Bio-lubricants: what are they and what formulating challenges do they present?

Mick Wragg – Senior Global Product Steward, Industrial Additives, Lubrizol

UKLA Biolubricants Seminar 6th July 2016
The content of this presentation is the personal interpretation of the author and no warranty concerning its accuracy is given by Lubrizol or any of its affiliates.
Outline

- What is a Bio-lubricant / Bio-based lubricant?
- Other environmental standards / drivers
- Formulating challenges
What is a Bio-lubricant?
Bio-lubricants / Bio-based lubricants are……..

- ‘Biodegradable’ lubricants
- ‘Environmental friendly’ lubricants
- Lubricants containing ‘biological’ substances
- Lubricants that have a lower impact on the environment
- Lubricants made from natural sources
- Lubricants that biodegrade rapidly and which are non-toxic for human beings and aquatic habitats
- Lubricants which are rapidly biodegradable and non-toxic to humans and other living organisms, especially in aquatic environments
- Lubricants made from a variety of vegetable oils, such as rapeseed, canola, sunflower, soybean, palm, and coconut oils
- Naturally lubricating chemicals extracted from animal fat, sunflower, soybean and rapeseed…non-toxic and biodegradable in nature
- Lubricants made from biodegradable synthetic materials
- Lubricants made using renewable biological resources
EU Commission Mandate 430 (2008)

- Commission Lead Market Initiative of “Accelerating the Development of the Market for Bio-based Products in Europe”
  - Bio-polymers
  - Bio-lubricants
- Standardisation thought to facilitate development of lead markets and harmonisation of the internal market
- Remove barriers to allow increased demand
- Technical Committee 19 (TC19) tasked with developing standard for Bio-lubricants
- Key criterion is renewable raw material content (Bio-based carbon)
- UK represented by British Fluid Power Association / BSI
EU Lead Market Initiative (LMI) for Bio-based products: relationship between the WGs for lubricants

**Mandate 429:**
Standardization programme for Bio-based Products to prepare a definition of the term “Bio-based”

**EU Commission – DG Enterprise & Industry**

**Ad-hoc Advisory Group for the LMI for Bio-based Products**

**Mandate 430:**
EU standards for Bio-polymers and Bio-lubricants in relation to Bio-based Product aspects

**CEN/BT/WG 209:**
"Bio-based Products"

**DIN NA 172-00-11AA:**
“Biobasierte” Produkte

**CEN/TC 19:**
"Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin"

**CEN/TC 19/WG 33:**
“Bio-lubricants”

**WG 1:**
Impact of legislation and policies (concerning raw materials and products)

**WG 2:**
Standards, labelling and certification

**WG 3:**
Market drivers and public procurement

**Proposals**

**Recommendations**

**Standards**

**Task**

© 2016 The Lubrizol Corporation, all rights reserved.
Developing a European Standard for Bio-lubricants and Bio-based lubricants

- **EN16807.2016** has been developed by Work Group 33
  - Convenor Dr. Rolf Luther (Fuchs)
- Contains definitions and other technical details establishing criteria
- Standard definition / criteria for value chain members and policy makers to refer to and for statistical reasons
- Builds on other European Standards associated with a biobased economy
- Complementary to, but not replacing, other EU ‘environmental’ standards (e.g. EU Ecolabel criteria for lubricants). Seen as an umbrella definition for all kind of lubricants
- Expected to be published as a finished standard during 2H2016
A Bio-lubricant / Bio-based lubricant:

- Contains a minimum of 25% (w/w) components obtained from renewable sources *(measured Bio-based carbon content)*

- Achieves ≥ 60% (lubricating oil) or ≥ 50% (lubricating grease) biodegradation
  - Measured over 28 days for lubricant
  - Standard test methods (freshwater or seawater)

- Is non-toxic to the aquatic environment (LC/EC/IC$_{50}$ > 100 mg/L *measured or calculated* using CLP rules)
  - Standard does *not* consider mammalian toxicity or toxicity to plants

- Meets the relevant performance specification

Criteria are for the finished lubricant as handled by end user.
EN16807 vs other EU environmental standards

- Renewable content is measured
  - $^{14}$C measurement by ASTM D6866-12 or equivalent
  - Only renewable carbon is measured
  - Renewable oxygen and nitrogen under evaluation by TC 411

- Renewable content requirement is lower than other standards (e.g. EU Ecolabel)

- No criterion for bioaccumulation potential of finished lubricant

- Covers a broader range of lubricant types than other standards (e.g. EU Ecolabel)
  - Industrial
  - Metalworking
  - Automotive
  - Temporary corrosion protection

- Only two existing lubricant specifications mention aquatic toxicity and biodegradability
  - ISO 15380 (Hydraulic oils)
  - ISO 8086 (Steam and gas turbine oils)
EN16807 - next steps for WG 33

- Validate biodegradation method for finished lubricant
  - Inter-laboratory study (ILS) has been approved and funded
  - Uses slightly modified, existing OECD methods
- Consider what might be in scope for a revision of the standard
  - Can EN16807 incorporate bioaccumulation of finished lubricant as a criterion
    - How to measure this property for complex mixtures?
    - Validate method using ILS
  - Effect of finished lubricant on terrestrial organisms (plants, soil dwellers etc)
    - Incorporate some form of life-cycle analysis
- Participate in discussion concerning revision of EU Ecolabel lubricants criteria
EU Ecolabel
The European Ecolabel scheme is a voluntary scheme to try to encourage business to provide more environmentally friendly products.

The scheme awards the flower logo to products that adhere to their criteria.

32 different and diverse product groups (3 more are being developed).

Goal is to reduce environmental effects in the product life-cycle.

Lubricants product group established 2005

- main criteria are low aquatic toxicity, high biodegradability and renewable content.

345 products have been awarded the flower logo in lubricants category.

<table>
<thead>
<tr>
<th>Category</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hydraulic fluid and tractor transmission oils</td>
</tr>
<tr>
<td>2</td>
<td>Greases and stern tube greases</td>
</tr>
<tr>
<td>3</td>
<td>Total loss lubricants (e.g. chainsaw, wire rope, stern tube oils, concrete release agents etc)</td>
</tr>
<tr>
<td>4</td>
<td>Two stroke oils</td>
</tr>
<tr>
<td>5</td>
<td>Industrial and marine gear oils</td>
</tr>
</tbody>
</table>

Source: [http://ec.europa.eu/environment/ecolabel](http://ec.europa.eu/environment/ecolabel) (last update March 2016)
EU Ecolabel - lubricants

- Lubricants product group currently concerns ‘loss’ lubricants
- Last updated 2011
  - Expanded to include tractor transmission oils, stern tube lubes and marine gear oils
  - Lubricant Substance Classification List (LuSC List) added
    - Non-exclusive list of ‘pre-approved’ substances and mixtures intended to help formulators
    - Components can be used to formulate lubricants up to the maximum treat rate shown alongside entry


- Experimental data needed to accompany application is subject to scientific review
- Application fee payable to Competent Authority where product first placed on market
- Annual maintenance fee depending on EU-wide sales
- Review of EU Ecolabel criteria for lubricants will begin October 2016

All lubricants bearing an EU Ecolabel are also ‘Bio-lubricants' by definition and qualify as “Environmentally Acceptable Lubricants” for US EPA VGP
### EU Ecolabel criteria – lubricants

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Test Method(s)</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Criterion 1 – Excluded or limited substances and mixtures</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No environmental or health risk phrases</td>
<td></td>
<td>No H phrases</td>
</tr>
<tr>
<td>No Substances Very High Concern &gt; 0.010% w/w</td>
<td></td>
<td>Meets</td>
</tr>
<tr>
<td><strong>Criterion 2 – Exclusion of specific substances (&gt; 0.010% w/w)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>No EU water priority substances (2000/60/EC)</td>
<td></td>
<td>Meets</td>
</tr>
<tr>
<td>No substances on the OSPAR list for priority action</td>
<td></td>
<td>Meets</td>
</tr>
<tr>
<td>No organic halogens, nitrite compounds, metals or metallic compounds except Na, K, Ca or Mg (Li or Al)</td>
<td></td>
<td>Meets</td>
</tr>
<tr>
<td><strong>Criterion 3 – Additional aquatic toxicity requirements</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquatic toxicity</td>
<td>OECD 201, 202 (203)</td>
<td>&gt; 100 mg/L or  &gt; 1000 mg/L</td>
</tr>
<tr>
<td><strong>Criterion 4 – Biodegradability and bioaccumulation potential (Each substance &gt; 0.10% w/w)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biodegradability (ultimate)</td>
<td>OECD 301 (302)</td>
<td>&gt; 60 % (&gt; 70%) in 28 days</td>
</tr>
<tr>
<td>Bioaccumulation (if required)</td>
<td>e.g. OECD 117</td>
<td>3 &gt; log K_{ow} &gt; 7</td>
</tr>
<tr>
<td><strong>Criterion 5 – Renewable raw materials</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Renewable carbon content</td>
<td></td>
<td>45 % minimum</td>
</tr>
<tr>
<td><strong>Criterion 6 – Minimum technical performance</strong></td>
<td></td>
<td>Meets</td>
</tr>
<tr>
<td>Technical criteria</td>
<td>Varies with category</td>
<td>Meets</td>
</tr>
</tbody>
</table>
Criterion 1 – Excluded or limited substances and mixtures

1a = hazardous substances and mixtures
• Long list of hazard class/category combinations that are restricted / prohibited in Ecolabel products
• No Carcinogen, Mutagen or Toxic to Reproduction (CMR) Category 1A or 1B present at > 0.010% w/w
• Derogation exists if finished lubricant does not have to be classified as hazardous (i.e. no H phrases)

1b = Substances listed in accordance with Article 59(1) of Regulation (EC) No 1907/2006 (REACH)
• No derogation for Substances of Very High Concern (SVHC) on ‘Candidate List’ if present at > 0.010% w/w regardless of product classification
 Criterion 2 - Exclusion of specific substances

Usage of certain substances is prohibited at > 0.010% w/w

- Substances contained in Union list of priority substances in the field of water policy (Annex X to Directive 2000/60/EC as amended)
- Substances contained in OSPAR List of Chemicals for Priority Action
- Organic halogen compounds
- Nitrite compounds
- Metals or metallic compounds
  - An exception exists for Na, K, Ca or Mg compounds or in the case of grease thickeners, Li or Al
Criterion 3 – Additional aquatic toxicity requirements

**Criterion 3.1 (finished lubricant and its main components)**

- Testing according to OECD 201 (algae), OECD 202 (daphnia) and OECD 203 (fish) required for finished lubricant
- Testing according to OECD 201 (algae) and OECD 202 (daphnia) required for each component present at > 5% w/w
- Marine or freshwater data accepted
- Water-accommodated fraction can be used to prepare dosing solution for complex mixtures / poorly soluble substances

<table>
<thead>
<tr>
<th></th>
<th>Category 1</th>
<th>Category 2</th>
<th>Category 3</th>
<th>Category 4</th>
<th>Category 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshly prepared lubricant; algae, daphnia and fish</td>
<td>&gt; 100 mg/L</td>
<td>&gt; 1000 mg/L</td>
<td>&gt; 1000 mg/L</td>
<td>&gt; 1000 mg/L</td>
<td>&gt; 100 mg/L</td>
</tr>
<tr>
<td>Main component; algae and daphnia only</td>
<td>&gt; 100 mg/L</td>
<td>&gt; 100 mg/L</td>
<td>&gt; 100 mg/L</td>
<td>&gt; 100 mg/L</td>
<td>&gt; 100 mg/L</td>
</tr>
</tbody>
</table>
Criterion 3.2 (each stated substance present at > 0.10% w/w)

- Chronic test data is preferred
  - Fish (e.g. OECD 210) and Daphnia (e.g. OECD 211)
- If chronic data is not available, acute aquatic toxicity data is acceptable
  - Algae (OECD 201) and Daphnia (OECD 202)
- Marine or freshwater data accepted
- Water-accommodated fraction can be used to prepare dosing solution for complex mixtures / poorly soluble substances
- Lubricant can contain up to a permitted amount of substances based on their toxicity (cumulative mass concentration % w/w)
  - Varies across product types
  - No product type can contain > 0.10% w/w of substances classified as very toxic to aquatic organisms (i.e. H400 or H410)
  - This lower limit is subject to multiplication factor where assigned
## Criterion 3.2 – Permitted amounts

<table>
<thead>
<tr>
<th>EEL class</th>
<th>Cumulative mass percentages (% w/w) of substances present in</th>
<th>Category 1</th>
<th>Category 2</th>
<th>Category 3</th>
<th>Category 4</th>
<th>Category 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not toxic</td>
<td>Acute toxicity &gt; 100 mg/L or NOEC &gt; 1 mg/L</td>
<td>D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Harmful Acute toxicity ≤ 100 mg/L or 1 mg/L &lt; NOEC ≤ 10 mg/L</td>
<td>E</td>
<td>≤ 20</td>
<td>≤ 25</td>
<td>≤ 5</td>
<td>≤ 25</td>
</tr>
<tr>
<td></td>
<td>Toxic Acute toxicity ≤ 10 mg/L or 0.1 mg/L &lt; NOEC ≤ 1 mg/L</td>
<td>F</td>
<td>≤ 5</td>
<td>≤ 1</td>
<td>≤ 0.5</td>
<td>≤ 1</td>
</tr>
<tr>
<td></td>
<td>Very toxic Acute toxicity ≤ 1 mg/L or NOEC ≤ 0.1 mg/L</td>
<td>G</td>
<td>≤ 0.1*</td>
<td>≤ 0.1*</td>
<td>≤ 0.1*</td>
<td>≤ 0.1*</td>
</tr>
</tbody>
</table>

* = permitted amount reduced where multiplication factor = 10, 100 etc

NOEC = No Effect Concentration
Criterion 3 – Additional aquatic toxicity requirements

Derogations from toxicity testing exist (Criteria 3.1 and 3.2):

- Substance is contained on Lubricant Substance Classification List (LuSC list) with an Ecolabel Environmental Label (EEL) hazard class
- A valid letter of compliance from a competent body can be submitted
- Substance is unlikely to cross a biological membrane
  - MM > 800 g/mol or
  - Molecular diameter > 1.5 nm (> 15 Å)
- Substance is a polymer with < 1% of molecular weight fraction below 1000 g/mol
  - Test method A19
- Substance is highly insoluble in water (< 10 μg/L)
  - OECD 105 or equivalent
Criterion 4 – Biodegradability and bioaccumulation potential

• Data is required for each substance intentionally added or intentionally formed at > 0.10% w/w

• Limit on substances that are inherently biodegradable (EEL classification = B) or non-degradable AND non-bioaccumulative (EEL classification = C)
  – Varies according to product category

• Finished lubricant cannot contain > 0.10% w/w non-degradable AND bioaccumulative substances
  – Same limit across all categories
  – EEL classification = X
## Criterion 4 – Permitted amounts

<table>
<thead>
<tr>
<th>EEL class</th>
<th>Category 1</th>
<th>Category 2</th>
<th>Category 3</th>
<th>Category 4</th>
<th>Category 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimately aerobically biodegradable</td>
<td>A</td>
<td>&gt; 90</td>
<td>&gt; 75</td>
<td>&gt; 90</td>
<td>&gt; 75</td>
</tr>
<tr>
<td>Inherently aerobically biodegradable</td>
<td>B</td>
<td>≤ 5</td>
<td>≤ 25</td>
<td>≤ 5</td>
<td>≤ 20</td>
</tr>
<tr>
<td>Non-biodegradable AND not bioaccumulative</td>
<td>C</td>
<td>≤ 5</td>
<td></td>
<td>≤ 5</td>
<td>≤ 10</td>
</tr>
<tr>
<td>Non-biodegradable AND bioaccumulative</td>
<td>X</td>
<td>≤ 0.1</td>
<td>≤ 0.1</td>
<td>≤ 0.1</td>
<td>≤ 0.1</td>
</tr>
</tbody>
</table>
Criterion 5 – Renewable material content

- Based on carbon content
  - Animal or plant
- No requirement to *measure* carbon content
- Differs depending on product category

<table>
<thead>
<tr>
<th></th>
<th>Category 1</th>
<th>Category 2</th>
<th>Category 3</th>
<th>Category 4</th>
<th>Category 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon content from renewable source</td>
<td>≥ 50% w/w</td>
<td>≥ 45% w/w</td>
<td>≥ 70% w/w</td>
<td>≥ 50% w/w</td>
<td>≥ 50% w/w</td>
</tr>
</tbody>
</table>
Criterion 6 – Minimum technical performance

• Technical performance standards exist for some product categories (fluid types)
  – Hydraulics = ISO 15380 Tables 2-5 (including which elastomers have been tested)
  – Industrial and marine gear oils = DIN 51517
  – Chainsaw oils = RAL UZ-48
  – Two-stroke oils for marine applications = NMMA TC-W3: Certification for Two-Stroke Gasoline Engine Lubricants
  – Two-stroke oils for terrestrial applications = ISO 13738:2000
• Lubricants in other product types must be ‘fit for purpose’
Criterion 7 – Information appearing on the label

- Optional
- Label with text box containing specific text:

  Reduced harm for water and soil during use
  Contain a large fraction of biobased material
EU Ecolabel formulating restrictions - additive

- The additive package has to satisfy the strict guidelines provided by EU Ecolabel.
- Finished lubricant cannot contain $> 0.010\%$ w/w of:
  - Carcinogens, Mutagens or Substances Toxic to Reproduction Category 1A or 1B
  - Substances on the ‘Candidate List’ (REACH Article 59) (SVHCs)
  - Substances present in OSPAR priority list or EU water policy list
  - Nitrites
  - Organic-halogen containing components
  - Metals or metal-containing components
    - Except Na, K, Ca, Mg (or Li, Al)

Formulating the additive with the right balance of components that give desired performance and comply with the EU Ecolabel criteria can be challenging.
Other EU environmental ‘standards’ exist for lubricants

- German Blau Angel (Blue Angel)
  - Biodegradable lubricants and hydraulic fluids (RAL-UZ 178)
- Swedish Standard
  - Hydraulic fluids (SS 15 54 34)
  - Greases (SS 15 54 70)
- Dutch VAMIL
- Nordic White Swan?
US EPA Vessel General Permit
US EPA Vessel General Permit (VGP)

• In 1990s, there was no agreed definition of Environmentally Acceptable Lubricants (EAL)

• In 1999, the US Army Corps of Engineers used the term “environmentally acceptable”

• In 2008 US EPA VGP encouraged ship owners to use EALs for all oil-to-sea interfaces
  – Applicable to all ships entering the waters around USA

• Mandatory requirement from December 2013
  – Also recommended for use in all above deck equipment
  – Derogation where use of EAL is ‘technically infeasible’

EALs should be biodegradable, minimally toxic and not bioaccumulative
For a lubricant to qualify as an EALs for VGP it must meet each of the following criteria:

- Lubricant must be biodegradable or contain $\geq 75\%$ w/w biodegradable components (greases) or $\geq 90\%$ w/w (other lubricant types)
  - The remaining components that do not meet the biodegradable requirement cannot be (potentially) bioaccumulative
- Lubricant should be not bioaccumulative
- Lubricant should be minimally toxic to algae, daphnia and fish or contain a limited amount of environmentally hazardous components
- Preferably contain no hazardous substances detailed in 40 CFR 401.15
Alternatively, a lubricant qualifies as an EAL if it is approved under other environmental labelling schemes:

- Blue Angel
- EU Ecolabel
- Nordic Swan (?)
- Swedish Standard (SS 15 54 34 or SS 15 54 70)
- OSPAR (component based or ‘approved for Norway?)
- EPA Design for Environment (DfE)

Compliance with VGP is self-certifying BUT vessel operators could be audited by US EPA so supporting documentation and data needs to be available.
VGP requirements: biodegradability based on components

- **Component is biodegradable if**
  - $\geq 60\%$ (O$_2$ consumption / CO$_2$ production methods)
  - $\geq 70\%$ (Dissolved organic carbon method)

- **Component is inherently biodegradable if**
  - $\geq 20\%$ but $< 60\%$ (any OECD 301-type method) or
  - $> 70\%$ OECD 302C

- **Component is non-biodegradable if**
  - $< 20\%$ (any OECD 301-type method) or
  - $< 70\%$ OECD 302C

<table>
<thead>
<tr>
<th></th>
<th>Lubricants</th>
<th>Greases</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Biodegradable</strong></td>
<td>$&gt; 90%$ w/w</td>
<td>$&gt; 75%$ w/w</td>
</tr>
<tr>
<td><strong>Inherently biodegradable AND not bioaccumulative</strong></td>
<td>$\leq 5%$ w/w</td>
<td>$\leq 25%$ w/w</td>
</tr>
<tr>
<td><strong>Non-biodegradable AND not bioaccumulative</strong></td>
<td>$&lt; 5%$ w/w</td>
<td></td>
</tr>
<tr>
<td><strong>Non-biodegradable AND bioaccumulative</strong></td>
<td>Not mentioned ($\leq 0.10%$ w/w)</td>
<td>Not mentioned ($\leq 0.10%$ w/w)</td>
</tr>
</tbody>
</table>

Only stated substances present at $> 0.10$ wt% need to be assessed

OECD = Organization for Economic Co-operation and Development
VGP requirements: aquatic toxicity based on lubricant and main component(s)

• Lubricant and *main constituent(s)* must pass acute toxicity or chronic toxicity tests
  • Acute toxicity = OECD 201 (algae), OECD 202 (daphnia) and OECD 203 (fish)
  • Chronic toxicity = OECD 210 (fish) and OECD 211 (daphnia)
• Measured \( \text{LC}_{50}/\text{EC}_{50} > 1000 \text{ mg/L} \) for greases, two-stroke oils and other total loss lubricants
• Measured \( \text{LC}_{50}/\text{EC}_{50} > 100 \text{ mg/L} \) for all other lubricants
Aquatic toxicity of lubricant can also be calculated based on the aquatic toxicity of individual components *(as long as algae, daphnia and fish toxicity data exists for all components?)*

<table>
<thead>
<tr>
<th>Acute toxicity</th>
<th>Cumulative mass percentages of substances present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acute toxicity &gt; 100 mg/L or NOEC &gt; 1 mg/L</td>
<td>Not limited</td>
</tr>
<tr>
<td>Acute toxicity ≤ 100 mg/L or 1 mg/L &lt; NOEC ≤ 10 mg/L</td>
<td>&lt; 20% w/w</td>
</tr>
<tr>
<td>Acute toxicity ≤ 10 mg/L or 0.1 mg/L &lt; NOEC ≤ 1 mg/L</td>
<td>&lt; 5% w/w</td>
</tr>
<tr>
<td>Acute toxicity ≤ 1 mg/L or NOEC ≤ 0.1 mg/L</td>
<td>≤ 1% w/w</td>
</tr>
</tbody>
</table>

NOEC = No Effect Concentration

© 2016 The Lubrizol Corporation, all rights reserved.
VGP requirements: bioaccumulation

- Bioaccumulation data is required for lubricant or all stated substances.
- **Not bioaccumulative** is defined as:
  - Polymer with molecular weight fraction below 1000 of <1%
  - Constituent with molecular size (MM) > 800 g/mole or molecular diameter > 1.5 nm
  - Measured bio-concentration factor (BCF) or bio-accumulation factor (BAF) < 100 L/kg
    - Measured by OECD 305-type method (fish)
    - ‘Field-measured’ BAF is also acceptable
  - Octanol : water partition coefficient (Log $K_{ow}$) <3 or >7
    - Measured by OECD method 107 or 117
    - Lubricant or constituent
VGP – an important market driver for (Bio)lubricants

• There is a growing demand for Environmentally Acceptable Lubricants to meet VGP requirements
• The additive technologies to enable development of lubricants and greases suitable for VGP are now readily available
• EAL suitable for VGP would not necessarily qualify as a Bio-lubricant / Bio-based lubricant in EU (based on EN16807 criteria)
Formulating Challenges
Start with the end in mind….

• Differences exist between the various environmental standards concerning “Bio-lubricants” or “environmental-beneficial fluids”

• What claims / OEM requirements are you trying to meet (or exceed) for your product?
  – Bio-lubricant / Bio-based lubricant (EN16807) and/or
  – EU Ecolabel lubricant and/or
  – Compliant with US EPA VGP and/or
  – Other EU environmental standards (e.g. Blue Angel RAL-UZ 178 or Swedish Standard SS 15 15 54 34 or offshore approval for hydraulic fluids)

• **Understand** the differences between the different standards
  – Easier to formulate against known criteria
  – It is often difficult to change a formulation (especially additive package) as we approach the end of the development phase
Finding the right balance: formulating challenge

Challenge is to balance all these factors
Formulating a Bio-lubricant

Individual components

Additive package

Bio-based base stock

Finished lubricant
Key formulating challenges - choice of base stock

- Bio-based lubricant base stocks are highly effective lubricants with excellent tribology properties BUT often have poor
  - Oxidative stability
  - Thermal stability
- Ester-based bio-lubricant base stocks can also be hydrolytically unstable
- Plant-derived base stocks often have high viscosity index (‘multi-grade’ lubricants)
- Non-additised Bio-lubricants / Bio-based lubricants are typically confined to total loss applications with low thermal stress
**Base stock selection**

- Selecting the right base stock is critical
- Responsible for meeting the biodegradation, renewability and toxicity criteria
- Saturated synthetic base stocks typically give better oxidation and thermal stability

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ester 1</th>
<th>Ester 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 40 °C, mm²/s</td>
<td>42.8</td>
<td>46</td>
</tr>
<tr>
<td>Viscosity at 100 °C, mm²/s</td>
<td>7.5</td>
<td>8.3</td>
</tr>
<tr>
<td>Viscosity Index</td>
<td>150</td>
<td>143</td>
</tr>
<tr>
<td>Biodegradability &gt; 60 % (OECD 301B)</td>
<td>67</td>
<td>85</td>
</tr>
<tr>
<td>Renewability content, &gt; 50 %</td>
<td>84</td>
<td>85</td>
</tr>
<tr>
<td>Algae &gt; 100 mg/L (OECD 201)</td>
<td>&gt; 1000</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Daphnia &gt; 100 mg/L (OECD 202)</td>
<td>&gt; 1000</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>Relative cost</td>
<td>£</td>
<td>££+</td>
</tr>
</tbody>
</table>
Sustainable base oils from renewable material

- **Plant derived base stocks**
  - Rapeseed oil
  - Sunflower oil
  - Soyabean oil

- **Plant derived components of synthetic and polymeric ester base stocks**
  - Tall oil fatty acid
  - Coconut oil
  - Azelaic acid
  - Sebacic acid

- **Sugar-derived base stocks**
  - There are an increasing number of novel base stocks on the market (e.g. estolides)
  - High renewable carbon content
  - From a sustainable source
Choosing the right base stock

- EU Ecolabel requires base stock to be either
  - On the LuSC list OR
  - > 60% biodegradable (OECD 301) and non-toxic to aquatic organisms and contain high level renewable content
    - Certified as bio-derived (with plant origin)

- VGP requires base stock to be either > 60% biodegradable (OECD 301) or > 70% biodegradable (OECD 302) and non-toxic to aquatic organisms
  - No requirement for minimum renewable material content
  - Suggestions are natural oils, synthetic esters and glycols

- Bio-lubricant / Bio-based lubricant requires base stock to be > 60% biodegradable (OECD 301) and non-toxic to aquatic organisms and at least partially renewable (>25%)
Biodegradability testing (OECD 301B)

- Lubricants are mixed with microorganisms in presence of oxygen
- Microorganisms decompose lubricants and release CO$_2$
- Measuring the evolved CO$_2$ over 28 days gives the % biodegradation

Some experts believe ‘rapid’ degradation of spilled lubricant can be potentially harmful for aquatic environment
Additive selection for Bio-lubricants / Bio-based lubricants

- Compatibility
  - With base stock and with other components
- Solubility in base stock
- Functionality
  - Do the blend of components provide the required performance
- Stability
  - Components that are labile/unstable in chosen base stock are no use
- Aquatic toxicity (if treat rate is > 2-3%)
- Non-bioaccumulative
- Other hazards (e.g. human health)?

Renewable content of additives is usually less important due to typically low treat rate
Challenging additive properties for formulators

**Not bioaccumulating**

- Persistence is a desirable property for additives that have to deliver performance under challenging conditions for a long time
- Lubricant components have to be more lipophilic than hydrophilic for many base stocks
- Lipophilic substances tend to partition to fat
- Substances that partition to fat often tend to bioaccumulate in organisms
- Limit on bioaccumulative, non-degradable substances in some Bio-lubricants (e.g. candidates for EU Ecolabel and US EPA VGP)
- Not currently a problem for fluids claiming to be a Bio-lubricant / Bio-based lubricant
A practical example: use of sulfurized olefin in a grease

- Sulfurized olefins are used to boost load carrying capacity and extreme pressure properties.
- Sulfurized olefins are usually non-biodegradable/poorly biodegradable and have potential to be bioaccumulative (oil soluble).
- Sulfurized olefins are typically UVCB substances so difficult to measure bioaccumulation potential by traditional methods.

The problem?
Hard to demonstrate that sulfurized olefin met Criterion 4 for EU Ecolabel (non-degradable and potentially bioaccumulative).

What should the formulator do?
Challenging additive properties for formulators

Performance vs toxicity profile
• The same functional groups that give a substance its desired performance characteristics are often toxicologically-active
• Need to balance performance vs toxicity (hazard) profile
  – Amount of hazardous substance that can be included depends on its hazard profile to avoid product labelling
  – Mammalian hazards preferable compared with environmental hazards for Bio-lubricants
• Currently in a period of rapid change in hazard profile for some substances
• Common misunderstanding that additive components contained in LuSC list are non-hazardous.

No zinc compounds (for EU Ecolabel)
• Traditionally ZDDPs have been very useful dual-function components (antiwear / anti-oxidant)
• 85% of all hydraulic fluids are zinc-based
• Zinc compounds prohibited above 0.10% (w/w)
A continually changing regulatory environment….

- **Key EU chemical control legislation #1**
  - Registration, Evaluation, Authorisation and restriction of CHemicals (REACH; Regulation 1907/2006)
- All substances currently produced in EU or imported into EU ≥ 1 MT **must** be registered by **end May 2018**
- REACH registration requires an amount of toxicology testing
  - Tiered testing requirement based on volume and hazard
- **Testing can throw up unexpected results**
- Most novel substances are also required to have a registration in place before production or import at ≥ 1 MT
  - EU and rest of world
- **Cost / benefit analysis of bringing new chemistry to market**
- Entry level cost for ≥ 10 MT **for EU** is **lower** than it used to be pre-REACH!

Estimated cost for **global approval** of a new substance at ≥ 10 MT is circa. €1M
A continually changing regulatory environment….

- Key EU chemical control legislation #2
  - Classification, Labelling and Packaging (CLP; Regulation 1272/2008)
- CLP provides rules for classifying mixtures (e.g. Bio-lubricants)
- CLP is updated every 2 years mirroring updates in UN Globally Harmonised System of Classification and Labelling (GHS)
  - New hazard classes introduced
  - Hazard criteria can change e.g. Skin sensitisers split into Category 1A and 1B with lower classification threshold for 1A (0.1% w/w)
  - Threshold for Substances of Very High Concern content much lower in EU Ecolabel criteria than cut-offs for mixture classification
What’s in your drum of bio-hydraulic fluid?

- Base stock: 98.5 - >99.0%*
- Performance Package: <1-1.5%*

Performance Package:
- Antiwear
- Antioxidant
- Rust inhibitor
- Demulsifier
- Antifoam
- Corrosion inhibitor / metal passivator

*Approximate ranges
Categorisation of hydraulic fluids (ISO 15380)

‘Environmentally acceptable’ hydraulic fluids (HE) - classified based on the major base stock component

<table>
<thead>
<tr>
<th>Fluid classification</th>
<th>Full name</th>
<th>Raw material</th>
</tr>
</thead>
<tbody>
<tr>
<td>HETG</td>
<td>Hydraulic Oil Environmental Tri-Glyceride</td>
<td>Vegetable oil</td>
</tr>
<tr>
<td>HEPG</td>
<td>Hydraulic Oil Environmental PolyGlycol</td>
<td>Polyalkylene glycol (PAG)</td>
</tr>
<tr>
<td>HEES</td>
<td>Hydraulic Oil Environmental Ester Synthetic</td>
<td>Saturated synthetic ester</td>
</tr>
<tr>
<td>HEPR</td>
<td>Hydraulic Oil Environmental Polyalphaolefin and Related Products</td>
<td>Poly-alphaolefin (PAO)</td>
</tr>
</tbody>
</table>

Not all these HE fluid types will necessarily qualify as a Bio-lubricant
### Table 1

- Biodegradability ≥ 60% (OECD 301-type test)
- Acute fish toxicity ≥ 100 mg/L (OECD 203)
- Acute daphnia toxicity ≥ 100 mg/L (OECD 202)
- Bacterial inhibition ≥ 100 mg/L (OECD 209)
- No renewable content requirement
- No algal toxicity requirement

Performance testing for a new biohydraulic fluid to meet ISO 15380 and OEM specifications are estimated at £1.5M

ISO 15380 Tables 2-5 concern performance-based criteria
What’s in your drum of bio-grease?

• Base Oils
  95-99.5%*

• Performance Package
  0.5-5%*

Performance Package

• Antiwear
• Antioxidant
• Rust Inhibitor
• Thickener

*Approximate ranges
Thickeners for bio-greases

- Main thickeners for lubricating grease are metallic soaps
  - Globally >90% (>92% Europe) thickeners are soap
  - These are mostly derived from castor oil
    - Hydrogenated castor oil
    - 12-Hydroxystearic acid
  - High renewable content
- Complexing acids can also be from renewable sources
  - Castor oil derivatives
    - Azelaic acid
    - Sebacic acid
  - Other naturally derived acids
    - Coconut oil used in calcium complex thickeners
Thickeners for bio-greases

- Lithium stearate and lithium 12-hydroxystearate pre-formed soaps are commercially available
  - Have to be heated to ~200 °C to melt the soap
  - Pre-formed complex soaps are not readily available

- Lithium 12-hydroxystearate is on the LuSC list and is suitable in greases seeking EU Ecolabel and/or US EPA VGP approval

- Lithium complex greases need sebacic acid as the complexing acid
  - Dilithium azelate is indicated to be toxic for the aquatic environment (EEL class = F) on LuSC List and therefore can only be used with caution (limited amount permitted in grease)
  - Sebacic acid also helps with corrosion protection
Drivers for Bio-lubricants, Bio-based lubricants and Environmentally Acceptable Lubricants
Drivers for environmentally friendly fluids

- **New** regulations that mandate the use of “Environmentally Acceptable Lubricants”
  - E.g. US EPA Vessel General Permit (VGP)

- **Existing** standards that define Environmentally Acceptable Lubricant criteria for some fluid types
  - E.g. EU Ecolabel, German Blue Angel and Swedish Standard

- **Green public product procurement**
  - E.g. United States Department of Agriculture (USDA) BioPreferred® program
  - Europe?

Environmental regulations and standards are key driving factors behind the demand for biodegradable fluids.
Final thoughts…..

• Formulating a Bio-lubricant to meet today’s performance and environmental standards is not as easy as it sounds……..
• UK industry can now be more certain about which fluids can be described as a Bio-lubricant for the EU market and which cannot
• A lubricant can be “environmentally-acceptable” but may not necessarily qualify as a Bio-lubricant (EN16807)
• A Bio-lubricant may not necessarily qualify for the EU ecolabel or other environmental awards (e.g. German Blue Angel)
• More incentives are needed to drive demand from the market for Bio-lubricants / “Environmentally Acceptable Lubricants” to offset higher cost
  – Regulatory incentives
  – Tax incentives
  – Incentives concerning disposal of waste lubricant and hardware contaminated with used lubricant
  – Green Product Procurement
Questions?

Thanks to my Lubrizol colleagues Shubhamita Basu and Gareth Fish for their help in preparing this presentation.
Working together, achieving great things

When your company and ours combine energies, great things can happen. You bring ideas, challenges and opportunities. We’ll bring powerful additive and market expertise, unmatched testing capabilities, integrated global supply and an independent approach to help you differentiate and succeed.