of pressing the pin to the disk). Rapeseed oil and rapeseed oil containing 4% aconitic acid trihexadecyl ester (AAE-additive) were used as a lubricant. The temperature of the lubricant supplied to the friction contact is equal to the ambient temperature 21°C.

Table 3 presents the results of measurements of friction coefficients at four load values.

Table 3. Results of measurements of friction force *Ft* and friction coefficient μ

No	Lubricating oil	Load, *F*							
		$F_1 = 60$ N		$F_2 = 100$ N		$F_3 = 140$ N		$F_4 = 220$ N	
		$P_{a1} = 21.2$ N/cm^2		$P_{a2} = 35.3$ N/cm^2		$P_{a3} = 49.5$ N/cm^2		$P_{a4} = 77.7$ N/cm^2	
		Ft_1 (N)	μ	Ft_2 (N)	μ	Ft_3 (N)	μ	Ft_4 (N)	μ
1	rapeseed oil	4.5	0.075	6	0.06	9	0.064	15	0.068
2	rapeseed oil + AAE-additive	2	0.03	4	0.04	6	0.042	10	0.045

Figure 7 shows the dependence of friction coefficients on the load.

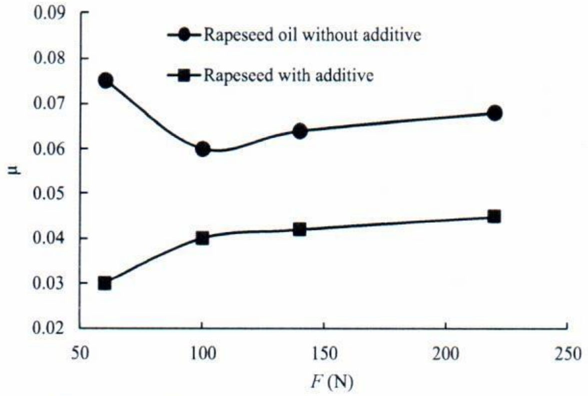

Fig. 7. Dependence of friction coefficient on the normal load

The diagram of the relative change of the friction coefficient $\bar{\mu}$ under different normal loads is shown in Fig. 8. The value of $\bar{\mu}$ is equal to the ratio of the friction coefficient for the oil with the additive to the friction coefficient for the original oil.

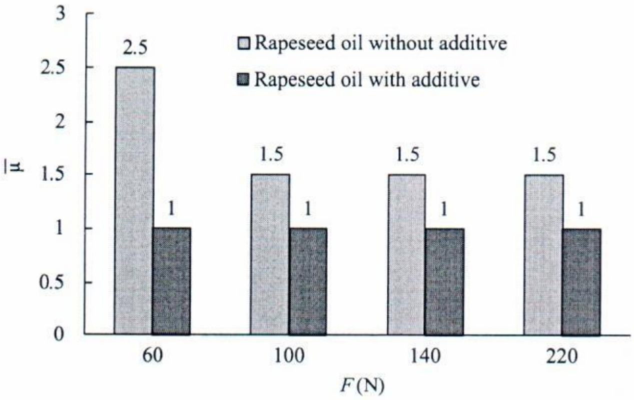

Fig. 8. Diagram of the relative change of the friction coefficient $\bar{\mu}$ under different normal loads

RESULTS AND DISCUSSION

The results of the experiments showed that the introduction of aconitic acid trihexadecyl ester (AAE-additive) into the composition of vegetable oil significantly improves the antiwear properties. The absence of the effect of this additive on the antifriction properties of the oil under the indicated conditions can be explained as follows. For hydrocarbon oils, the introduction of AW/EP additives usually leads to increased anti-friction properties in transitional and boundary friction modes. This is due to the influence of the adsorbed additive layer on the rheological parameters of the adjacent liquid layers. Vegetable oils (rapeseed or sunflower) consist of triglycerides containing oxygen. Due to the presence of dipole moments, bonds between triglycerides are stronger than bonds between hydrocarbons. Thus, vegetable oils are initially more structured liquids than hydrocarbon oils. The effect of the adsorbed layer of the polar component extends to an extremely thin layer of liquid.

Under conditions of modelling a radial bearing, hydrodynamic pressures provide a separating layer of lubricant even at high contact pressures. The friction force is due in this case to the rheological parameters of the oil. In the case of friction of plane surfaces, the friction force is determined by the parameters of an extremely thin layer of lubricant. Under these conditions, the effect of the presence of the polar component is manifested. Thus, determining the effect of potential AW/EP additives on vegetable oil requires modelling the parameters of the technical friction units for which this lubricant is intended.

CONCLUSIONS

The results show that aconitic acid trihexadecyl ester (AAE-additive) demonstrates antiwear properties in vegetable oil at high contact pressures. Aconitic acid ester can be used when it is necessary to enhance the AW/EP properties of vegetable oil-based lubricants in cases where toxicity and biodegradability are particularly important. For example, it can be used in a food processing equipment.

This additive can be used as a prototype for the synthesis of more effective additives with low toxicity.

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