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RESEARCH

Ester Based Lubricants Deriwed From Renewable Resources

The development of lubricants like, e.g. engine and hydraulic oils was traditionally based on mineral oil as a base fluid. This fact is related to the good technical properties and the reasonable price of mineral oils. A disadvantage of mineral oil is its poor biodegradability and thus its potential for long-term pollution of the environment.

Subsequently, innumerable synthetic esters have been synthesized by systematic variation of the fatty acid and the alcohol components. Whereas the alcohol parts of the environmentally adapted synthetic esters are usually of petrochemical origin, the fatty acids are almost exclusively based on renewable resources. The physical-chemical properties of biobased synthetic esters can cover the complete spectrum of technical requirements for the development of high-performance industrial oils and lubricants. From the technical point of view, and disregarding overall costs, more than 90% of all present-day lubricants could be formulated to be environmentally adapted.

Keywords: *Environmentally adapted lubricants, ester oils, oxidation stability, friction, wear.*

1. INTRODUCTION

Some of the first detailed experiments on friction were performed at the end of the seventeenth century by Guillaume Amontons (1663-1705). Amontons main findings were that the force of friction is directly proportional to the applied load and that the force of friction is independent of the apparent area of contact. The specimens tested were copper, iron, lead and wood in various combinations. In each experiment the surfaces were coated with old pork fat. Since pork fat is primarily composed of saturated and unsaturated glycerol esters, one may conclude that Amontons was one of the first to study the friction of esters [1].

In recent years, increasing attention has again been focused on the sources of raw materials that were used before mineral oils became available in the late 19th century. In those days, lubricating oils were based mainly on rapeseed, castor and whale oil. There are several reasons for the current interest in such oils: there is a large overproduction of plants whose seeds could be used to produce oils on an industrial scale, the raw materials are relatively cheap, and they are renewable [2,3].

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The interest in the development of novel products from plant sources is not only because of their renewable and sustainable character, but also because these products have equal or even superior technical performance characteristics to mineral-oil products. From an ecological point of view, the prospects for the use of renewable resources are favorable, provided the full potential of natural synthesis by means of energy from the sun is used. The production of vegetable oils constitutes a cycle in which no net release of carbon dioxide occurs.

The vast majority of environmentally adapted lubricants available today are based on saturated or unsaturated ester oils. In chemical terms, native and synthetic esters exhibit the same structure. The raw materials used for the production of synthetic ester base stocks are alcohols and fatty acids. Most of the alcohols are derived from petrochemicals, while most of the fatty acids used are prepared from renewable raw materials, such as vegetable oils and animal fats [4,5].

2. SAMPLE PREPARATION

2.1 Oil samples

Vegetable oils are attractive base stocks for environmentally adapted lubricants. By chemical nature, vegetable oils are exclusively long-chain fatty-acid triesters of glycerol, typically involving three fatty acids. The vegetable oil most used as lubricating base is rapeseed oil and its physical and chemical properties have been well documented [6]. It is available throughout Europe and has fatty acid profiles suitable for common lubricant applications. The fatty acid composition of test basestock for formulation Bio 1 is presented on Tab. 2.

Table1. Test oils

Oil code	Base oil type	Oil type	Kinematic viscosity [mm²/s] at 40°C	at 100°C	IV
Bio 1	Unsaturated ester	Rapeseed oil	48.8	10.4	209
Bio 2	Saturated ester	Complex ester	46.7	8.1	147
Bio 3	Unsaturated ester	TMP-trioleate	46.9	9.3	186
Min 1	Mineral oil	Paraffin mineral oil	57.6	9.3	143

Two types of synthetic base oils were selected for this study. The first synthetic formulation Bio 2 was based on a saturated complex ester consists of the petrochemical derived di-acids and some shorter chain (C8 – C10) fatty acids from natural resources.

The second synthetic formulation Bio 3 was based on unsaturated trimethylolpropane (TMP) -trioleate, the most widely applied material for environmentally adapted hydraulic fluids at present. It was largely biobased, consisting from fatty acids derived from renewable resources, Tab. 2.

Table 2. Fatty acid composition of test base stocks.

Fatty acid content [%]		Bio 1	Bio 3
	Palmitic, C 16:0	6.1	5.5
	Stearic, C 18:0	2.5	2.2
	Oleic, C 18:1	49.1	62
	Linoleic, C 18:2	32.2	20.5
	Linolenic, C 18:3	6.9	8
	Other	3.2	1.8

C X:Y - fatty acid chain of length X and containing Y double bonds; e.g. C 18:3 is an 18-carbon chain fatty acid with three double bonds

Test formulations Bio 1, Bio 2 and Bio 3 were made from ester oil base along with a unique blend of additives typical for hydraulic fluids. All three formulations are highly biodegradable and of low ecotoxicity.

The properties of formulated environmentally adapted ester based oils were compared to the conventional paraffinic mineral oil labeled as Min 1.

3. TEST EQUIPMENT AND PROCEDURES

3.1 Oxidation stability

The oxidation performance of test oils is demonstrated by a laboratory test similar to a modified Baader test according to DIN 51 554, Part 3. Test oils are aged for six days in a glass vessel at constant temperature of 95 °C. The condition of the oil was monitored by measurements of kinematic viscosity on 72 hours periods.

3.2 Friction and wear test

The friction and wear tests described in this study were performed using a ball-on-disk configuration,Fig.1.

Table 3. Ball-on-disc test conditions

Properties	Unit	Value				
Normal force	N	10				
Sliding distance	m	1750				
Sliding speed	cm/s	0.445	1.71	4.73	13.11	23.8
Contact radius	mm	6	6	7	10	11
Duration	h:m:s	109:13:00	28:40:31	10:16:00	03:42:00	02:02:00

As the disc rotates, the ball is pressed eccentrically against it with a known force. This makes a circular track on the disc. The balls were DIN 100Cr6 steel, 12.7 mm diameter, 8.3 GPa hardness and 0.02 µm roughness. The disks were DIN 100Cr6 steel, 24 mm outer diameter, 8.3 GPa hardness and 0.06 µm roughness. Test conditions are summarized in Table 3.

The experiments were performed at room temperature with the test oil covering the ball and the disc completely in the sample chamber. Friction is measured continuously during the test, while wear is determined subsequent to the test by profilometry. The wear of both disc and ball or pin is expressed in a so-called wear coefficient. This is a standardized ratio for the wear volume (mm^3) to the sliding distance (m) and the load (N). The smaller the wear coefficient, the greater is the wear resistance.

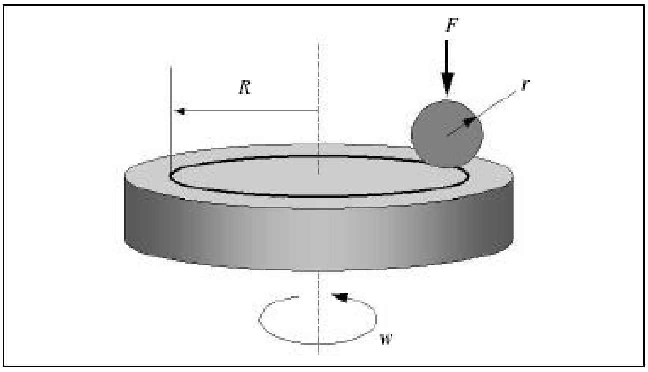

Figure 1: Ball-on-disc configuration.

3.3 Film thickness and damage criterion

The minimum lubricant film thickness h_{min}, together with the surface roughness, determines when full fluid film lubrication begins to break down. It is useful to define the ratio of the minimum film thickness to the roughness of the surfaces and this ration is often designated the lambda ratio (λ) or a film parameter [7]:

$$\lambda = \frac{h_{\min}}{\sqrt{(R_{q,a}^2 + R_{q,b}^2)}} \quad (1)$$

h_{min} = minimum lubricating film thickness
$R_{q,a}$ = rms surface finish of surface a
$R_{q,b}$ = rms surface finish of surface b

Mixed lubrication is present when $1<\lambda<3$ and boundary when $\lambda<1$ the mixed lubrication condition is only valid at sufficiently high sliding speeds and as long as the surface roughness is unaffected by wear. Wear tests in this study were performed in λ value interval 0.1 to 1.6, therefore in the boundary and mixed lubrication regime.

4. TEST RESULTS AND DISSCUSION

4.1 Oxidation stability

It is well known that ester based oils may show problems with oxidation and thermal stability. Vegetable oils are by their chemical nature long chain fatty acid triesters of glycerol. The rate of oxidation depends on the degree of unsaturation of a fatty-acid chain and the "β-CH group" of the glycerol, Fig 2.

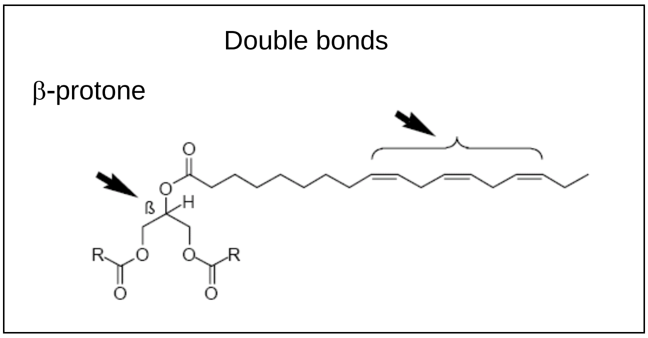

Figure 2: Triglyceride structure.

The double bonds in the alkenyl chains easily react with the oxygen, therefore lower unsaturation result in better oxidation stability. The beta proton in "β-CH group" is relatively easily eliminated from the molecular structure, weakening the middle carbon-oxygen bond and resulting in the formation of a carboxylic acid, which leads to further degradation [4,8]. Figure 3 illustrated this with rapeseed formulation Bio 1 in comparison with a complex ester based formulation Bio 2 and TMP-oleate based formulation Bio 3 where the glycerol and consequently the beta hydrogen proton is replaced by other polyols with quaternary carbons. At constant oil temperature of 95 °C the formulation based on natural ester Bio1 shows very poor oxidation stability. It was also observed that oxidation stability of formulation Bio 2 based on saturated synthetic ester is better in comparison with the formulation Bio 3 based on unsaturated synthetic ester, mainly because short, linear molecular chains tend to give better thermal stability than long, branched chains contained in TMP-oleate. Oxidation stability of saturated ester based formulation Bio 2 is comparable to the oxidation stability of reference mineral oil formulation Min 1.

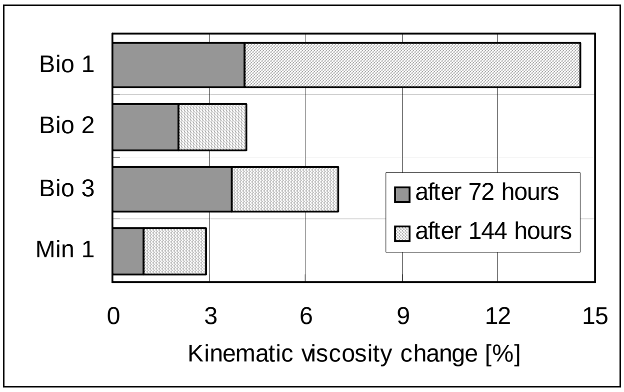

Figure 3: Oxidation stability.

4.2 Friction and wear measurements

The friction coefficient measurements during the wear test, shows substantial differences between ester based lubricants and the mineral oil based reference lubricant. Both ester based formulations Bio 2 and Bio 3 resulted in lower friction compared to the mineral oil Min 1. It is clear from the Fig. 4 that coefficient of friction for unsaturated ester formulation Bio 3 is significantly lower compared to the saturated ester formulation Bio 2. Unsaturated ester contains organic long straight-chain compounds with polar end groups. These polar end groups are adsorbed on the metal surface, which decreases the surface energy and causes a reduction of the coefficient of friction.

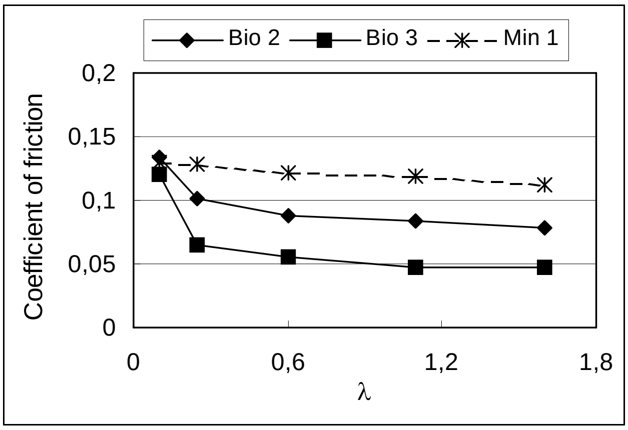

Figure 4: Effect of film parameter on coefficient of friction.

Wear coefficient is largely dependent on the sliding speed and sharply decreases with increase of λ ratio, especially when film parameter is low, Fig. 5. The wear measurement showed that saturated synthetic ester formulation Bio 2 resulted in a higher wear compared to mineral oil formulation Min 1 and unsaturated ester based formulation Bio 3 when λ ratio is low. As λ raises to 0.27 and higher the difference in wear coefficient between formulations Bio 2 and Min 1 becomes smaller. With increasing speed, in mixed lubrication regime the wear coefficient is almost of the same value for all three test oils.

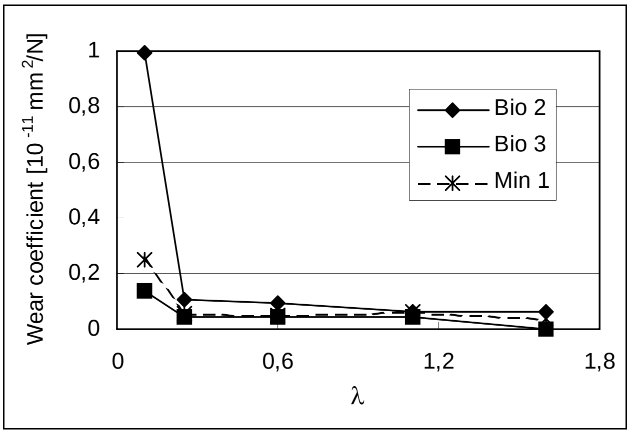

Figure 5: Effect of film parameter on wear coefficient

Narrow-minded the best anti-wear protection shows formulation Bio 3, based on unsaturated ester. Unsaturated esters react more easily than saturated esters or mineral oils and have the highest content of polar functional groups that make physical and chemical interaction with the metallic surfaces under high load and sliding contact.

Figure 6 presents the wear tracks obtained on the disc surfaces at □ratio 0,27. The wear profile with Bio 3 (Fig. 6 (b)) is hardly visible with the naked eye and separate grooves formed are not very deep. Excellent antiwear protection of unsaturated ester based formulation Bio 3 is also supported from results of friction and wear measurements presented on Figs. 4 and 5.

The wear track for oil Bio 2 (Fig. 6 (a)) is wider with deep grooves than the wear track with oil Min 1 (Fig. 6 (c)).

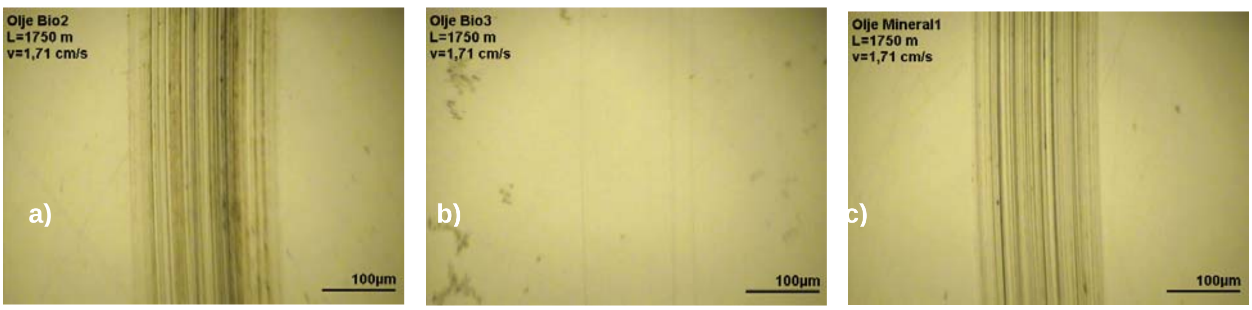

Figure 6: The worn contact surfaces of the bottom disc specimen photographed in an optical microscope (λ ratio, 0.27; speed, 1.71 cm/s; radius on disc, 6 mm): (a) Bio 2, (b) Bio 3, (c) Min 1

The unsaturated ester based formulation Bio 3 results in lower friction and better anti-wear properties than saturated formulation Bio 2. Polar functional groups in the unsaturated molecule of ester based oil in conjunction with oil-additive-metal interaction during the metal rubbing process can significantly improve the wear resistance and extreme-pressure lubrication. Unsaturated sites react more easily with the mating surfaces and it is found to be much more effective in reducing friction and wear than esters with saturated fatty groups. Short chain compounds of saturated ester Bio 2 are better for oxidation stability than long chain compounds, but are less effective in lubricant protective film formation. In this study, the effect of additives is excluded, because the same additive system is used for both ester based formulations.

5. SUMMARY

The following conclusions can be derived from this study:

• The oxidation stability of saturated based ester formulation is better compared to the unsaturated ester based formulations. Especially regarding with the rapeseed oil based formulation. The sensitivity to oxidative attack is caused mainly by multiple unsaturated (double) bonds present in the fatty acid part of the molecule and also by the "β-CH group" of the glycerol. Oxidation stability of saturated ester formulation can be compared to the oxidation stability of reference mineral oil formulation.

• Ester based oils formulations exhibit less friction than mineral based oil. The lowest friction coefficient is obtained with the formulation based on unsaturated synthetic ester through the whole λ value interval performed in this study.

• Unsaturated based synthetic ester formulation exhibits the best antiwer protection, especially in the boundary lubrication regime. At higher sliding speeds, wear coefficient is comparable for all test oils.

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