Evaluating Lubrication Capability of Soybean Oil with Nano Carbon Additive

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\textbf{ABSTRACT}

This paper presents the influence of adding black carbon nanopowder (average size 13 nm, PlasmaChem) in soybean oil in different massic concentration (0.25 \%, 0.50 \% and 1 \%) on several tribological parameters: friction coefficient and wear scar diameter. Tests are done on a four-ball machine. The test parameters were load: 100 N, 200 N and 300 N and speed 1000 rpm, 1400 rpm, 1800 rpm. The test balls are lime polished, made of chrome alloyed steel, having 12.7±0.0005 mm in diameter, with 64-66 HRC hardness. The sample oil volume required for each test was 8±1 ml. This type of anti-wear additive, because the particle distribution is not evenly in contact during the running, could not help improving the tribological behavior. It does not reduced the friction coefficient and wear scar diameter as compared to the neat soybean oil. The authors estimate that the additive should be bonded (physically or chemically) on the triboelements for having better results.

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1. INTRODUCTION

Soybean oil could become a source for the base oil in fields of activities that require non-polluting processes and materials [1-5]. As other vegetal oils, this one, too, has low viscosity [6] and research has been done for additivating it in order to increase its viscosity or/and to protect the rubbing surfaces by specialized additive (especially anti-wear and extreme pressure additives) [7]. But vegetal oil-based lubricants have several disadvantages as compared to mineral and synthetic ones, including low viscosity that not encourage the generation of a continuous film when the tribosystem runs, consequently, implying a mixt or boundary lubrication. This is why the additivation of such vegetal oils is of great interests for researchers, producers and users [2].

Recent reviews of the mechanisms of friction reduction and anti-wear of nanoparticles in lubricants were published, pointing out lubrication mechanisms as rolling, protective film, mending and polishing [8-10]. Shahnazar et al. [11] presented a classification of nano additives in lubricants. Those based on carbon were included in four main allotropic classes: zero-dimensional (fullerene), one-dimensional (nanotubes, nanowires, nanorodes), two-
dimensional (graphene), three-dimensional (graphite, nano-sized diamonds) [12, 13]. Hwang [14] concluded that lubricants with nano additives improve the tribological behavior as compared to microaddition in the same base oils. The nanoparticles play the role of nano ball bearings. He used several carbon-based additives tested on a disk-on-disk tribotester and for black carbon, the size was 54 nm. Hu et al. [15] investigated the efficacy of the carbon black as an engine soot substitute and concluded that wear scar diameter increased with the content of black carbon in the range of 0...8% for a certain grade of engine oil, but for the other, the same parameter has lower values as those for the neat oil. Tested time was 0.5 h. Also, the friction coefficient depends on the base oil and carbon concentration. Many research reports used a pin-on-disk tribotester for evaluating the anti-wear additives [16], but also, the four ball tribotester is favorable to compare experimental results [17].

This paper aims to report the influence of nano black carbon as additive in soybean oil on the tribological behavior of the formulated lubricants by the parameters friction coefficient and wear scar diameter.

2. TESTING METHODOLOGY AND MATERIALS

The lubricants formulated with soybean oil additivated and nano black carbon in different concentrations (0.25 wt%, 0.50 wt% and 1 wt%) were tested on a four-ball machine. The sample oil volume for each test was 8±1 ml. The nano black carbon was supplied by PlasmaChem and has the following characteristics [18]: average particle size ~13 nm, specific surface ~550 m²/g, ash content < 0.02 %, bulk density ~120 g/L. Table 1 presents the typical composition of this oil. The degumming and refining process of oil is done at Prutul SA Galati and prevents oil to form gum deposit and to ferment [19].

The test balls are lime polished, made of chrome alloyed steel (Table 2), having 12.7±0.0005 mm in diameter, with 64-66 HRC hardness. The test method for investigating the lubricating capacity is given in SR EN ISO 20623 [20].

The test parameters were: speed (1000 rpm, 1400 rpm and 1800 rpm, corresponding to the following sliding speeds 0.383 m/s, 0.537 m/s and 0.691 m/s, respectively), normal force on the machine shaft (100 N, 200 N and 300 N), testing time 1 hour.

Table 1. Typical fat acid composition for the tested soybean oil.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Symbol</th>
<th>Concentration, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristic acid</td>
<td>C14:0</td>
<td>0.11</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>C16:0</td>
<td>12.7</td>
</tr>
<tr>
<td>Palmitoleic acid</td>
<td>C16:1</td>
<td>0.13</td>
</tr>
<tr>
<td>Heptadecanoic acid</td>
<td>C17:0</td>
<td>0.05</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>C18:0</td>
<td>5.40</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>C18:1</td>
<td>21.60</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td>C18:2</td>
<td>52.40</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>C18:3</td>
<td>5.70</td>
</tr>
<tr>
<td>Arachidic acid</td>
<td>C20:0</td>
<td>0.25</td>
</tr>
<tr>
<td>Gondoic acid</td>
<td>C20:1</td>
<td>0.20</td>
</tr>
<tr>
<td>Eicosadienoic acid</td>
<td>C20:2</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Table 2. Chemical composition of the steel the balls are made of (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel grade EN31</td>
<td>1.0</td>
<td>1.3</td>
<td>0.5</td>
<td>0.35</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The formulated lubricants were obtained in a small quantity of 200 ml each. The steps followed in this laboratory method were:

- weighting the additive and the dispersing agent with an accuracy of 0.1 mg,
- mechanical mixing of additive and equal mass of guaiacol (supplied by Fluka Chemica), chemical formula being \( C_{66}H_{46}(OH)OCH_3 \) (2-methoxyphenol), for 20 minutes; this dispersing agent is compatible with both additive and vegetal oils,
- adding gradually the soybean oil, measured for getting 200 g of lubricant with the desired concentrations of additive,
- stirring with a magnetic homogenizing device for 1 hour,
- sonication + cooling of 200 g lubricant for 5 minutes with the help of sonicator Bandelin HD 3200 (Electronic GmbH & KG Berlin); the lubricants are heating at approximately 70 °C; the cooling time was 1 hour; this step of sonication + cooling is repeated 5 times for obtaining a total sonication time of 60 minutes. The parameters of sonicating regime are: power 100 W, frequency 20 kHz±500 Hz, continuous regime.
3. RESULTS

The plots of the friction coefficient in Figs. 1-3 is done using a moving average of 200 values, the sampling record being 2 values per second.

The discussion upon the evolution of friction coefficient in time is based on comments done by Czikos [21].

Thus, the friction coefficient measured for soybean oil has a tendency to gradually increase in time for low speed and to remain in a narrow range, at almost the same value for the higher speed (Fig. 2). For the additivated lubricants, the tendency is to decrease the friction coefficient after a running period of 10…15 minutes.

Analysing Fig. 3, one may notice that, at a concentration of 1 % of nano black carbon, the friction coefficient (COF) becomes lower for higher load (F = 300 N) and high speed (v = 1800 rpm). Also, this regime gives the less influence on the wear scar diameter (WSD) (see Fig. 4). Under the lowest tested load (F = 100 N) the range of friction coefficient oscillations are the greatest.
Fig. 3. Evolution of friction coefficient in time for soybean oil +1% nano black carbon.

All maps in Figs. 4 and 6 were plotted using a cubic interpolation and the surfaces are “obliged” to include the experimental data. A point on a map represents a test for the same set of parameters (F [N], v [rpm], C [%]), where F is the normal load on the four ball tester, v is the rotational speed (1000 rpm, 1400 rpm and 1800 rpm) and C is the massic concentration of the black carbon (0, 0.25 %, 0.5 %, 1.0 %).

In Fig. 4, the friction coefficient (COF) is the average value obtained during a test of one hour. COF is slightly reduced for the additivated lubricants and this tendency is more visible for the higher speed (1800 rpm). Taking into account the map shape for 1400 rpm, it seems there are some changes in the regime, especially for the neat oil. The increase of load and speed makes the friction coefficient to increase for the soybean oil.

Fig. 4. The friction coefficient as a function of additive concentration and test conditions.

Wear scar diameter (WSD) is the average values of six measurements, two of each fixed ball of a test. For each ball, there were measured the wear diameter in the sliding direction and perpendicular to it (see Fig. 5).

Fig. 5. Exemple of wear scar diameter measurement. Test conditions: 1000 rpm, F = 200 N, time 1 h, lubricant: soybean oil + 1% nano black carbon, ball 1.
For the additivated lubricants, wear scar diameter is less sensitive to concentration, especially for $F = 300$ N. The non-additivated soybean oil could be recommended for mild regimes (equivalent to $F = 100...200$ N and speed $v = 1000...1800$ rpm). The almost linear dependency of the WSD to load in each map in Fig. 6 suggests an abrasive wear due to a mixt regime.

SEM investigations reveal that the black carbon is on the rubbing surfaces as nanoagglomerations, unevenly distributed on the surface texture. The particles or their agglomerations seem to be rolled and it is very probable that they act like nano rolling elements, this explaining the low values of friction coefficient during the test (see Fig. 7).

Fig. 6. Wear scar diameter as a function of additive concentration and test conditions.

Fig. 7. Particles of nano black carbon. Test conditions: 1000 rpm, $F = 200$ N, time 1 h, lubricant soybean oil +1 % nano black carbon.

The problem is that, as one may notice, the particles are not evenly distributed on the contact surfaces, producing preferential wear on the zone without particles. As the particles migrate in running, these zones prone to direct contact are changing, this could be the explanation for the variation of the friction coefficient in time and with high amplitudes (Fig. 7).

4. CONCLUSIONS

For the tested regimes ($F = 100$ N...300 N and $v = 1000...1800$ rpm), the results are not in the favour of the additivated lubricant formulations.

The addition of nano black carbon increases the wear scar diameter. As comparing only the additivated oils, it seems that under low speed, when the load increases, the wear scar diameter increases, too. Under the loads of 200 N and 300 N, wear scar diameter is less depending on speed and load for the concentrations of 0.5 wt% and 1 wt% black carbon.

It seems that this anti-wear additive - nano black carbon, does not have a very clear influence on
improving the tribological behaviour of the soybean oil. Even if the mechanism of reducing friction exists in the presence of the additive, that is interposing nano particles of black carbon between the rubbing surfaces and having a third body friction, the migration of these particles (because they are not bonded to the surfaces) and their uneven distribution in contact make the tribosystem to behave more unstable than when using the neat soybean oil. In a statistical approach, at a moment there could enough particles in contact to reduce friction and wear but, during running, there could be moments when this number is low enough to have mixt regime and the oscillations between these two situations could explain the variations of the friction coefficient and the higher values for wear scar diameter.

This type of anti-wear additive, because the particle distribution is not even in contact during the running, could not help improving the tribological behaviour, as it does not reduce the friction coefficient and wear scar diameter as compared to the neat soybean oil. The authors think that the additive should be bonded (physically or chemically) for having better results.

REFERENCES

