DEVELOPMENT OF LOW PHOSPHORUS ENGINE OILS

Patel\(^a\), As swath\(^b\), P.B., Elsenbaumer\(^b\), R.L.

\(^a\) Materials Science and Engineering, The University of Texas at Arlington, Arlington, TX-76019
\(^b\) Platinum Research Organisation, 2828 Rout h St. Dallas, TX-75021
as swath@uta.edu

ABSTRACT
ZDDP is the industry standard anti wear additive used by oil formulators for the past 50 years to provide the antiwear and load bearing capacity of engine oil. The breakdown of ZDDP results in the formation of sulfides and phosphates which provide anti-wear protection. In addition to its role as an antiwear additive ZDDP also performs the role of an antioxidant. The performance of ZDDP is reduced by other parts of the additive package which include dispersants, pH stabilizers, and detergents. These constituents stabilize ZDDP and reduce its activity.

The breakdown of ZDDP also creates S and P that can poison catalytic converters resulting in higher hydrocarbon and NOx emissions. GF-4 oils have lower ZDDP content to meet federal emission standards. In addition, to meet CAFÉ fuel economy standards, the industry is moving towards lower weight 5W-20 oil. The lower weight base oil coupled with lower ZDDP content have put additional constraints in developing high performance GF-4 oil. An additive package developed by Platinum Research Organization and the Tribology Group at University of Texas at Arlington is evaluated. This additive package enhances the activity of ZDDP and increases its anti-wear performance.

This paper presents results from bench top tribology tests that were conducted to evaluate the performance of GF-4 oils with different amounts of ZDDP, additive package and an Fe based active ingredient. Results are discussed with respect to the extent of wear for a fixed number of wear cycles in a ball on cylinder test conducted under boundary conditions. In the presence of FeF\(_3\) active ingredient fully formulated oils with as little as 0.01% P exhibits antiwear performance comparable to oils with as much as 0.05% P and oils with 0.05%P are comparable to oils with 0.1%P. Differential scanning calorimetry indicates that the decomposition temperature of ZDDP is reduced by as much as 20°C in the presence of FeF\(_3\). This reduced decomposition temperature results in the efficient formation of anti-wear films even with lower ZDDP amounts.

INTRODUCTION
Zinc dialkyldithiophosphates (ZDDPs) are widely used lubricant additives to provide antiwear and antioxidancy and from their origin in late 1930s till today, ZDDPs have successfully stimulated research [1]. Although extensively used, ZDDPs is responsible for poisoning catalytic converters and a trend of lower phosphorus levels in engine oils is fast emerging [2]. Along with the need to reduce the detrimental effects of phosphorus a need for improved antiwear protection, durability of engine components and extension of engine oil useful life is important [3]. Efforts to reduce the level of phosphorus, to 0.03% have been initiated in context to antiwear characteristic of ZDDP [4].

This paper discusses the possibility of phosphorus reduction to as low as 0.01% in engine oil to provide equal or greater antiwear performance as compared to 0.05%P or 0.1%P. A matrix of ball-on-cylinder boundary condition tests performed on Plint Tribometer indicates that inclusion of an active ingredient, FeF\(_3\), enhances the performance of ZDDP in engine oils and allows the amount of the phosphorus to drop to as low as 0.01% and still maintain the antiwear performance. Differential Scanning Calorimetry studies have shown that the decomposition temperature of ZDDP can be decreased by almost 20 deg C when reacted with FeF\(_3\), thus providing the wear protection before any catastrophic wear occurs.

Experimental Set-up & Materials
All the wear tests were carried out on the Plint T53 Slim model to approximate engine performance. The tribometer, as-received was modified to use standard Timken Roller Tapered Bearing cylinder [SAE TIMKEN LM67010 with 67.5(HRC) outer surface hardness, 60mm inner diameter and surface roughness of 0.2-0.3 microns Ra] where the outer surface of the cylinder was used for wear testing. The tribometer was designed to carry out the tests as per the Gear Oil Scuff Test (GOST) standards. Tungsten Carbide ball [1/2” diameter, 79 (HRC) hardness] was used as a stationary body. Details of the oils evaluated are listed in Table 1. All the tests were conducted at 297 N loading under boundary condition at 700
rpm. Only 50µl of oil formulation was applied at the contact path between ball and cylinder and the cylinder was hand-rotated to ensure a continuous boundary film of oil. Test materials were cleaned with acetone-hexane mixture before the test. Wherever mentioned, “Pre-activation” of ZDDP and FeF₃ was carried out by heating both the materials at 125 deg C for 4hrs and then adding this mixture to the fully formulated oil. At least two replicates of each test were carried out to confirm the reproducibility and consistency of results.

Results
Results of the wear tests including details of the oils used, duration of tests are displayed in Table 1.
Comparison of the tests conducted in GF3 oils indicate that wear performance comparable to that seen in 0.1%P oils can be achieved in the oils with 0.05%P with the addition of 0.4wt% FeF₃. SEM results of the wear surface indicate the formation of a stable tribofilm in the presence of FeF₃. Corroborating DSC results on the stability of ZDDP with and without additives and in the presence and absence of FeF₃ indicate that FeF₃ helps in the decomposition of ZDDP resulting in formation of an efficient tribofilm at lower levels of phosphorus.

![Figure 1- Wear Volume Comparisons](image)

**Table 1**

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Type of Oil</th>
<th>Test duration (No. of cycles)</th>
<th>Details of oils tested</th>
<th>Wear Track Depth (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GF3</td>
<td>42K</td>
<td>Fully formulated oil(0.05%P)</td>
<td>3.27</td>
</tr>
<tr>
<td>2</td>
<td>GF3</td>
<td>42K</td>
<td>Fully formulated oil(0.1%P)</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>GF3</td>
<td>42K</td>
<td>Oil #1 + 0.4%pwd, masticated catalyst</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>GF4</td>
<td>100K</td>
<td>Fully formulated oil(without ZDDP)</td>
<td>3.4</td>
</tr>
<tr>
<td>5</td>
<td>GF4</td>
<td>100K</td>
<td>Oil #4 + 0.01%P added</td>
<td>2-2.5</td>
</tr>
<tr>
<td>6</td>
<td>GF4</td>
<td>100K</td>
<td>Oil #4 + 0.4%pwd masticated catalyst</td>
<td>1-1.2</td>
</tr>
<tr>
<td>7</td>
<td>GF4</td>
<td>100K</td>
<td>Oil #4 + Catalyst(0.4%pwd, masticated) &amp; ZDDP(0.01%P) pre-mixed and added to the oil</td>
<td>1.2-2</td>
</tr>
<tr>
<td>8</td>
<td>GF4</td>
<td>100K</td>
<td>Oil #4 + [Catalyst(0.4%pwd, masticated) &amp; ZDDP (0.01%P)] PRE-ACTIVATED</td>
<td>≤1</td>
</tr>
</tbody>
</table>

Figure 1 shows a comparison of wear volumes of all the tests mentioned in Table 1.

The results in GF4 oils are even more dramatic where a significant drop in the depth of wear track and the wear volume both, when just 0.01%P is added to GF4 oils and also when just 0.4wt% FeF₃ is added with 0.01%P is seen. Results are further improved when the ZDDP is preactivated with the catalyst prior to its addition to fully formulated GF4 oils. It is well known that various additives in engine oil like dispersants and detergents have and antagonistic effect on ZDDP and reduce its performance. When ZDDP is premixed with FeF₃ and baked at 125 deg C for 4 hours it complexes with it and reduces its interaction with the other additives. This complex is then delivered to the wear surface resulting in a stable tribofilm formation.

Conclusions
The results of the ball on cylinder bench test studies indicate that phosphorus reduction to as low as 0.01% is possible in engine oils. As is widely accepted, ZDDPs are responsible for providing antioxidancy along with antwear. Authors believe that this characteristic can be achieved by other ashless antioxidants available in market. Efforts are underway to analyze the performance of low phosphorus (0.01%) engine oils in real engine tests.

**REFERENCES**