Low Temperature Assessment of Current Engine Oils

Charles K. Dustman
Evonik Oil Additives USA, Inc.
Outline

- An Overview of Evonik Industries
- Importance of Lubricant Low Temperature Flow Performance
- Low Temperature Performance of Oils from the Americas Region
- Pour Point Depressant (PPD) Fundamental and Selection Criteria
- Effect of Oil Aging Oil Process on Oil Low Temperature Flow Property
- GF-6 Impact on Low Temperature Performance
- Summary
### Evonik’s 2015 figures

<table>
<thead>
<tr>
<th>Employees December 31, 2015</th>
<th>33,576</th>
</tr>
</thead>
<tbody>
<tr>
<td>Profitability (EBITDA margin)</td>
<td>18.2%</td>
</tr>
<tr>
<td>€2,4 billion (\text{Adjusted EBITDA})</td>
<td>(\text{Return on capital employed (ROCE)}) (\text{sales})</td>
</tr>
<tr>
<td>€13.5 billion</td>
<td></td>
</tr>
</tbody>
</table>
A modern structure

Evonik

Segments

Nutrition & Care
- Animal Nutrition
- Baby Care
- Comfort & Insulation
- Health Care
- Household Care
- Interface & Performance
- Personal Care

Resource Efficiency
- Active Oxygen
- Catalysts
- Coating Additives
- Coating & Adhesive Resins
- Crosslinkers
- High Performance Polymers
- Oil Additives
- Silanes
- Silica

Performance Materials
- Acrylic Monomers
- Acrylic Polymers
- Agrochemicals & Polymer Additives
- CyPlus Technologies
- Functional Solutions
- Performance Intermediates

Services

Technology & Infrastructure
- Logistics
- Site Management
- Technical Service
- Process Technology & Engineering

Other Services
- Utilities and Waste Management
# Oil Additives Product Overview

<table>
<thead>
<tr>
<th>Category</th>
<th>Subcategories</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic fluid</td>
<td>Mobile, Industrial, Shock Absorbers, Aviation, Fire Resistant</td>
</tr>
<tr>
<td>Engine oil</td>
<td>Gasoline, Passenger Car Diesel, Heavy Duty Diesel, Railroad</td>
</tr>
<tr>
<td>Driveline</td>
<td>Gear, Transmissions: Manual, Automatic, Continuously Variable, Rear Axle, Dual Clutch</td>
</tr>
<tr>
<td>Biodegradable</td>
<td>Motorcycle, Scooter, Chain Saw Oils, Saw Mill Oils</td>
</tr>
<tr>
<td>Refinery</td>
<td>Dewaxing, Declining</td>
</tr>
<tr>
<td>Biodiesel</td>
<td>B100, Bio</td>
</tr>
</tbody>
</table>

- **VISCOPLEX®** pour point depressants
- **VISCOPLEX®** viscosity index improvers
- **VISCOPLEX®** defoamer additives

**Main Drivers**
- Resource Efficiency
- Fuel Economy
- Reduced Carbon Emissions
- Higher demand in emerging regions

**Technology**
- DYNAVIS®
- VISCOBASE® synthetic base fluids
Evolution of Low Temperature Performance Standards

Low temperature testing has become more diverse over time to account for new issues.

1980
SAE J300 listed
MRV BPT

1986
SAE J300 listed
MRV TP-1

1994
SAE J300 lowered
MRV TP-1 temp. by 5°C

1996
ILSAC GF-2 defined max. gelation index

1999
SAE J300 lowered
CCS temp. by 5°C

2004
ILSAC GF-4 introduced aged oil low temp. viscosity spec.

2010
ROBO method listed in ILSAC GF-5

2012
ACEA 2012 listed CEC L-105 method, considering low temp. impact by biodiesel dilution

Future
GF-6 and other formulated oil standards in development

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Future GF-6 and other formulated oil standards in development
Several low temperature phenomena can limit oil flow to the engine and lead to engine damage:

- **Oil flow limited due to high viscosity**
  - MRV TP-1 viscosity

- **Air binding phenomenon due to yield stress**
  - MRV TP-1 Yield Stress
A test database of 249 commercially available engine oils from the Americas region gave the following results for the key low-temperature tests.

<table>
<thead>
<tr>
<th>Country</th>
<th>TP-1 Viscosity</th>
<th>TP-1 Yield Stress</th>
<th>Gelation Index</th>
<th>Failing TP-1 and/or GI³ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentina</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0 (0 %)</td>
</tr>
<tr>
<td>Brazil</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>4 (20%)</td>
</tr>
<tr>
<td>Canada</td>
<td>0²</td>
<td>1</td>
<td>0</td>
<td>1 (3%)</td>
</tr>
<tr>
<td>Mexico</td>
<td>0²</td>
<td>1</td>
<td>1</td>
<td>2 (20%)</td>
</tr>
<tr>
<td>United States</td>
<td>2²</td>
<td>2</td>
<td>9</td>
<td>9 (5%)</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>16 (6.4%)</td>
</tr>
</tbody>
</table>

2. One additional sample was a borderline pass.
3. Samples often fail more than one test, so the number of fails may not be the total of the preceding columns.
Characteristics of the Oils in the Study

Most of the 249 oils were multi-grade, lower viscosity, and often synthetic. The Brazilian samples were similar, and so it is noteworthy that the regional failure rate of key low-temperature tests exceeds 6%.
A test database\(^1\) of 240 commercially available engine oils from the Americas region gave the following results for the key low-temperature tests.

<table>
<thead>
<tr>
<th>Country</th>
<th>TP-1 Viscosity</th>
<th>TP-1 Yield Stress</th>
<th>Gelation Index</th>
<th>Failing TP-1 and/or GI(^3) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argentina</td>
<td></td>
<td>Not Sampled in this Database</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brazil</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>5 (25%)</td>
</tr>
<tr>
<td>Canada</td>
<td>0</td>
<td>Not Measured</td>
<td>0</td>
<td>0 (0%)</td>
</tr>
<tr>
<td>Mexico</td>
<td>0(^2)</td>
<td>1</td>
<td>1</td>
<td>2 (20%)</td>
</tr>
<tr>
<td>United States</td>
<td>4</td>
<td>6</td>
<td>12</td>
<td>13 (7%)</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>20 (8.3%)</td>
</tr>
</tbody>
</table>

2. One additional sample was a borderline pass.
3. Samples often fail more than one test, so the number of fails may not be the total of the preceding columns.
Overall, a total of 4 oils (20% of sample set) failed either the MRV TP-1 or the gelation index requirements:

- 0 W → 1 oil (17% of 0W tested)
- 5 W → 1 oil (10% of 10W tested)
- 10W → 2 oils (67% of 20W tested)

The MRV TP-1 viscosity and/or yield stress failures result from ill-controlled gelation/crystallization processes.

A solution to this challenge consists in a careful selection of adequate Pour Point Depressant (PPD) technology that balances the effects of other formulation components.
Pour Point Depressants Control Oil Low Temperature Flow

Without PPD

Wax molecules start to crystallize below the cloud point.

Wax crystals continue to grow, forming needle and/or plate shapes.

Flow is hindered when a 3-D wax network structure, with crystal size > 100 micron, hinders oil flow.

With PPD

Wax molecules co-crystallize with the PPD.

PPD modifies the growth of wax crystals, forming more numerous but smaller crystals.

The lack of a wax crystal network structure removes yield stress and facilitates flow.

Decreasing Temperature
Modern PPDs typically consist of a polymer backbone with side chains capable of interacting with wax molecules.

The properties of the PPD can be modified by changing the nature of the side chains:

- Adjusting the side chain type and length alters the wax interaction properties of the PPD
- Optimal PPD selection requires the careful matching of the wax interaction properties of the PPD with those of the rest of the formulation components.
Considerations in PPD Selection

An optimal PPD choice matches the “waxiness” of the PPD to that of the formulation. Major factors influencing the PPD choice are shown below:

- Additive Components
- Formulation Viscosity Grade
- Oil Aging
- Base Oils
- Biodiesel Contamination
Matching “Waxiness” of Oils and PPDs

SAE 5W-30 Formulations

- High
- Medium High
- Medium
- Medium Low
- Low

MRV TP-1 Viscosity, mPa.s

- 0
- 20000
- 40000
- 60000
- 80000
- 100000

Gelation Index

- 0
- 2
- 4
- 6
- 8
- 10
- 12

Viscosity

Gelation Index
### Effect of Viscosity Grade on Low Temperature Properties

<table>
<thead>
<tr>
<th>Test</th>
<th>Viscosity Grade</th>
<th>5W-30</th>
<th>10W-30</th>
<th>20W-50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pour Point (ASTM D97)</td>
<td>-33, -30</td>
<td>-36</td>
<td>-27</td>
<td>-24</td>
</tr>
<tr>
<td>MRV TP-1 (ASTM D4684)</td>
<td>44,000, 35,000</td>
<td>22,000</td>
<td>23,600</td>
<td>21,600</td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Yield Stress, Pa</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Scanning Brookfield (ASTM D5133)</td>
<td>5, 6</td>
<td>5</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>
## Effect of Base Oil on Low Temperature Properties

<table>
<thead>
<tr>
<th>Test</th>
<th>Group II Source</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PPD Type</strong></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Pour Point</strong> (ASTM D97)</td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>MRV TP-1</strong> (ASTM D4684)</td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Viscosity, mPa.s</strong></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Yield Stress, Pa</strong></td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td><strong>Scanning Brookfield</strong> (ASTM D5133)</td>
<td></td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Effect of Additive Components on Low Temperature Properties

SAE 5W-30 Formulations, DI package 1

- Decreasing PPD Waxiness
- VM Crystallinity: VM 1 > VM 2
Effect of Additive Components on Low Temperature Properties

SAE 5W-30 Formulations, DI package 2

Decreasing PPD Waxiness

VM Crystallinity VM 1 > VM
Oil Aging Effects Incorporated into ILSAC Standards

- ILSAC established an aged oil low temperature standard to address viscosity increase due to engine oil oxidation ➔ ILSAC GF-4

- ILSAC GF-4 required Sequence IIIGA engine test method to generate aged oil for MRV TP-1 (ASTM D4684)

- Based on aged oil CCS viscosity, decide MRV TP-1 temp.
  - Viscosity < 60,000 cP
  - Yield Stress < 35 Pa
## Effect of Oil Aging on Low Temperature Properties

<table>
<thead>
<tr>
<th></th>
<th>PPD</th>
<th>Untreated</th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fresh Oil</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MRV TP-1 (ASTM D4684) @ -35°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Treat Rate</td>
<td></td>
<td>0.0%</td>
<td>0.4%</td>
<td>0.4%</td>
</tr>
<tr>
<td>Pour Point (ASTM D97, °C)</td>
<td></td>
<td>-18</td>
<td>-33</td>
<td>-30</td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td></td>
<td>17,600</td>
<td>17,000</td>
<td>17,000</td>
</tr>
<tr>
<td>Yield Stress, Pa</td>
<td></td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>MRV TP-1 (ASTM D4684) @ -40°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td></td>
<td>134,000</td>
<td>60,000</td>
<td>60,000</td>
</tr>
<tr>
<td>Yield Stress, Pa</td>
<td></td>
<td>&lt;105</td>
<td>&lt;35</td>
<td>&lt;35</td>
</tr>
<tr>
<td>Scanning Brookfield (ASTM D5133)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gelation Index</td>
<td></td>
<td>5.0</td>
<td>5.0</td>
<td>5.5</td>
</tr>
<tr>
<td><strong>Aged Oil (by ROBO)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MRV TP-1 (ASTM D4684) @ -300°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Viscosity, cP</td>
<td></td>
<td>Solid</td>
<td>128000</td>
<td>44000</td>
</tr>
<tr>
<td>Yield Stress, Pa</td>
<td></td>
<td>&lt;105</td>
<td>&lt;35</td>
<td>&lt;35</td>
</tr>
</tbody>
</table>
Biodiesel Fuel Contamination
CEC L-105

- Pumpability field failures - winter 2008/09
  - 3 OEMs
  - Light & heavy duty
  - Oils passed fresh oil TP-1

- Biodiesel contamination
  - Regeneration of the DPF
  - Less volatile biodiesel passes to oil

- CEC L-105
  - Predicts failing oils from the field
  - Mandatory for all ACEA heavy & light duty categories except A3/B3
ACEA 2012 added CEC L-105 test to evaluate impact of biodiesel dilution on low temperature properties of aged diesel engine oil.

## Effect of Biodiesel Contamination on Low Temperature Properties

### Increasing PPD Waxiness

<table>
<thead>
<tr>
<th></th>
<th>PPD</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fresh Oil</strong></td>
<td>PPD Treat Rate</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
<tr>
<td>MRV TP-1 (ASTM D4684) @ -25°C</td>
<td>Viscosity, cP</td>
<td>Fail</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>Yield Stress, Pa</td>
<td>Fail</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td><strong>Aged Oil by CEC L-105</strong></td>
<td>PPD Treat Rate</td>
<td>0.2%</td>
<td>1.0%</td>
<td>0.5%</td>
<td>0.2%</td>
</tr>
<tr>
<td>MRV TP-1 (ASTM D4684) @ -250°C</td>
<td>Viscosity, cP</td>
<td>Bad Fail</td>
<td>Pass</td>
<td>Fail</td>
<td>Pass</td>
</tr>
<tr>
<td></td>
<td>Yield Stress, Pa</td>
<td>Bad Fail</td>
<td>Fail</td>
<td>Fail</td>
<td>Pass</td>
</tr>
</tbody>
</table>
Summary

- A significant percentage of commercial engine oils do not meet modern low temperature performance standards

- Modern engine oils must have robust cold flow performance to prevent engine failure from inadequate oil pumpability.
  - Low temperature tests are now defined for fresh, aged, and fuel-contaminated engine oils

- Selection of an appropriate PPD allows an oil to meet these extensive requirements.
  - Factors affecting the engine oil low temperature performance include base stocks, additives, viscosity grade, aging and fuel contamination effects