Additive Components
What happens without lubrication?
Outline

• The function of additives
  – What do they do?

• Destructive processes in the engine
  – What are these processes?
  – How do additives minimize them?

• Types of additives
  – Which additives are commonly used?
  – How do they work?
The function of additives

Why do we add additives?

– Enhance lubricant performance
– Minimise destructive processes in the engine
– Extend oil life time
Destructive processes in the engine

What destructive process are present in the engine?

• Mechanical
  – Wear of engine parts
  – Shear affecting lubricant properties

• Chemical
  – Corrosion of engine parts
  – Oxidation of lubricant
Destructive processes in the engine

Friction and wear

- Both are caused by relative motion between surfaces
- **Friction** is the loss of energy – dissipated as heat
  - Types – sliding, rolling, static
- **Wear** is loss of material
  - Types – abrasion, adhesion, corrosion, fatigue
  - Changes geometry of contacts
  - Changes equipment performance
  - Introduces metal oxidation catalysts
Destructive processes in the engine

Rust and corrosion

- **Rust** refers to ferrous (iron) metals
  - Oxidative process
  - Catalysed by water and acids

  \[ 2\text{Fe} + 1.5\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 \]

- **Corrosion** refers to non-ferrous metals
  - Chemical attack, examples include

  \[ \text{Cu} + \text{S} \rightarrow \text{CuS} \]
  \[ \text{Pb} + \text{acid} \rightarrow \text{Pb-salt} \]
Destructive processes in the engine

Fuel combustion

- **Ideal situation** – Complete combustion of fuel with oxygen
  
  \[
  \text{Fuel + Air} \rightarrow \text{Energy} + \text{CO}_2 + \text{H}_2\text{O}
  \]

- **What actually happens** – Incomplete combustion of fuel produces undesirable by-products
  
  \[
  \text{Fuel + Air} \rightarrow \text{Energy} + \text{CO}_2 + \text{H}_2\text{O} + \text{NO}_x + \text{SO}_x + \text{CO} + \text{HC} + \text{Particulate Matter (PM-Soot)} + \text{Radicals}
  \]

- **Result** – accelerate the oxidation and degradation of engine oil, viscosity increase, acid build-up, corrosive wear and deposits
Destructive processes in the engine

• Destruction of molecules by exposure to oxygen at elevated temperatures

• Initiated by **radicals**
  • Molecular fragments with an unpaired electron
  • Very unstable and reactive

• Radicals attack and ‘pull apart’ the base stock molecules
  • To pair their lone electron
  • Process can produce more radicals leading to a chain reaction

• The process can be **catalysed** by metals
Destructive processes in the engine

Oxidation – What effect does oxidation have on the lubricant?

- Oxidation is fluid degradation
- Measured as
  - Oxygen consumption
  - Viscosity change
  - Acid number build-up
  - Increase in C=O IR absorption
  - Increase in polar materials (pentane insolubles)
- Affected by
  - Base stock
  - Conditions (temperature, catalyst etc.)
  - Additive system
Balance of additives and base oil

Key is balancing the additives for the application
Balance of additives and base oil

Key is balancing the additives for the application

- Base Oil: 60-90%
- Viscosity Modifier & flow improver: 5-15%
- Additive Package: 5-25%
- Dispersant
- Detergent
- Antiwear
- Antioxidant
- Friction Modifier
- Others
Dispersants and detergents

1. **General surfactants properties** – individual molecules
   - Formed by molecules with both polar and non-polar sections
   - Aggregate with orientation based on polarity of medium
   - At a water/oil interface;
     - Polar ends in water, non-polar ends in oil
2. General surfactants properties – micelles

- In three dimensions these form a spherical environment = Colloid
  - Solid in the middle = sol
  - Liquid in the middle = emulsion
Dispersants and detergents

3. Basic dispersant and detergent structure
• Both are surfactants, consisting of 2 parts;

- Differences
  - Ashless vs. metal
  - Length of “tail”
  - Strength of “head”

Polar ‘head’ Non-Polar ‘tail’

Dispersant

Detergent
Dispersants and detergents

4. ‘Metal’ detergents

- Functions:
  - Neutralise acidic species (sulfur oxides and organic acids)
  - Reduce lacquer, carbon and varnish deposits on the engine’s pistons
  - Prevent ring sticking under severe high-temperature operating conditions

- Typical compositions – colloidal
  - Alkylated metal sulfonates, sulfurised phenates, salicylates
  - Neutral or overbased (Excess base)
5. Ashless dispersants

- Functions
  - Suspend soot (carbonaceous particles)
  - Inhibit and disperse sludge
  - Reduce formation of deposits
  - Keep things clean

- Typical composition
  - Metal free (ashless)
  - Polyisobutene succinimide (PIBSA PAM)

![Chemical structure of Ashless dispersants]

$$\text{Polyisobutylene} \quad \text{Succinic acid} \quad \text{Polyalkylene amine}$$

= PIBSA/PAM
Balance of additives and base oil

Key is balancing the additives for the application
Antiwear agents

1. General function and types
   • Function
     – Reduce metal-metal wear
   • Types
     – Zinc-based: zinc dialkyldithiophosphates (ZDDP)
       • Engine oils
     – Molybdenum-based: molybdenum dithiocarbamates (MoDTC)
     – Phosphorus-based: tri-cresyl phosphate
       • ATF, gear, aviation
     – Extreme pressure: highly reactive sulphur-phosphorus compounds
       • Gear oils
Antiwear agents

2. Mechanism of antiwear protection by ZDDP

Hydrodynamic contact
- Thick oil film
- No metal/metal contact
- Phosphate layers won’t form but would be maintained if formed previously

Boundary contact
- Oil film insufficient to separate surfaces
- Glassy poly-phosphate film forms as high temp/pressure increases contact
- Phosphate layer liquefies at high temperature contact point
- Phosphate layer is lost sacrificially to protect the metal surface
### Antiwear agents

#### 3. Aspects of ZDDP structure and performance

<table>
<thead>
<tr>
<th></th>
<th>Primary</th>
<th>Secondary</th>
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</thead>
<tbody>
<tr>
<td>Lower molecular</td>
<td>Better wear protection</td>
<td></td>
</tr>
<tr>
<td>weight</td>
<td></td>
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<tr>
<td>Higher molecular</td>
<td>Improved stability</td>
<td>Better wear protection</td>
</tr>
<tr>
<td>weight</td>
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</tr>
</tbody>
</table>

- Alcohol type and molecular weight have an effect on properties
- Typically used at 0.5 to 1.5 mass % in the oil – specifications limit amount
Balance of additives and base oil

Key is balancing the additives for the application
Antioxidants

1. General functions and classes
   • Functions
     – Reduce and control oxidation
     – Reduce the consequences of oxidation
   • Negative results of oxidation
     – Viscosity increase
     – Organic acids
       • Attack engine surfaces
       • Particularly copper-lead bearings
     – Insolubles
       • Form deposits
       • Sludge and varnish
     – Additive depletion
   • Types
     – Primary antioxidants
     – Secondary antioxidants
Antioxidants

2. Specific examples

- Primary antioxidants (chain stopping, radical traps)
  - Hindered Phenols
  - Alkylated DiPhenyl Amines (DPA)

- Secondary antioxidants (peroxide decomposers)
  - Zinc Dialkyl Dithiophosphates (ZDDP)
  - Molybdenum Dialkyldithiocarbamates (MoDTC)
  - Thioethers

\[ \text{ROOH} + \text{PD} \rightarrow \text{ROH} + \text{PD}[O] \]

Where:
ROOH = Peroxide
PD = Peroxide decomposer
ROH = Alcohol
PD[O] = Oxidised peroxide decomposer
Balance of additives and base oil

Key is balancing the additives for the application
Friction modifiers

1. General function

• Operate under boundary lubrication conditions
• Give a low coefficient of friction by providing a low shear surface
• Can be defined as “surface active chemicals that affect friction coefficient”
• Almost all additive components fit this broad definition!
• For our purposes friction modifiers can be defined as “chemicals that when added to a lubricating oil, at a concentration less than 1%, significantly affect the coefficient of friction”
What are friction modifiers

- Long chain hydrocarbons with polar end groups
  - Surfactants
- They work by adsorbing to metal surfaces
- Molecules designed to:
  - Adhere to metal surfaces
  - Rather than soot, for example
  - ‘Stand’ upright into bulk oil
- Friction coefficient is affected by:
  - Type, concentration, temperature, speed, load
2. Organic friction modifiers

- Molecular geometry is similar to detergents (surfactant)
- Act “intact” (not chemically transformed at the surface)
- Examples include oleic acid and glycerol monooleate (GMO)

![Glycerol monooleate](image.png)

- Friction modifier film
- Oxide layer
- Metal surface

Moving asperity
Friction modifiers animation
3. Solid friction modifiers

- Molecular geometry describes a “flat plate”
- Act after chemical transformation at the surface
- Examples include molybdenum disulphide (MoS$_2$) from molybdenum trimer (MoDTC)
Balance of additives and base oil

Key is balancing the additives for the application
‘Others’

• Antifoamant
  – High viscosity silicone fluid to prevent foaming
    • Beer – foaming; champagne – aeration

• Demulsifiers
  – Various surfactant chemistries to stop emulsions forming if water gets into the oil (condensation or coolant leaks)

• Emulsifiers
  – More typically used in metal-working applications to form an emulsion

• Rust inhibitors
  – Inhibition of ferrous metal corrosion either by surfactant coating the surface or improving acid neutralisation – especially in factory-fill oils

• Corrosion inhibitors
  – Inhibition of non-ferrous metal corrosion such as soft metals (lead, copper) such as film-forming agents as tolyl triazole

• Seal compatibility agents
  – Control polarity of the oil \( \rightarrow \) control extend of seal swelling or shrinking
Relative sizes of things

Log (Meters)

-10 -9 -8 -7 -6 -5 -4 -3

<table>
<thead>
<tr>
<th>Material</th>
<th>Size Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>-10</td>
</tr>
<tr>
<td>Soap</td>
<td>-9</td>
</tr>
<tr>
<td>Friction Modifier</td>
<td>-8</td>
</tr>
<tr>
<td>Colloid</td>
<td>-7</td>
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<tr>
<td>Virus</td>
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<tr>
<td>Dispersant</td>
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<td>Viscosity Modifier</td>
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<tr>
<td>Surface Roughness</td>
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</tr>
<tr>
<td>Soot Particle</td>
<td>-2</td>
</tr>
<tr>
<td>Oil Film Thickness</td>
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<tr>
<td>Bacteria</td>
<td>0</td>
</tr>
<tr>
<td>Human Hair</td>
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</tr>
</tbody>
</table>

Angstrom = Å
Nanometer = nm
Millimeter = mm
Micrometer = micron = μm

Performance you can rely on.
Formulation Science

Dispersant | Detergent | FM

Antioxidants | “The Oil” | LOFI
ATF | PCMO | HDD
TPEO | MDCL | VM
Gear Oil | 2Stroke | Base Stock

Corrosion Inhibitor
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