Abstract

This work presents the results of wear prevention tests carried out with mixtures of a polyalphaolefin (PAO 6) and two esters (TMP-05 and Sunflower oil, SO), on a four-ball machine tester. Results show that esters are excellent wear reducers when they are mixed with a low viscosity polyalphaolefin. The optimum ester percentages in PAO 6 were 5% and 15% for TMP-05 and SO, respectively. Better results than in pure PAO 6 occurred in all mixtures. The addition of esters (less than 15%) to PAO 6 hardly changed volume viscosity.

Notation

EHL elastohydrodynamic lubrication
E´ reduced Young’s modulus [Pa]
h minimum film thickness [m]
k dependent on type and geometry of contact
POME palm oil methyl ester
R´ reduced radius of curvature [m]
U entraining surface velocity [m/s]
W contact load [N]
VI viscosity index
α pressure-viscosity coefficient [m²/N]
η₀ dynamic viscosity at atmospheric pressure [Pa-s]

1. INTRODUCTION

Certain facets of the world lubricants market will change in the future. World demand for lubricants seems set to grow by 2.8% (2010) and 15% (2020) compared to the 1998 figures, with fastest growth likely to occur in the industrial lubricant sector, which is forecast to increase by 17.1% and 35% for 2010 and 2020, respectively (1). Furthermore, a number of functions that are normally performed by additives will increasingly have to be performed by base oils. When base oils with a high viscosity index (VI) are used they perform the most important rheological functions of VI improvers so, by carefully selecting base oil mixtures, the need for VI improvers can be partially or totally eliminated (e.g. engine oils, gear oils, high VI hydraulic oils). Due to their polarity, and in contrast with hydrocarbon-based oils, esters perform tribological functions in boundary lubrication conditions. Base oils with outstanding cold flowing characteristics such as PAOs or some esters do not need pourpoint
depressants or other cold flow improvers. The higher thermal-oxidation stability of some base oils simplifies their stabilization with antioxidants, although these will still be needed (2).

Although the initial cost of synthetic oil is higher than conventional mineral oils, they can nevertheless deliver a cost saving in the longer term. The high performance and environmental acceptability of esters and other synthetic lubricants offer benefits that can be exploited throughout the supply chain. As esters are very polar materials they tend to migrate to metal surfaces and form physical bonds with the surface oxide layer. They therefore have the potential to be used as friction-reducing additives in low polarity base oils such as PAOs and mineral oils. Mixed synthetics (multi-component composite blends of different synthetic lubricants, e.g. PAO/ester, Poly Alkylene Glycol (PAG)/ester) are also being employed to obtain an optimum balance of lubricating properties (3).

2. THEORETICAL CONSIDERATIONS

Lubricant film thickness is a very important parameter of a lubricated contact. It has an important influence on friction, pressure peaks (fatigue life), wear, lubrication regimes, and so on. The Hamrock-Dowson relation (Equation 1) seems to suggest that only two lubricant properties are related to film thickness, although this only refers to isothermal conditions.

\[
\frac{h}{R^*} = k \left( \frac{U \eta}{E' R^*} \right)^a \left( \frac{\nu}{E' R^*} \right)^b \left( \frac{W}{E' R^*} \right)^c
\]

where:  
\( a = 0.66-0.74 \)  
\( b = 0.5-0.6 \)  
\( c = -0.1 \)

In contrast, Kassfeldt and Larsson (4) claim that other parameters influence film thickness, friction, wear, pressure peaks, and so on. These researchers believe that the temperature-viscosity coefficient (\( \beta \)), thermal conductivity (\( \lambda_0 \)), heat capacity per unit volume (\( \rho c_p \)), compressibility (B), and EHL friction coefficient (\( \gamma \)) all play their part. The suggested influence of these factors on film thickness, friction and pressure peaks (contact fatigue) is shown in Table 1.

Despite the fact that each of the parameters mentioned in the previous paragraph is involved in lubricant oil mixtures, no mention of them is made either by Masjuki and Maleque (5), or Spikes and Guangteng (6, 7), who limit themselves to a consideration of film forming and anti-wear properties.

As these parameters are related to the tribological behaviour of lubricants, it is interesting to see how different percentages of esters in binary mixtures influence rheological properties like viscosity and wear prevention.
3. LUBRICANTS, APPARATUS AND PROCEDURE

3.1 Lubricants
The properties of the oil samples used in this study can be observed in Table 2. The PAO 6 was mixed with 5%, 10% and 15% by weight of TMP-05 and SO.

3.2 Apparatus and procedure
The oil mixtures were tested to quantify their viscosity (40 and 100°C). Wear tests were then carried out on a Falex Roxana four-ball machine in line with the ASTM D 4172-88 standard (speed: 1200 rpm, load: 392 N, time: 60 min). The ball test material was 12.7 mm diameter AISI 52100 steel with a hardness of about 65 HRC. Further wear tests were also run with loads of 264.6 N and 490 N at the same speed. The region of optimum mixture composition was then calculated from the results and wear scar diameter (WSD) was measured under an optical microscope.

4. RESULTS AND DISCUSSION

Figure 1 results are caused by the higher viscosity and pressure-viscosity coefficient of esters compared to polyalphaolefin. The relationship between the minimum film thicknesses of TMP-05 and SO (Equation 2, 40°C) was calculated at 1.016. Both film thicknesses are therefore similar, and the influence of thermal conditions on the contact and film forming capacity of esters is obvious.

\[
\frac{h_{mm}^{TMP - 05}}{h_{min}^{SO}} = \frac{\eta_{0}^{0.67} \alpha_{0.53}^{TMP - 05}}{\eta_{0}^{0.67} \alpha_{0.53}^{SO}}
\]

where:
\[
\eta_{0}^{TMP - 05} = 41 \text{ mPa·s} \\
\eta_{0}^{SO} = 34 \text{ mPa·s} \\
\alpha_{0.53}^{TMP - 05} = 14.4 \text{ GPa}^{-1} \\
\alpha_{0.53}^{SO} = 17.5 \text{ GPa}^{-1}
\]

Typical values of the pressure-viscosity coefficient for polyalphaolefins, vegetable oils and polyesters can be observed in Figure 2 (8). Although viscosity can be modified over a relatively wide range for each lubricant type, the pressure-viscosity coefficient is relatively constant within each group of lubricants (4).

Figure 2 clearly indicates that the polyalphaolefin has the lowest pressure-viscosity coefficient and vegetable oils have the highest; the better wear test behaviour of TMP-05 under testing can be attributed to the viscosity exponent in the Dowson-Hamrock equation being higher than the pressure-viscosity coefficient.
Figure 3 shows the appearance of wear scar on the ball specimens from tests using pure oils. TMP-05 and SO can be seen to provide better wear behaviour when measured on the scale that is being used in this study.

Figures 4 and 5 show the results of wear tests (ASTM D 4172) with mixtures. An interesting result was obtained when the viscosity for the oil mixtures was determined (ASTM D 2162). The addition of less than 15% of TMP-05 and SO in a low viscosity polyalphaolefin (PAO 6) had practically no influence on viscosity. In these cases, the difference between PAO 6 and their mixtures were always less than 4.5% at both temperatures (40 and 100ºC). This result shows that the volume properties of the mixtures are similar to PAO 6 and that any difference is explained by different surface behaviours caused by the higher polarity of esters compared to polyalphaolefins. The polarities of these two families of oils were calculated by Larsson and Kassfeldt (4) in their “non-polarity index”, provided in Table 3.

Although wear results improve as the amount of polyester increases (which is only to be expected given the results for pure oils), it is nevertheless noteworthy that this behaviour is non-linear, and that the best results were generally obtained at concentrations of between 5% and 15%.

Figures 6 and 7 illustrate wear scar on the ball specimens for each mixture for the 392 N test. Figure 6 clearly shows that the lowest wear was obtained with 5% of TMP-05, whilst the worst result was for a concentration of 10% of TMP-05. For PAO 6/SO mixtures (Figure 7), the best result occurred at 15% of SO, and the worst behaviour occurred for 10%.

The tendency in wear behaviour for the best mixtures can be seen in Figures 8 and 9. According to Figure 8, the mixture of PAO 6 and 5% TMP-05 performs best under load. According to Figure 9, the mixture of PAO 6 and 15% SO is the best. When the load is higher (490 N) the surface SO film breaks and the PAO 6 with 5% SO behaves similarly to pure PAO 6. The mixture can be selected by considering these results and by taking into account stresses in the tribological contact.

In general, adding an ester to a low viscosity polyalphaolefin acts as a wear reducer at any load. The best mixtures were obtained with 5 and 15% of TMP-05 and SO, respectively. The difference between TMP-05 and SO performance can be attributed to the higher viscosity of TMP-05 and its viscosity exponent in Equation 1, which offsets and neutralises the effect of the higher pressure-viscosity coefficient of the vegetable oil family compared to TMP. The 5% TMP-05 mixture exhibited the best wear performance under load.

5. CONCLUSIONS

The following conclusion can be drawn from this study:

- Adding less than 15% (in wt.) of an ester (TMP-05 or sunflower oil –SO-) to a low viscosity polyalphaolefin has practically no influence on volume viscosity, although lubricity is greatly enhanced.
- The addition of a natural or synthetic ester (TMP-05 or SO) to a low viscosity polyalphaolefin acts as a wear reducer.
- The results obtained with each mixture were better than with pure PAO 6.
The best results were obtained when the percentage of TMP-05 and SO in the mixture ranged between 5% and 15%, respectively.

6. REFERENCES


Table 1: Optimum magnitude [as high or as low possible] of seven parameters in order to obtain beneficial effects on the three lubrication mechanisms.

<table>
<thead>
<tr>
<th>Film thickness</th>
<th>η₀</th>
<th>α</th>
<th>β</th>
<th>ρc₁₀</th>
<th>λ₀</th>
<th>B₀</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Friction</td>
<td>low</td>
<td>low</td>
<td>high/low</td>
<td>?</td>
<td>high/low</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td>Pressure peaks</td>
<td>high/low</td>
<td>low</td>
<td>?</td>
<td>?</td>
<td>?</td>
<td>low</td>
<td>low</td>
</tr>
</tbody>
</table>

Table 2: Oil sample properties.

<table>
<thead>
<tr>
<th>Oils</th>
<th>Density (g/cm³) 15.6°C</th>
<th>Viscosity (cSt) 40°C</th>
<th>Viscosity (cSt) 100°C</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAO 6</td>
<td>0.826</td>
<td>31.0</td>
<td>5.90</td>
<td>135</td>
</tr>
<tr>
<td>TMP-05</td>
<td>0.919</td>
<td>47.5</td>
<td>9.60</td>
<td>192</td>
</tr>
<tr>
<td>SO</td>
<td>0.917</td>
<td>38.42</td>
<td>8.42</td>
<td>202</td>
</tr>
</tbody>
</table>
Figure 1: Wear test of pure oils (ASTM D 4172).

Figure 2: Pressure-viscosity coefficients of studied group of lubricants.
Figure 3: Wear scar appearance in test at 392 N. a) PAO 6  b) TMP-05  c) SO

Table 3: Polarity of polyalphaolefin and esters.

<table>
<thead>
<tr>
<th>Type of oil</th>
<th>Non-polarity index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyalphaolesin</td>
<td>&gt;300</td>
</tr>
<tr>
<td>TMP-05</td>
<td>185</td>
</tr>
<tr>
<td>Rapeseed oil</td>
<td>170</td>
</tr>
<tr>
<td>Pine tree oil</td>
<td>170</td>
</tr>
</tbody>
</table>
Figure 4: Wear test results in PAO 6/TMP-05 mixture.

Figure 5: Wear test results in PAO 6/SO mixture.
Figure 6: Wear scar appearance in test at 392 N: a) PAO 6/5% TMP-05; b) PAO 6/10% TMP-05; c) PAO 6/15% TMP-05 (scale: 100 μm).
Figure 7: Wear scar appearance in test at 392 N: a) PAO 6/5% SO; b) PAO 6/10% SO; c) PAO 6/15% SO (scale: 100 μm).

Figure 8: Tendency in wear behaviour for PAO 6/TMP-05 mixture.
Figure 9: Tendency in wear behaviour for PAO 6/SO mixture.