Change of Coefficient of Friction due to Ageing of Biological Esters

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In order to investigate the influence of a single tribo system on the ageing of lubricants, a so-called Tribo-Oxidationtest has been designed at IFAS. It consists of a disc on disc tribometer integrated into the pressure vessel of an oxidation test according to ASTM D 2112. The coefficient of friction $\mu$ of different friction partners is discussed in this paper. The attempts are done with biological esters which are synthesized in a collaborative research centre. Due to biological aspects they contain no additives. It has been shown that there is an influence of oil ageing on friction coefficient but also a big influence of viscosity on friction coefficient.

Keywords: tribology, friction, ageing, oxidation, hydrolysis, coefficient of friction

1. Introduction

Ageing behaviour of customary oils is defined through complex additive packages. So lifetime of pure crude oils is often not observed. But the use of biological esters presupposes special additives, which affect biological degradability of these oils.

At IFAS there are many possibilities to determine ageing behaviour. Inter alia there is the so-called Tribo-Oxidationtest, which enables the investigation of the influence of a single tribo system on the ageing of lubricants. It consists of a disc on disc tribometer integrated into the pressure vessel of an oxidation test according to ASTM D 2112. With this test mainly oxidation behaviour can be analysed. But further examinations yield information about friction or hydrolysis for example. The coefficient of friction $\mu$ of different friction partners is discussed in this paper.

2. Ageing behaviour of esters

There are many influences on the ageing behaviour of oils. Each influence leads to different mechanisms of ageing. Fig 1. The influences in hydraulic circuits are multifarious. High temperatures and pressures, catalytic influences from materials used, waste, water as well as other impurities, and shear stress in friction gaps are the main influences on ageing. Only radiation does not usually occur, except for light radiation in vision panels.

Mechanisms of ageing cannot be separated clearly. Water leads to hydrolysis. Thereby acidic components and alcohols are generated. Solved and unsolved air leads to oxidation which cracks the molecular chains and generates acidic components too.

![Fig. 1 Progress of ageing](image)

High temperature leads to polymerization. Supported by catalytic surfaces the average molecular mass rises so that viscosity usually increases. High pressure and shear stress in contact areas show an opposite effect on viscosity, because molecules are cracked.

Often the materials used exhibit a catalytic influence on the progress of ageing. Especially brass components lead to interactions with the fluid, so that both can be affected.
Ageing can be determined with different tests. Until now there is no possibility to analyse the influence of a single tribosystem. With the Tribo-Oxidationtest this gap has been closed.

3. Test rack assembly

The design of the Tribo-Oxidationtest is based on the rotating vessel Oxidationtest (RVOT) according to ASTM D 2112. Basic features like mass of oil of 35 g, rotation speed of 100 rpm, oxygen pressure of 0.625 MPa, are kept constant. Temperature is lowered to 120 °C and no water or catalysts are added. Additionally a disc on disc tribometer is integrated into the test vessel, Fig. 2. Pretension of 1 N/mm² is generated by cup springs, which are located in the upper sealing and pretension unit. To avoid leakage of oxygen a sealing unit consisting of two radial shaft seal rings is used. The space between these is filled with water for cooling and lubrication. Oil cannot be used for this application, because of the pure oxygen atmosphere.

![Assembly of Tribo-Oxidationtest](image)

The discs with an outer diameter of 43 mm and an inner diameter of 22.5 mm can easily be changed so that different materials can be tested. The lower disc is fixed with the draw and torsion bar and acts as a stator. The rotor is the upper disc. For each test new discs have been used, to prevent any influence of corrosion layers.

4. Tests

4.1. Oils

Within the framework of the collaborative research centre 442 environmentally friendly fluids are being developed. Two esters, named HISM and HIGTS, with different viscosities are synthesized. The double bond is substituted by two alcohols so that oxidation stability increases. HISM is shown in Fig. 3.

![Hydroxy-Isobutoxy-Stearic-Methylester](image)

The Tribo-Oxidationtest rig is filled with 0.625 MPa oxygen before it is placed into the heating bath, so that pressure increases. Due to oxidation reactions oxygen is used up and pressure decreases. A drop of 0.175 MPa from its maximum marks the end of lifetime. The faster the oxidation reactions take place the shorter the lifetime.

Therefore there is no defined test duration. After

<table>
<thead>
<tr>
<th>No.</th>
<th>Oil</th>
<th>kinematic viscosity at 40 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mixture of two HISM</td>
<td>21 mm²/s</td>
</tr>
<tr>
<td>2</td>
<td>Pure HISM</td>
<td>22 mm²/s</td>
</tr>
<tr>
<td>3</td>
<td>Mixture of Oil 1 and 5</td>
<td>32 mm²/s</td>
</tr>
<tr>
<td>4</td>
<td>Mixture of Oil 1 and 5</td>
<td>100 mm²/s</td>
</tr>
<tr>
<td>5</td>
<td>Pure HIGTS</td>
<td>256 mm²/s</td>
</tr>
<tr>
<td>6</td>
<td>Pure HIGTS</td>
<td>653 mm²/s</td>
</tr>
</tbody>
</table>

Viscosity can be adjusted by mixing these fluids. For this paper six mixtures have been used. Some of them are mixtures and some are pure oils. Table 1 gives an overview of the oils and their viscosities.

4.2. Discs

Three different friction partners have been examined. The stator was always made of 42CrMo4-steel. A combination of steel against brass acts as reference. Further tests were carried out using rotors made of 42CrMo4 coated with either Chromium aluminum nitride (CrAIN) or graded zirconium carbide (ZrCg). Both coatings were applied through a PVD-process by the surface engineering institute of RWTH Aachen University. CrAIN is a very hard layer with a metastable cubic phase. It is characterised by its high hardness and Young`s modulus. ZrCg is not as hard as CrAIN. Its graded carbon content leads to an increase of hardness with ascending distance to the layer surface. This enables a running-in behaviour of the coated part, so that tolerances for manufacturing can be designed less demanding.

4.3. Test condition

Test duration depends on the oxidation stability of the investigated oil. The progress of pressure is recorded and analysed in the same way as with the RVOT, as shown in Fig. 4.

![Progress of pressure at oxidation test](image)
reaching the end of lifetime the test is aborted and the test rig dissembled. Usually, a test takes about 45 min.

A torque support of the length $l$ at the upper end of the test rig leads the friction torque into the frame of the test rack. A built in load cell records the support force $F_R$. By eq.(1) the coefficient of friction $\mu$ can be calculate from pretension $p$, contact area $A$ and the middle diameter $D_m$.

\[
\mu = \frac{2 \cdot l \cdot F_R}{p \cdot A \cdot D_m}
\]  

(1)

5. Results

5.1. Lifetime

The influence of friction on the ageing of oil has been proven in previous papers. Lifetime drops about 40%, if there is a pretension of the discs of 1 N/mm². This effect can be traced back to different causes. There are high flash temperatures in the contact zone, mechanical load on the molecules, a bigger catalytic surface due to wear, and other influences.

As shown in Fig. 5 there is a catalytic influence of different materials on the ageing behaviour. ZrC leads to a slightly shorter lifetime than brass or CrAlN. Good results can be achieved with brass. But change of oil properties is strong. Viscosity increases and especially copper and zinc content are significantly higher after testing. This can affect ecotoxicological behaviour.

5.2. Coefficient of friction $\mu$

Fig. 6 shows exemplary results achieved with oil 1 of low viscosity. Length of progress of coefficient of friction accords the lifetime of the test. So brass against steel and CrAlN against steel lead to higher lifetimes than ZrC against steel.

The combination brass against steel shows the highest values and biggest variations. Both can be explained with wear. First the corrosion layer has to be removed by the discs. This demands high friction. When there are impurities in the gap, the coefficient of friction can increase until particles are removed or destroyed.

The coefficient of friction of ZrC against steel starts at the same level as brass against steel. It ascends slightly and descends slowly after reaching its maximum. There are no abrupt changes.

CrAlN against steel features the lowest start level.

Due to the hard layer which does not permit a running-in the coefficient of friction rises slowly. The final value is comparable to the start level of brass against steel which acts as a reference.

The drop of the coefficient of friction of brass and ZrC can be traced back to different causes. First of all, viscosity increases due to oxidation processes. This results in thicker lubricating films and better lubrication. Another reason is the wear of the discs. The extension of the cup springs lowers their pretension. Thus the contact force is reduced.
that, wear comes to a rest and the coefficient of friction approaches a final and constant value.

The influence of viscosity on the coefficient of friction is also noticeable for oil 3 and 5. As explained before, higher viscosities yield lower coefficients of friction. The viscosity index of the tested oils is about 110. So the ratios of viscosities at 120 °C are comparable to those at 40 °C.

The influence of viscosity can be seen in Fig. 9, too. Especially the coefficient of friction of brass against steel is more than half as low as that of oil 1 for low viscosities. The peak at the beginning can be traced back to impurities from production.

Steel against CrAlN shows lower friction than steel against ZrCg. This may be due to less wear which inhibits a loss of normal force due to the relaxation of the pretension springs. Decrease of friction coefficient in the second half can be traced back on increase of viscosity.

\[
\text{Fig. 9} \quad \text{Progress of friction coefficient for Oil 6}
\]

5.3. Change of viscosity

The relevance of viscosity can be proven by its change. The ageing mechanisms offer different effects on viscosity so a forecast is not possible.

The different effects can be seen in Fig. 10. The low viscosity oils are getting more viscous, while the high viscosity oils are getting thinner. This leads to the presumption that either polymerisation or cracking dominates.

\[
\text{Fig. 10} \quad \text{Change of viscosity}
\]

6. Summary and outlook

The newly developed Tribo-Oxidationtest enables multifarious new investigations of the ageing behaviour of oil. It has been shown that PVD coatings feature lower coefficients of friction than brass. The influence of viscosity of esters containing no additives on the coefficient of friction is clear. The higher the viscosity, the better the lubrication.

A change of the friction coefficient can be caused by oil ageing but also through a loss of normal force due to wear and a successive relaxation of the cup springs. To investigate the influence of age on the coefficient of friction, a new version of the tribo-oxidationtest is being designed. The pretension unit will consist of a pneumatic clamping cylinder. Therefore, preload can be kept constant during the whole test and the friction coefficients dependency on the oil can be determined exclusively.

7. Acknowledgement

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8. References