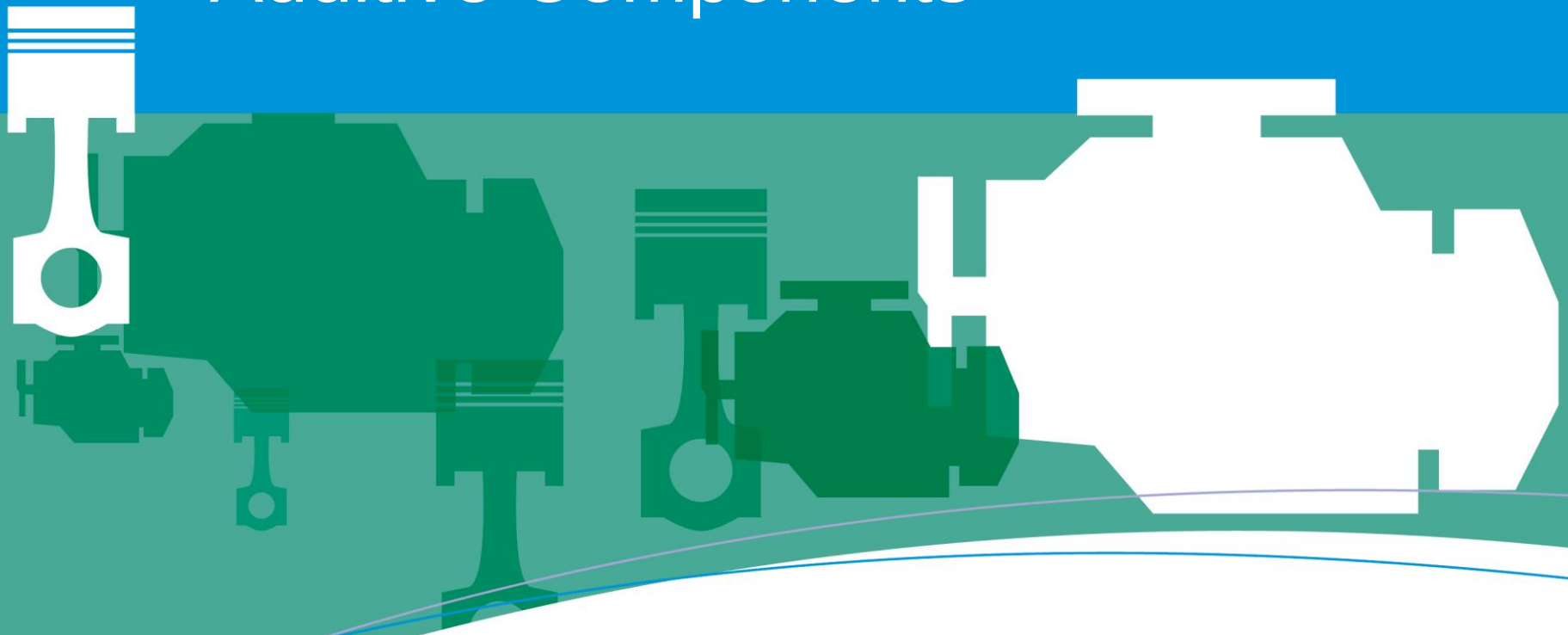
Performance you can rely on.

Additive Components



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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

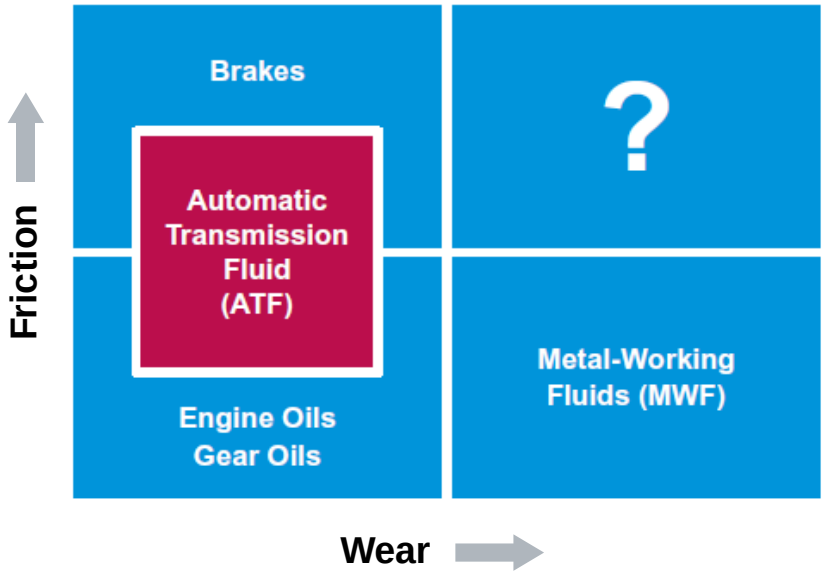
What destructive process are present in the engine?

- 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

$$2Fe + 1.5\,O_2 \rightarrow Fe_2O_3$$

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

$$Cu + S \rightarrow CuS$$

$$Pb + acid \rightarrow Pb\text{-}salt$$

Destructive processes in the engine

Fuel combustion

- **Ideal situation** – Complete combustion of fuel with oxygen

$$\text{Fuel} + \text{Air} \longrightarrow \text{Energy} + CO_2 + H_2O$$

- **What actually happens** – Incomplete combustion of fuel produces undesirable by-products

$$\text{Fuel} + \text{Air} \longrightarrow \text{Energy} + CO_2 + H_2O + NO_x + SO_x + CO + HC + \text{Particulate Matter (PM-Soot)} + \text{Radicals}$$

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

Destructive processes in the engine

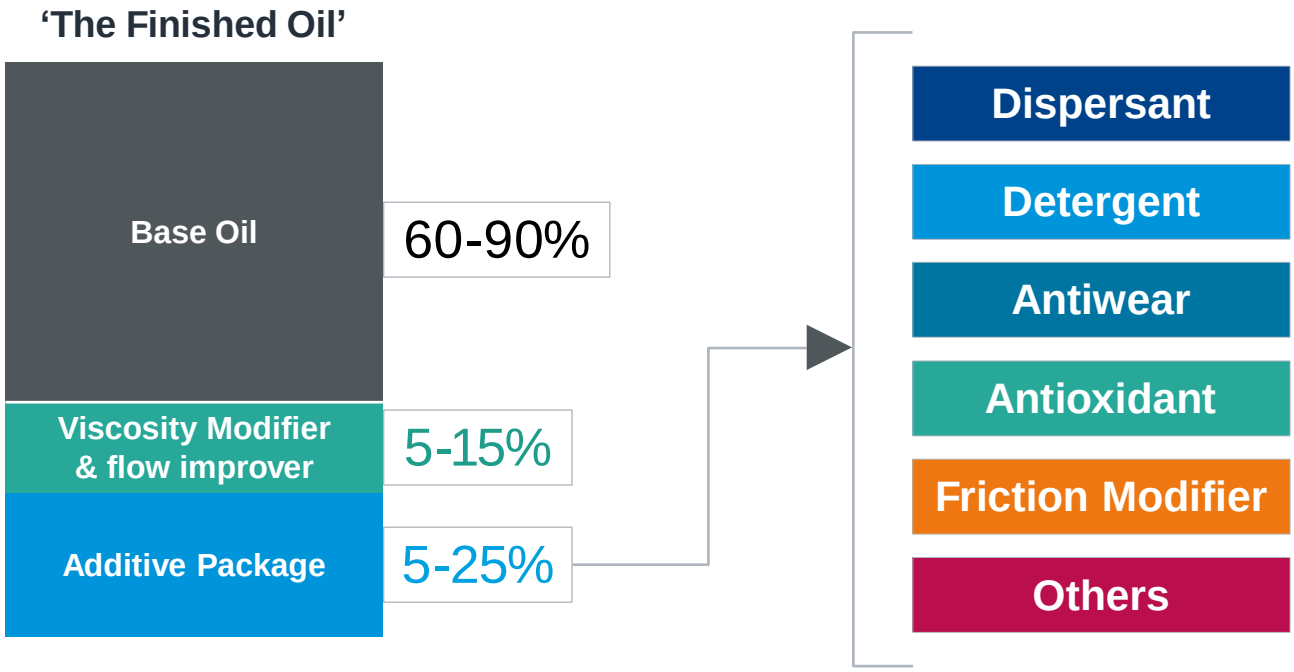
- Destruction of molecules by exposure to oxygen at elevated temperatures
- Initiated by **radicals**
  - Molecular fragments with an unpaired electron
  - Very unstable and reactive
- Radicals attack and ‘pull apart’ the base stock molecules
  - To pair their lone electron
  - Process can produce more 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?

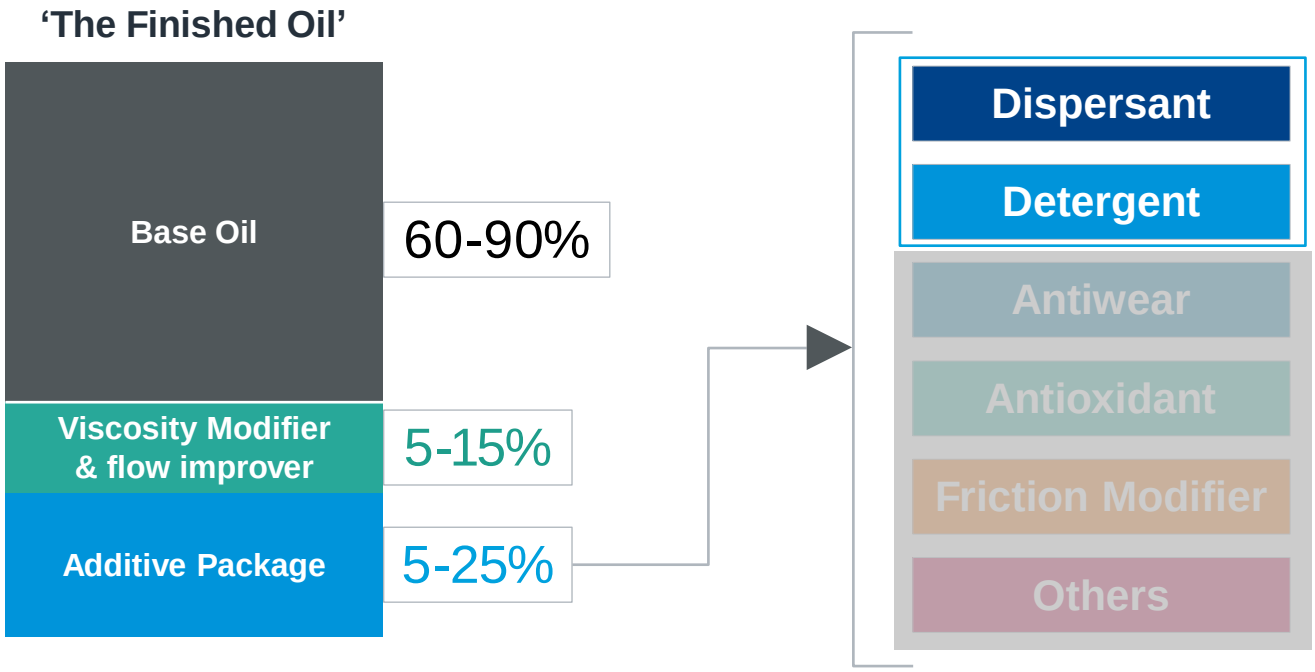
- Oxidation is fluid degradation
- Measured as
  - Oxygen consumption
  - Viscosity change
  - Acid number build-up
  - Increase in C=O IR absorption
  - Increase in polar materials (pentane insolubles)
- Affected by
  - Base stock
  - Conditions (temperature, catalyst etc.)
  - **Additive system**

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

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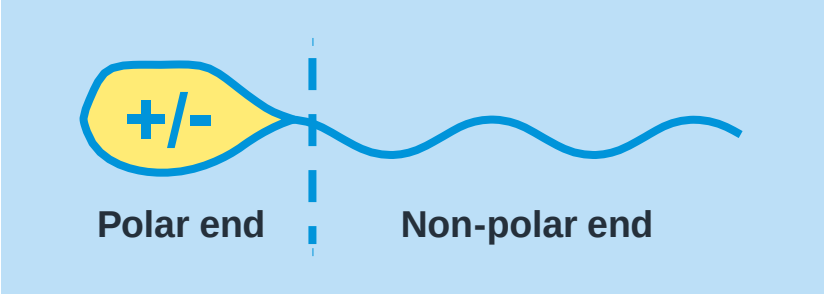
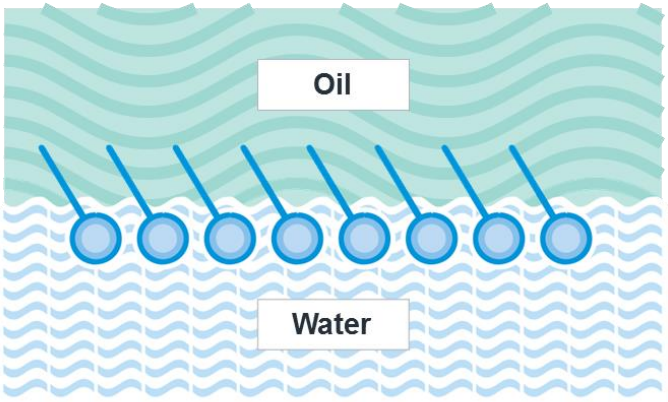
Dispersants and detergents

1. General surfactants properties – individual molecules

- Formed by molecules with both polar and non-polar sections



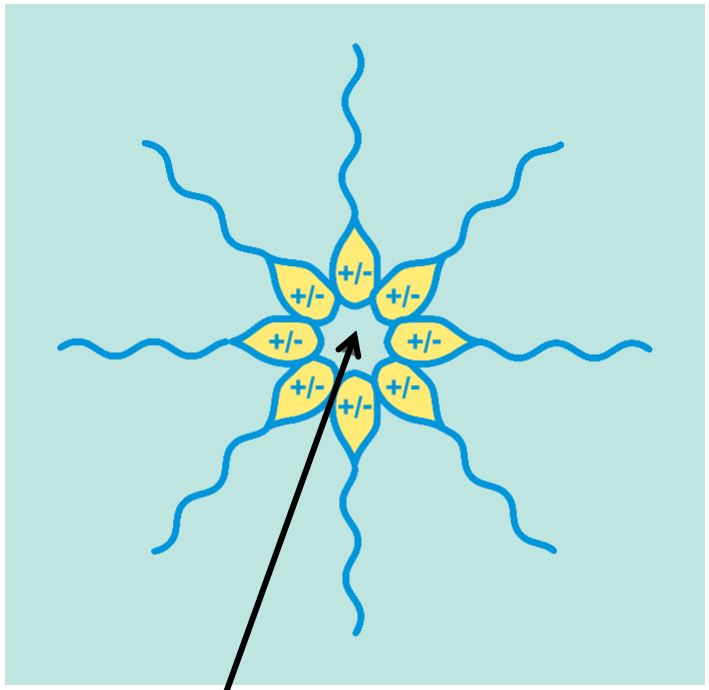
- Aggregate with orientation based on polarity of medium
- At a water/oil interface;
  - Polar ends in water, non-polar ends in oil



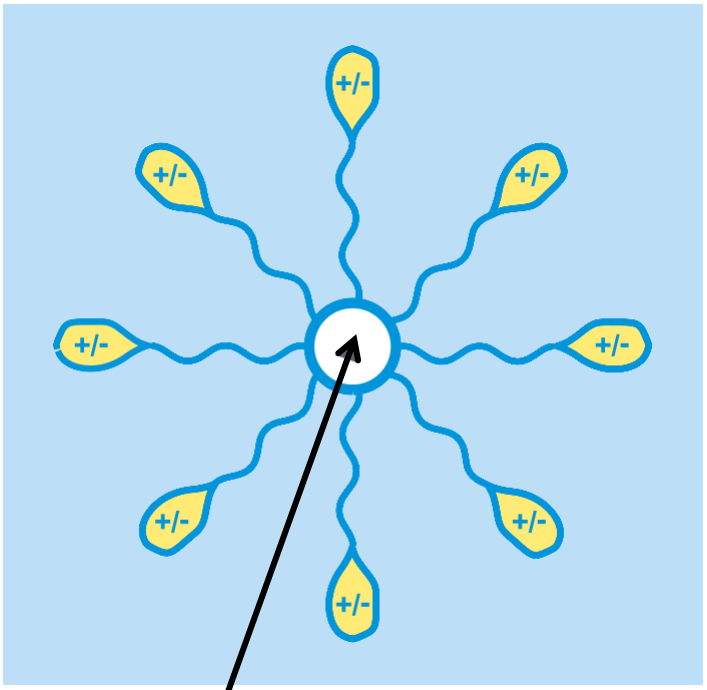
Dispersants and detergents

2. General surfactants properties – micelles

In Oil



In Water

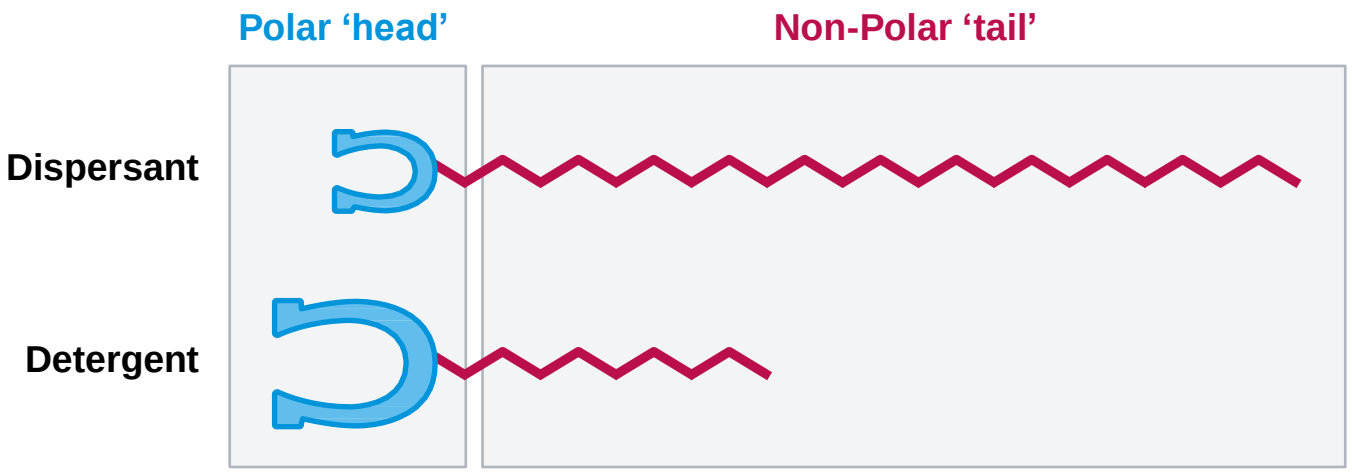


- In three dimensions these form a spherical environment = **Colloid**
  - Solid in the middle = **sol**
  - Liquid in the middle = **emulsion**

Dispersants and detergents

3. Basic dispersant and detergent structure

- Both are surfactants, consisting of 2 parts;

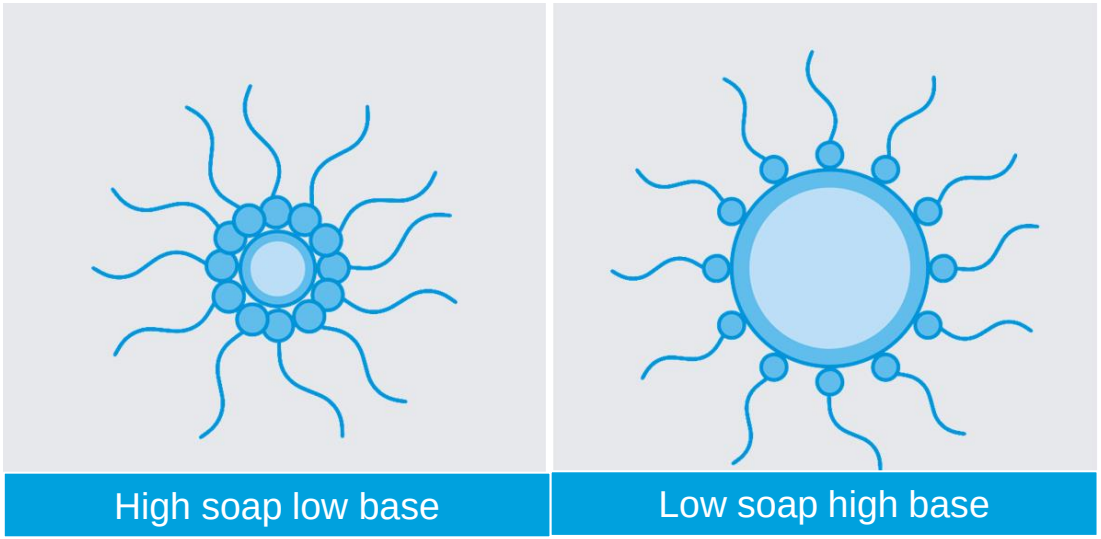


- Differences
  - Ashless vs. metal
  - Length of “tail”
  - Strength of “head”

Dispersants and detergents

4. ‘Metal’ detergents

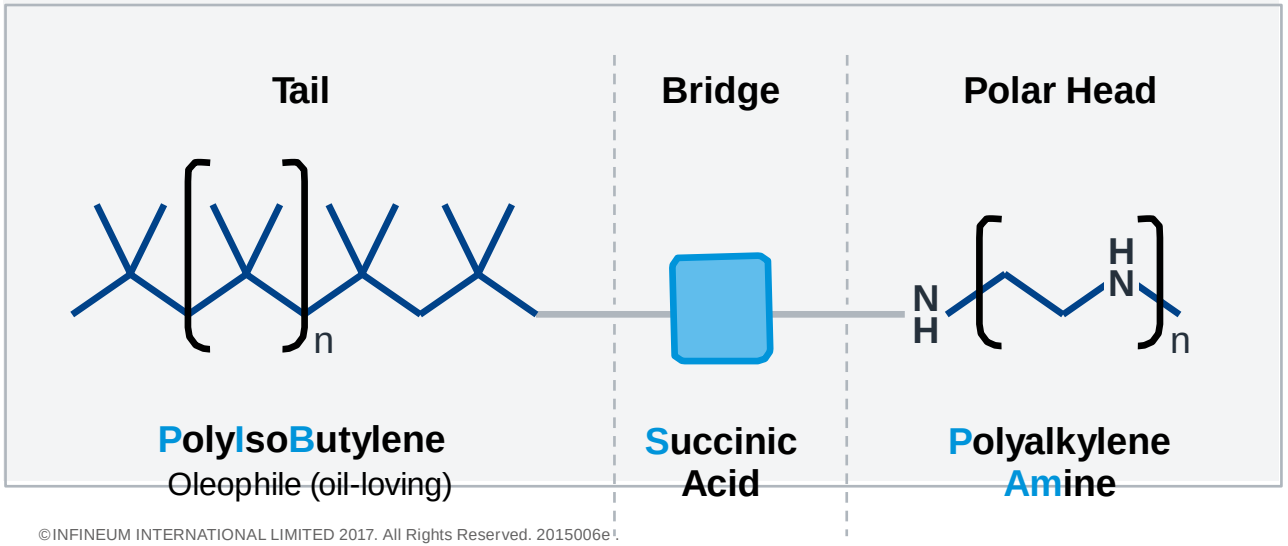
- Functions:
  - Neutralise acidic species (sulfur oxides and organic acids)
  - Reduce lacquer, carbon and varnish deposits on the engine’s pistons
  - Prevent ring sticking under severe high-temperature operating conditions
- Typical compositions – colloidal
  - Alkylated metal sulfonates, sulfurised phenates, salicylates
  - Neutral or overbased (*Excess base*)



Dispersants and detergents

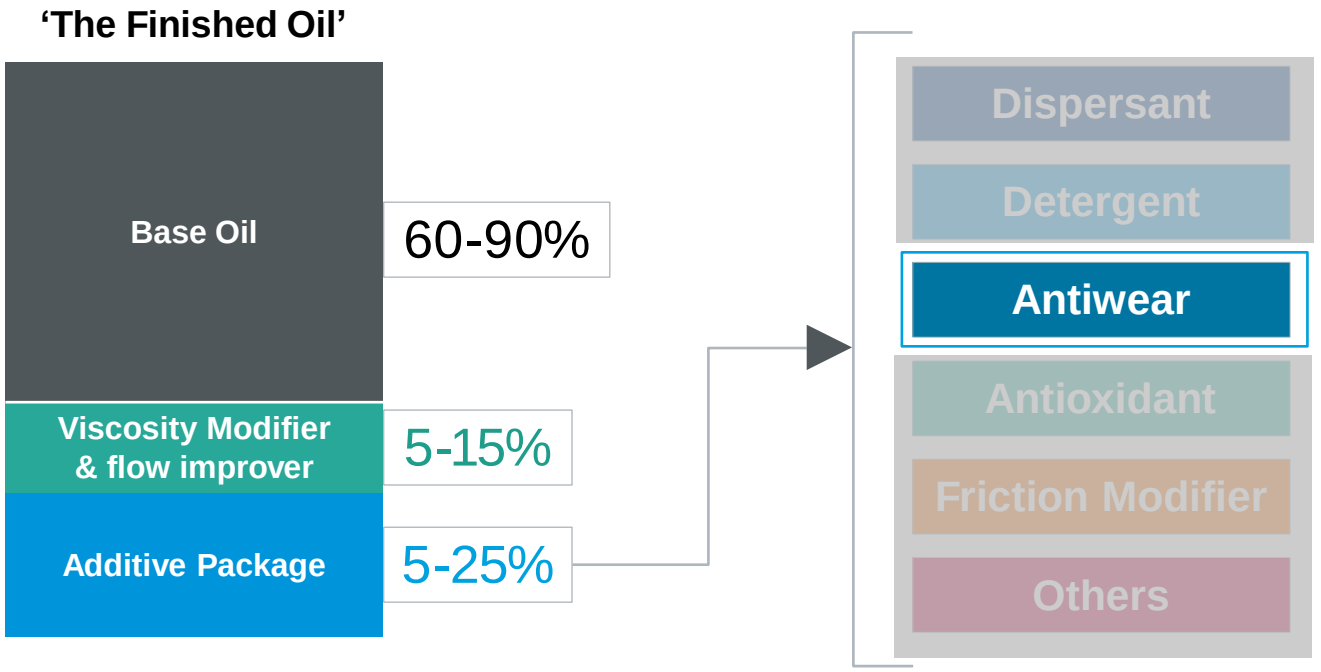
5. Ashless dispersants

- 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)



= PIBSA/PAM

Balance of additives and base oil



Key is balancing the additives for the application

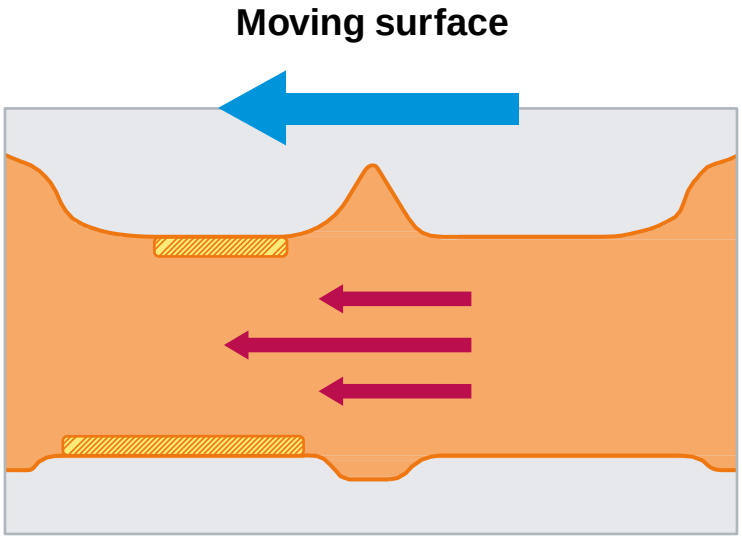
Antiwear agents

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

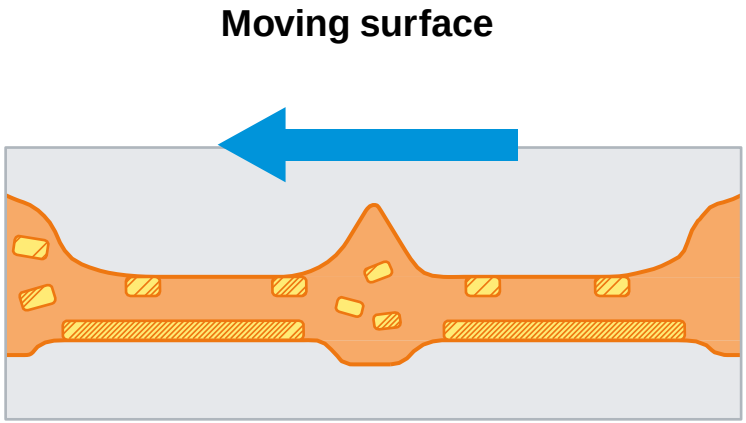
Antiwear agents

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

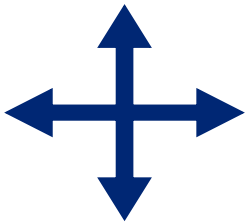


Boundary contact

- 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

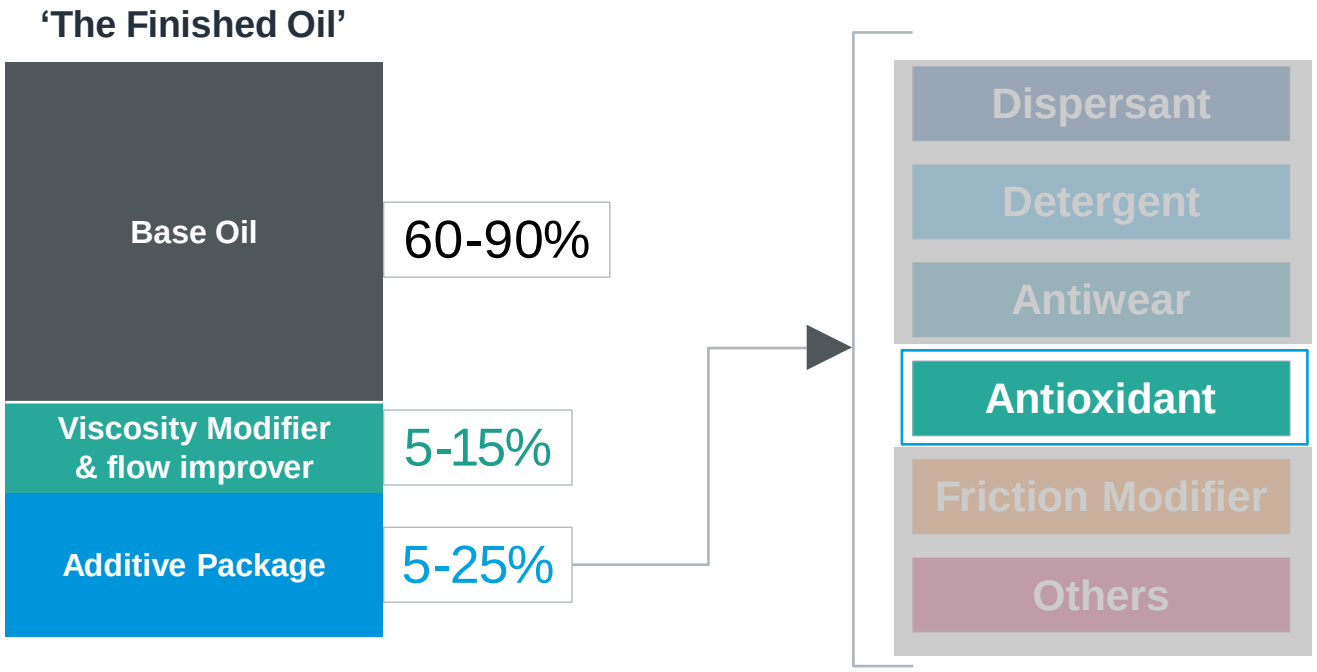
Antiwear agents

3. Aspects of ZDDP structure and performance

	Primary		Secondary
Lower molecular weight		Better wear protection	
	Improved stability		Better wear protection
Higher molecular weight		Improved stability	

- 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

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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 **DiP**henyl **A**mines (DPA)

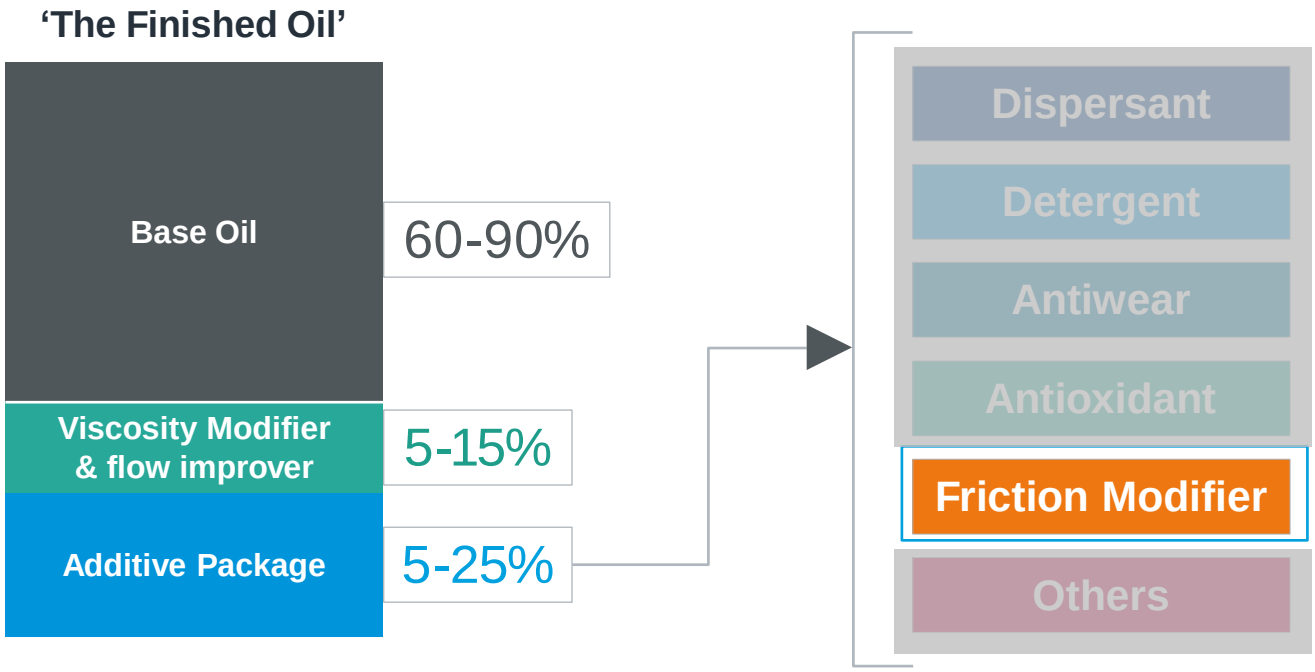
Where: In-H = inhibitor

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

ROOH + PD → ROH + 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

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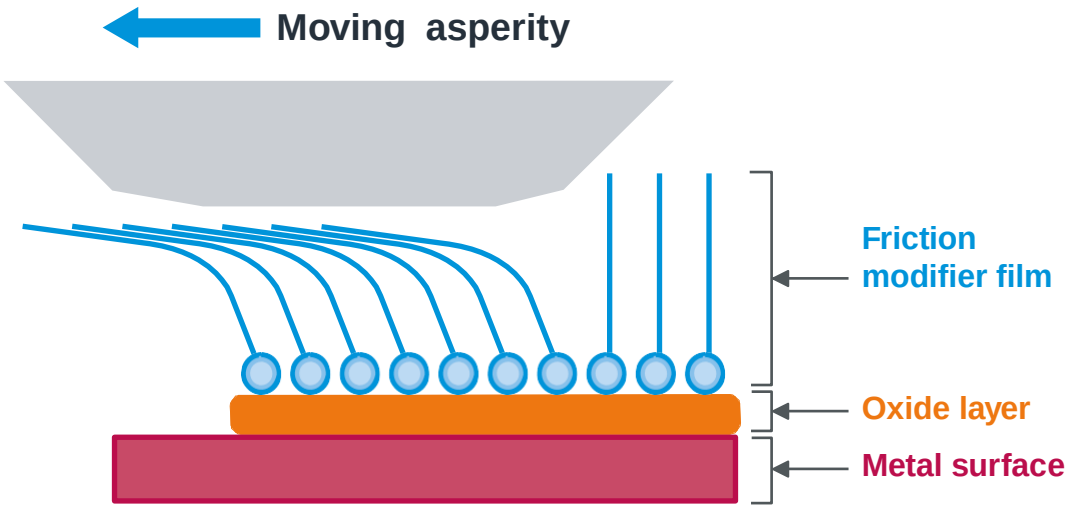
Friction modifiers

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

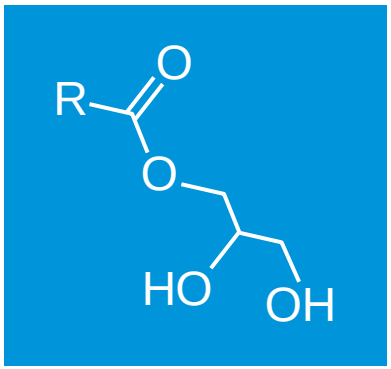
- Long chain hydrocarbons with polar end groups
  - Surfactants
- They work by adsorbing to metal surfaces
- Molecules designed to:
  - Adhere to metal surfaces
    - Rather than soot, for example
  - ‘Stand’ upright into bulk oil
- Friction coefficient is affected by:
  - Type, concentration, temperature,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



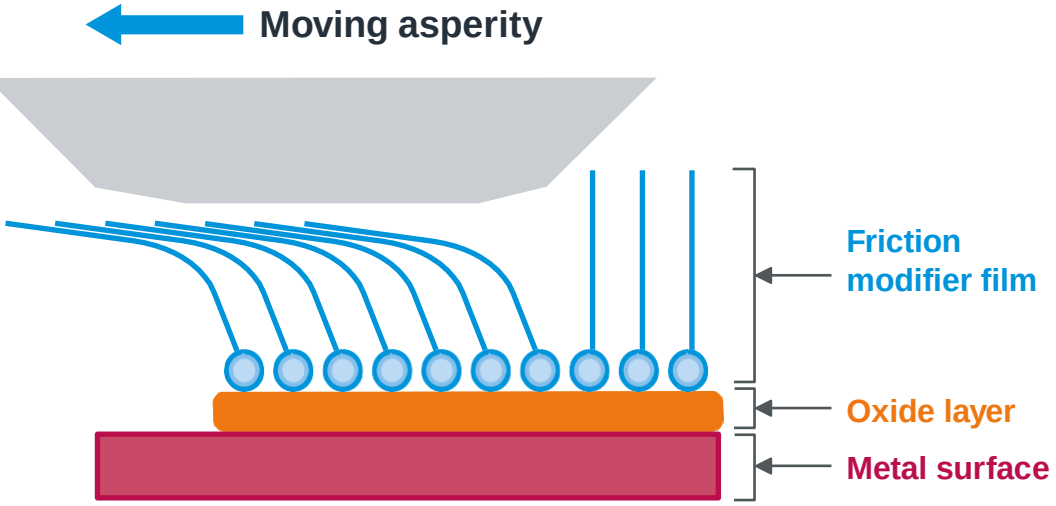
Friction modifiers

2. Organic friction modifiers

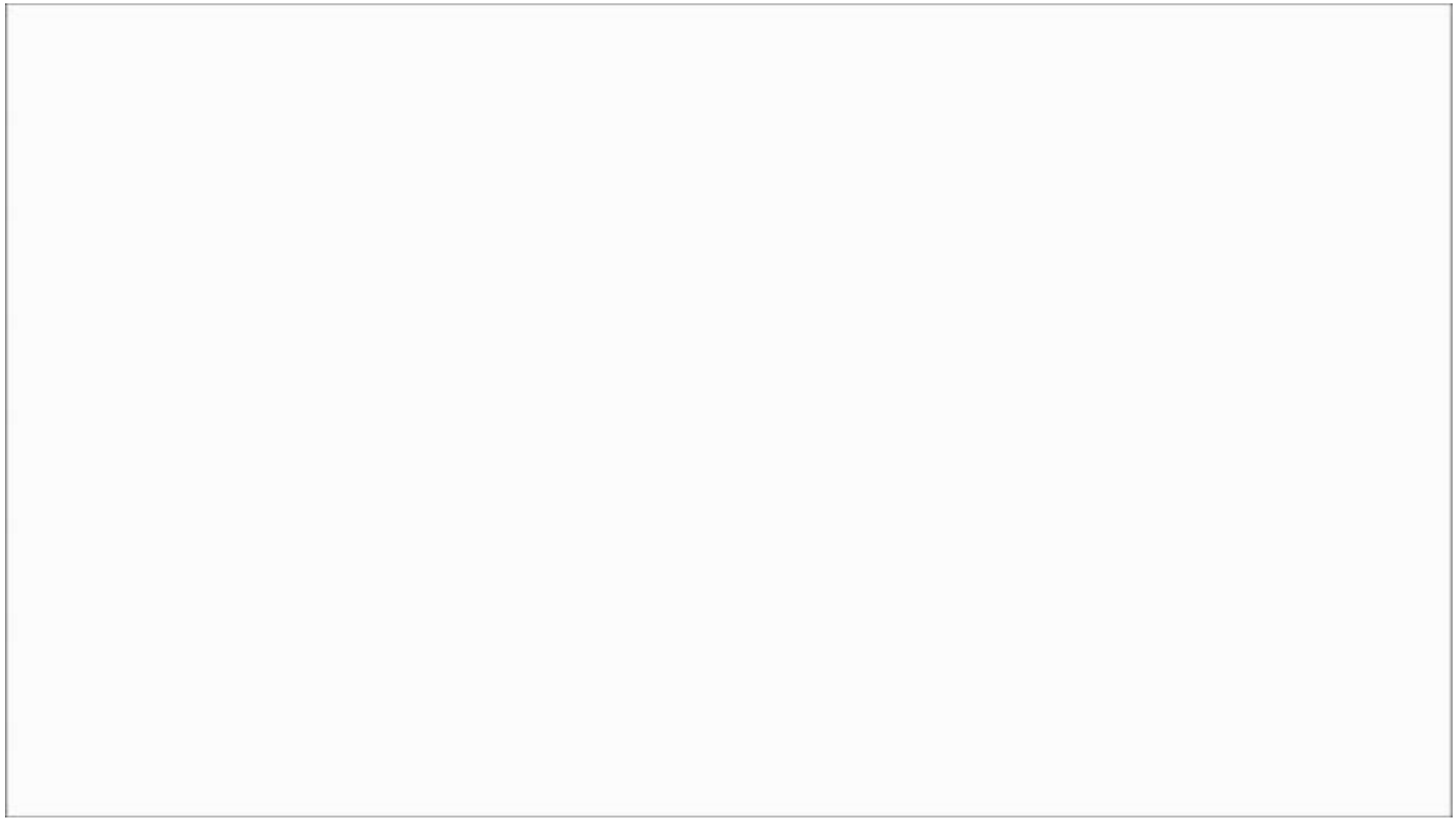
- Molecular geometry is similar to detergents (surfactant)
- Act “intact” (not chemically transformed at the surface)
- Examples include oleic acid and glycerol monooleate (GMO)



Glycerol monooleate



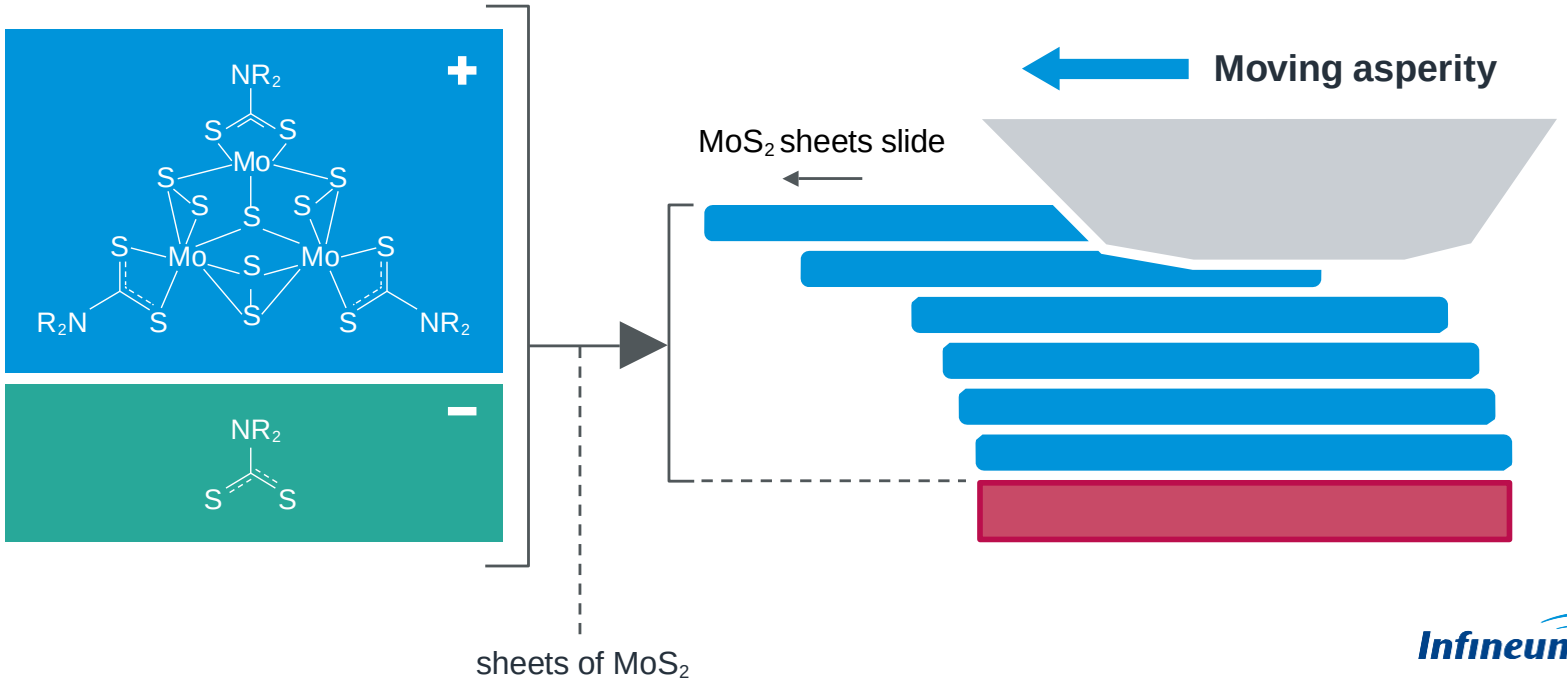
Friction modifiers animation



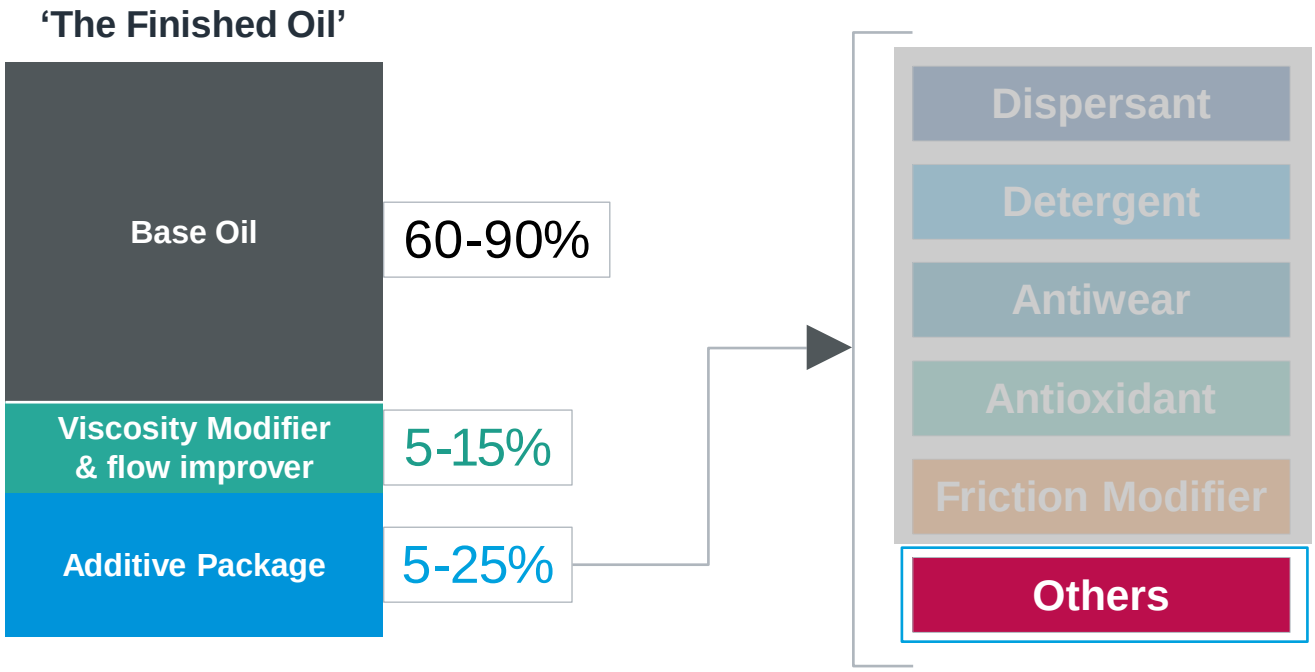
Friction modifiers

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)



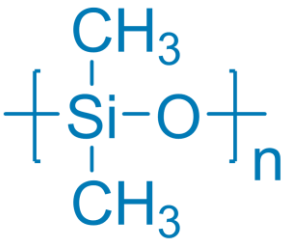
Balance of additives and base oil



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 → control extend of seal swelling or shrinking

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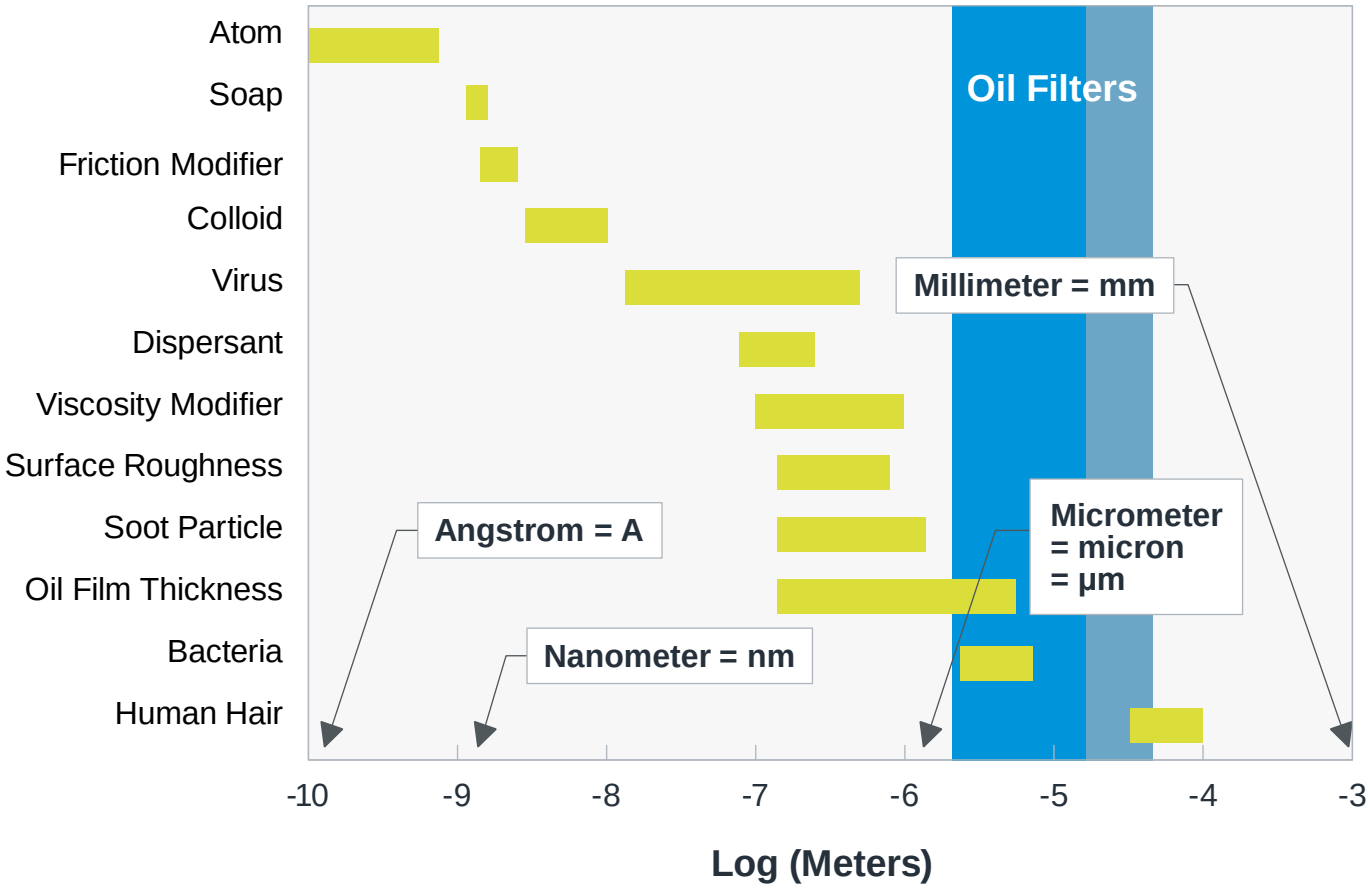
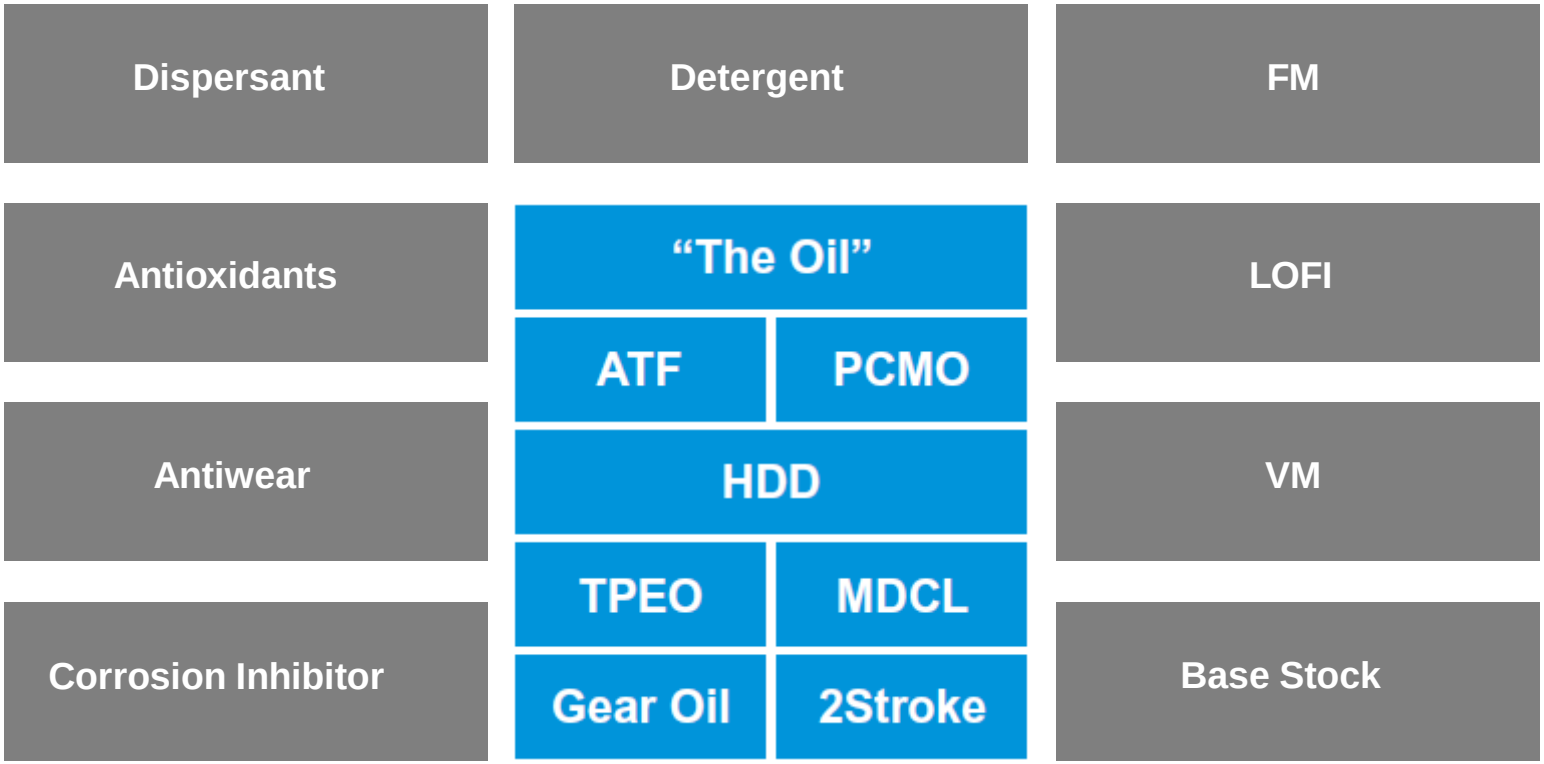
Relative sizes of things



Formulation Science



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