Biorefinery Technology: New, High-Performance Approaches in Lubricant Base Stocks

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1. Introduction
Elevance Renewable Sciences, Inc. announced the start up and shipment of commercial products in 2013 from a jointly owned world-scale biorefinery with Wilmar International Limited located in Gresik, Indonesia. The biorefinery was constructed based on proprietary Nobel Prize-winning olefin metathesis technology capable of converting renewable natural oils (e.g., palm, soybean, canola, mustard, algal, etc.) into high-value specialty difunctional molecules, olefins and oleochemicals with a capacity of 180 kMT. There are large established markets for oleochemicals and olefins in place to provide off take, however, it is the advantaged specialty chemicals that create technology options and value for Elevance partners. This paper reviews the development and design of a new, synthetic base stock obtained through a polymerisation reaction of difunctional ester building blocks. These novel materials enable Elevance to effectively address the lubricants and additives market by addressing both bio-content and, more importantly, differentiated performance.

2. Drivers
There are three drivers steering the lubricant industry today. 1) Regulations continue to tighten, with higher requirements on fuel economy and emissions. 2) Original equipment manufacturers (OEMs) are responding to the regulations in part by redesigning engines to deliver more power from smaller displacement engines and, as a result, increasing the performance requirement on lubricants. The fundamental driver influencing society, politicians, consumers and the lubricant industry, however, is 3) the environment. Consumers want more sustainable products and this is driving more environmental solutions across societies worldwide. The net result is that lubricants are shifting in technology, mostly towards higher quality and performance and the lubricant industry is becoming more complex with an increasingly diverse range of performance targets, portfolio of OEMs and customer locations.

3.1 Elevance Inherent™ Building Blocks
Within Elevance, using our metathesis catalyst, we simply “unlock” the unsaturated sites in the long carbon chains present in nature’s triglycerides to create novel, difunctional and renewable building blocks and renewable olefins. Metathesis is the rearrangement of unsaturated carbon bonds (Figure 1). Historically limited to molecules without important functional groups, “Grubbs catalysts” represent a significant breakthrough – opening the chemistry to plant oil applications.

Inherent™ C10 methyl ester (ME) is an exciting new platform chemical (Figure 2). With its alpha olefin, carboxylic acid groups and commercially important chain length, it provides functionality for derivatization and a variety of innovation possibilities. Like acrylic acid (a product with a similar difunctional structure) we see this platform chemical and those like it that we produce at scale in our biorefinery as exciting building blocks for a wide variety of applications and industries. This new, difunctional material can be modified to achieve unique functionality via branching, oligomerisation or polymerisation, functional group insertion or exchange.
3.2 Elevance Aria™ WTP 40
An early example of using Inherent™ chemical building blocks to reengineer base stocks is in the functionalisation of polyalphaolefin (PAO). Elevance engineers have synthesised olefinic ester technology where PAO-type architecture is combined with ester functionality to create an ester functionalised PAO. A new material offering novel and differentiated performance from PAO, esters and PAO ester blends, Elevance Aria™ WTP 40 is a novel synthetic base stock that is an ester-functionalised polyalphaolefin. Its unique molecular architecture is devised by the use of Elevance Inherent™ renewable carbon-based building block C10 ME.

The oligomerisation of alpha olefins with our C10 methyl ester creates a PAO structure but with a covalently bonded ester. This branching has decene length and the ME is at the terminal carbon. We can also use these synthesis tools to efficiently manage polarity. Some formulators and additive producers feel group I and group II polarity are the ideal, so we targeted polarity to match these two base stocks, targeting an aniline point of around 100.

This base stock, developed for use in synthetic lubricants, has a number of unique attributes (Table 1), which include inherent additive solvency, ability to lower friction — hence reduce wear, inhibit foam formation and provide deposit control in a finished lubricant. Its low pour point and high viscosity index delivers performance across a broad range of temperatures and lubrication regimes, clean operation and better lubricity, leading to equipment durability and extended lubricant life. Because of its high viscosity, this high-performance molecule is especially designed to formulate high viscosity grade lubricants.

The initial evaluation of our material for industrial use was to study additive compatibility. PAO high viscosity base oils have typical aniline points greater than 120 which requires formulators to commonly blend with esters as compatibilisers. We have also included PAO/ester blends to replicate how lubricant formulations are done in practice. The clarity and colour of additised samples of Elevance Aria™ WTP 40 versus PAO shown in Figure 4 demonstrates the solubility advantage of Elevance Aria™ as compared to PAO and PAO/ester blends.
4. Performance Data of Formulated Elevance Aria™ WTP 40

Gear lubricants are designed to perform in all three types of lubrication environments: boundary, mixed film and full film. Boundary lubrication occurs when the gear sets start or stop. When the gears are operating at slow speeds, they are in mixed lubrication regime and when they are operating at high speeds, they are in full film lubrication regime. Of course, the introduction of pressure or load into this equation alters the nature of the lubrication. For example, high loads on gears operating in full film regime will change the lubrication regime to mixed film and the higher loads for those operating in the mixed film regime will alter the regime to boundary.

To gain insight on how the new architectures may impact lubricant industry trends mentioned earlier in terms of equipment durability (using wear as a proxy), we made typical formulations using commercially available GL-5 additive package and other commercial materials. We made two formulations at equal viscosity. We compared Elevance Aria™ WTP 40 to a blend of PAO 40 and ester, as per the additive package producer recommendations. We then utilised the MTM and found the Elevance formulation demonstrated less wear in this controlled test under conditions designed to mimic gear operations (Figure 5).

The MTM was then used to measure the traction forces transmitted across a lubricant film under varying amounts of sliding while controlling load, speed and temperature (Figure 6). The actual traction coefficient measurement over a range of slide-to-roll ratios shows that Elevance Aria™ WTP 40 has even lower friction than a high-performance PAO/ester blend gear lubricant. While these systems are not optimized, this initial data demonstrates that the new synthetic base stock architecture may bring users improved friction and wear. These attributes, in turn, may lead to improved, in-use performance compared to typical mineral and group IV oil-based products.

5. Application Data

Automotive gear oils are designed to provide wear protection to driveline components, such as manual transmissions, drive axles (differentials) and non-drive parts, such as steering and rear axles in front-drive vehicles. Their primary functions are to reduce friction between the gear surfaces in contact, dissipate heat and provide protection against damage due to extreme operating pressures. Unlike automotive gear oils that are classified by SAE viscosity grades, industrial gear oils are classified by ISO viscosity grades. Suitable viscosity is determined by the minimum viscosity that maintains hydrodynamic lubrication at operating temperature. Because of this, suitable ISO viscosity grades for industrial gear oils are 100 and above.

The KRL roller bearing test method is used to determine the mechanical shear stability of lubricating oils with polymer additives, such as gear oils, engine oils, damper oils and automatic transmission fluids (Figure 7). This test was used to compare Elevance Aria™ WTP 40 versus conventional PAO/ester neat and in formulation. Elevance Aria™ WTP 40 was formulated with <10% PAO4 and GL-5 gear oil additive package to make 80W140 grade oil. The results show that in both cases Elevance Aria™ WTP 40 offers improved film strength under high shear and temperature conditions.
The L-37 automotive test is used to evaluate the load-carrying, wear protection and extreme-pressure proper-ties of gear lubricants in final hypoid drive axles. The severity of the test was increased to challenge Elevance Aria™ WTP 40 to the absolute limits in gear lube performance. Test conditions were low-speed, high-torque for 24 hours at 135°C. Elevance Aria™ WTP 40 was formulated similar to prior testing (vide supra). The L-37 wear test results in Table 2 indicate strong pass.

<table>
<thead>
<tr>
<th>Gear Rating</th>
<th>Pinion</th>
<th>Ring</th>
<th>API GL-5 MT-1 Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wear</td>
<td>7.0</td>
<td>8.0</td>
<td>5 min.</td>
</tr>
<tr>
<td>Rippling</td>
<td>9.4</td>
<td>10.0</td>
<td>8 min.</td>
</tr>
<tr>
<td>Ridging</td>
<td>9.4</td>
<td>10.0</td>
<td>8 min.</td>
</tr>
<tr>
<td>Pitting + Spalling</td>
<td>9.9</td>
<td>9.9</td>
<td>9.3 min.</td>
</tr>
<tr>
<td>Scoring</td>
<td>10.0</td>
<td>10.0</td>
<td>10</td>
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<td>Deposits</td>
<td>10</td>
<td>10</td>
<td>Report</td>
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<tr>
<td>Corrosion</td>
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<td>Report</td>
</tr>
<tr>
<td>Discoloration</td>
<td>9</td>
<td>8</td>
<td>Report</td>
</tr>
<tr>
<td>Overall Rating</td>
<td>PASS</td>
<td>PASS</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. L37 Automotive drive axle test

In automotive differentials the ring and pinion are spiral-cut, hypoid gears. They slide more on each other than other types of gears. Extreme-pressure additives are used to protect these gears when the lubricant film is wiped away or ruptured. The photos in Figure 8 complement the data showing very little wear, pitting and scoring and no corrosion or deposition. These results demonstrate that the inherent polarity of Elevance Aria™ WTP 40 allows for additive solvency without disrupting the additive designed interaction with the metal surface. We’re seeing that the formulation flexibility with Elevance Aria™ WTP 40 allows these additives to perform at their most optimal level.

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The L-60-1 automotive gear oil test measures an oil’s resistance to thermal/oxidative degradation under high temperature conditions. In addition to the evaluation of the gear components (see photos in Figure 9), the L-60-1 test evaluated the viscosity change and sludge generated of the used oil. The Elevance Aria™ WTP 40 formulation passed all of the GL-5 specifications while it also outperformed the PAO/ester formulation in varnish measurement.

6. Conclusions
Elevance renewable building blocks offer a new tool for synthesising novel, high-performance lubricant base stocks. Elevance Aria™ WTP 40 is a base stock that can help meet today’s high-performance base stock demands for severe applications. The molecular design of Elevance Aria™ with chemically bound ester shows advantages over the PAO/ester blend in additive compatibility, seal compatibility, foam control, friction, wear, cleanliness and tribological performance. The improved performance of Elevance Aria™ WTP 40 could be attributed to its stronger and thicker adsorbed fluid film and intramolecular interactions. Elevance Aria™ WTP 40 is showing great promise and more formulating and testing will help demonstrate the ideal applications.

References
[4] DIN 51350-6

References
[4] DIN 51350-6

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