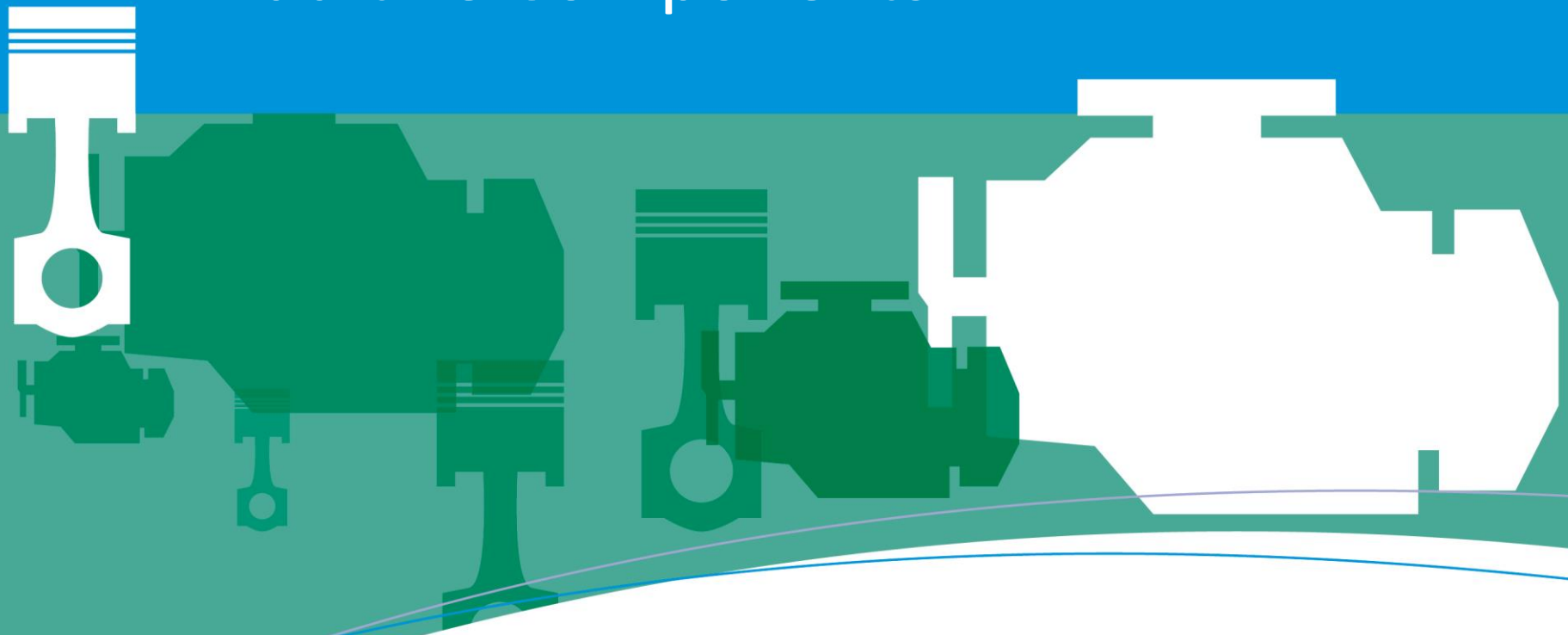
Performance you can rely on.

Additive Components



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Multifunctionality…

Drawing Parallels…

Lubricants dealing with different tasks

Friction

Wear

Oxidation

Multifunctional mixture

Thanks to additives

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Introduction

Reliability

Performance

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Agenda

01 | **Destructive processes.** The necessity for additives

02 | **Functions of additives**

03 | **Types of additives**

Enhance lubricant performance

Minimise destructive processes in the engine

Extend engine and oil life time

Balance of Additives and Base Oil

Lubricant
Commercially available product

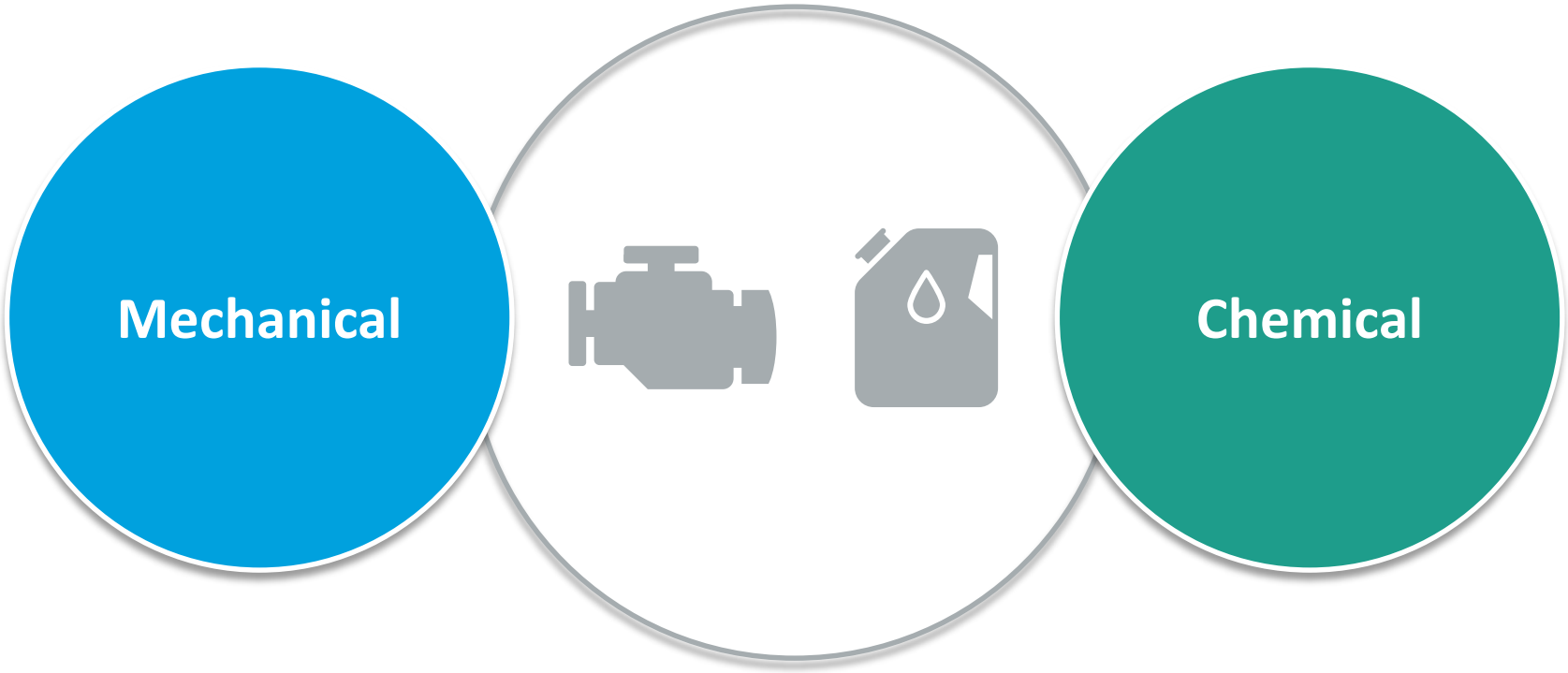
'Finished Oil'

Base Oil	60-90%
Viscosity Modifier & flow improver	5-15%
Additive Package	5-25%

- Dispersant
- Detergent
- Antiwear
- Antioxidant
- Friction Modifier
- Others

Key is balancing the additives for the application

Destructive Processes



These processes affect **both** the engine and the lubricant

Destructive Processes

Mechanical

Both caused by relative motion between surfaces

Friction

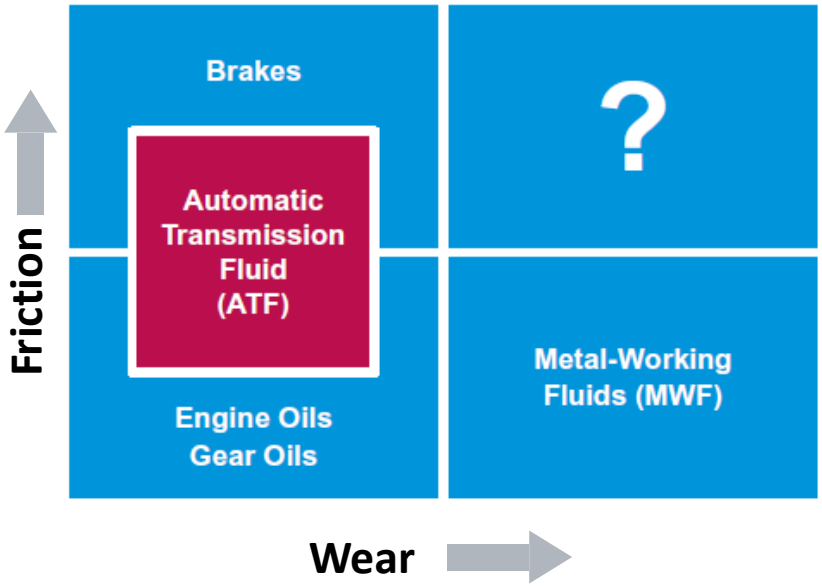
loss of energy – dissipated as heat

- Types – sliding, rolling, static

Wear

loss of material

- Types – abrasion, adhesion, corrosion, fatigue
- Changes geometry of contacts
- Changes equipment performance
- Introduces metal oxidation catalysts



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Destructive Processes

Chemical

Rust

to ferrous (iron) metals

- Oxidative process
- Catalysed by water and acids

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

Corrosion

to non-ferrous metals

- Chemical attack
- Examples include:

$$Cu + S \rightarrow CuS$$

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

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Destructive Processes

Fuel combustion

Ideal situation
Complete combustion

$$Fuel + O_2 \rightarrow Energy + CO_2 + H_2O$$

Reality
Incomplete combustion

$$Fuel + Air \rightarrow Energy + CO_2 + H_2O$$

$$+$$

$$NO_x + SO_x + CO + HC + Particulate\ Matter\ (PM\text{-}Soot) + Radicals$$

Result
Acceleration of oil oxidation and degradation, viscosity increase, acid build-up, corrosive wear and deposits

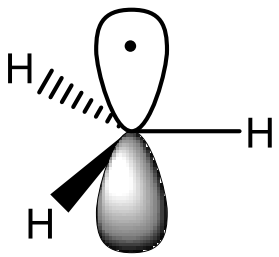
Oxidation

In the Lubricant

Destruction of molecules by exposure to oxygen at elevated temperatures

Initiated by **radicals**

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



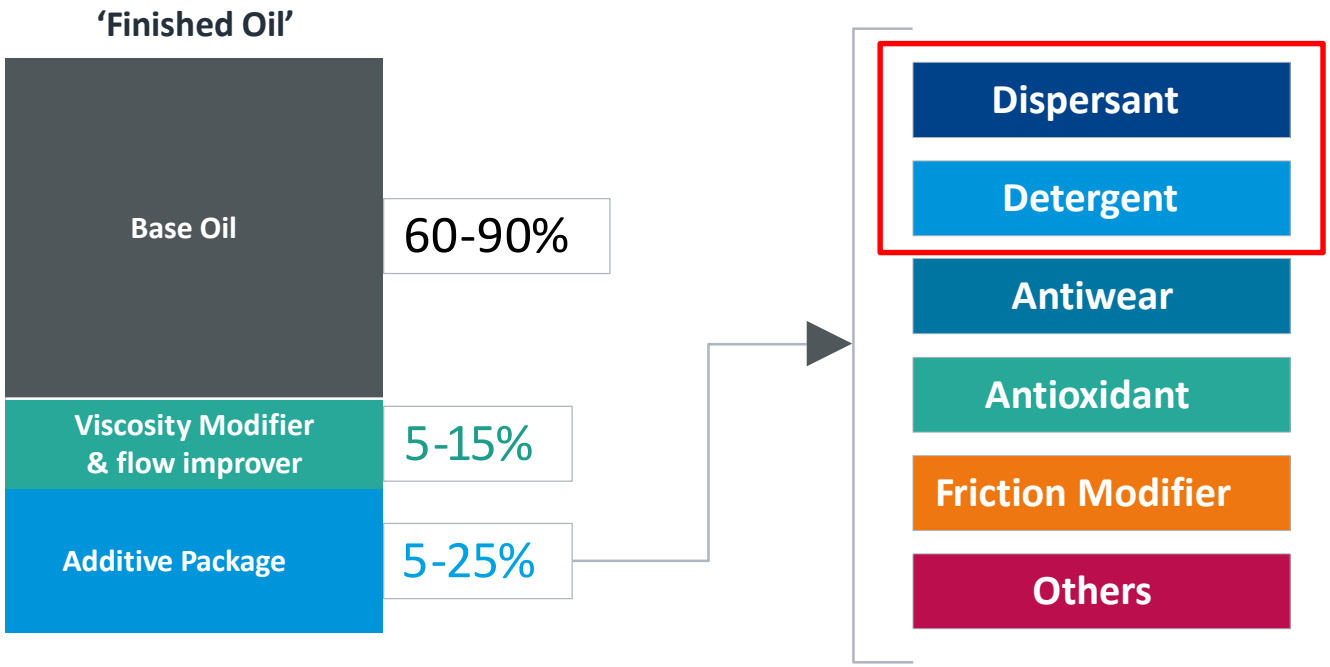
Methyl Radical

sp^2 hybridised carbon atom

The process can be **catalysed** by metals

Consequences

Balance of Additives and Base Oil



- Solubilisation of different moieties
- Inhibition of deposit formation

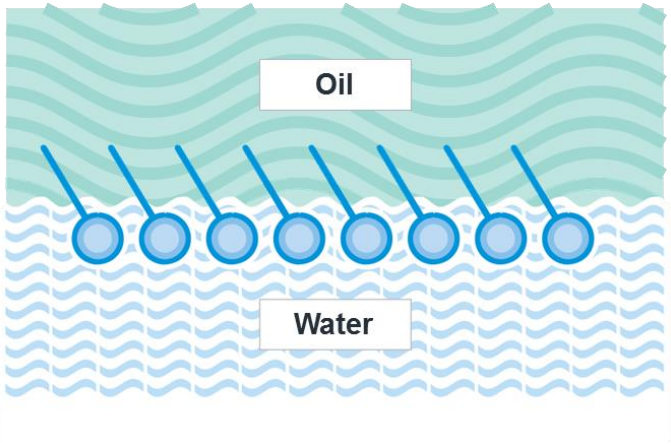
Dispersants and Detergents

Properties

Molecules with a polar and a non-polar section

Non-polar tail Polar end

Tend to aggregate forming polar or non-polar core micelles

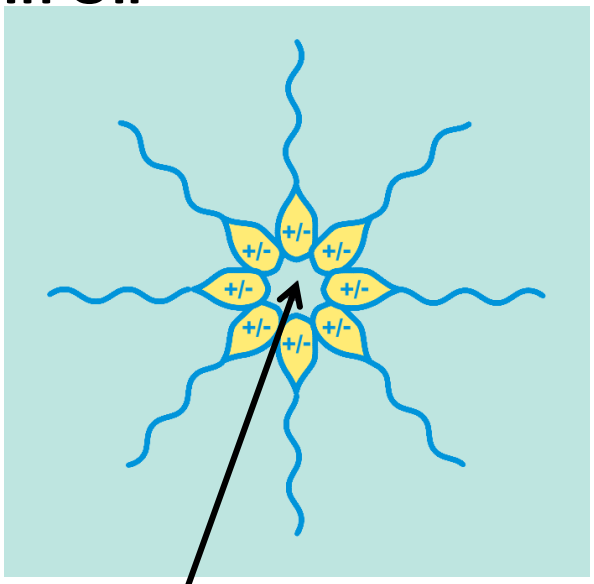


Dispersants and Detergents

Aggregation

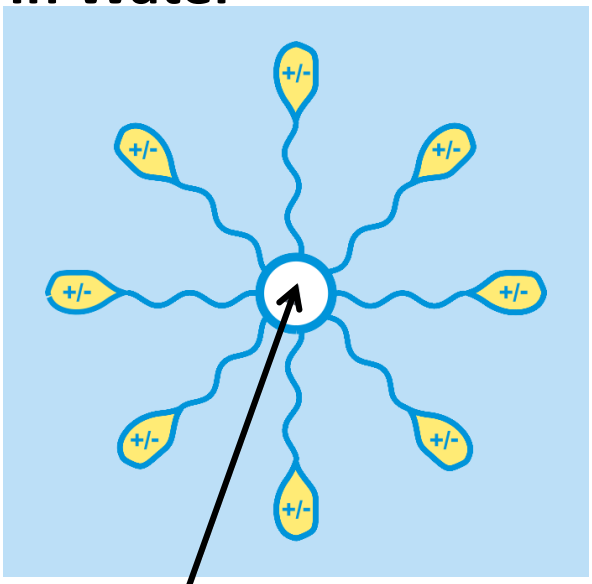
Micelles

In Oil



Polar core

In Water

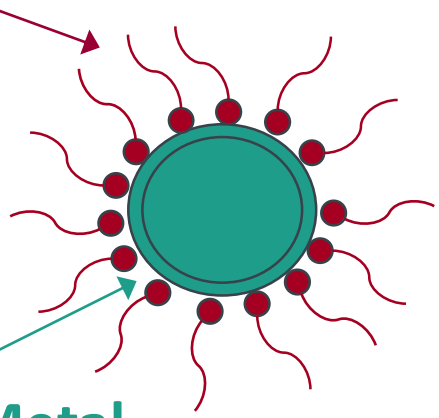


Non-polar core

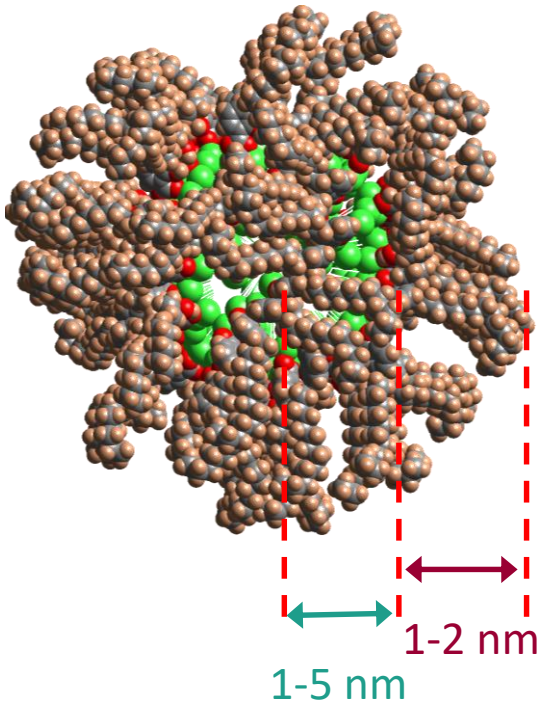
Metal-containing Detergents

Colloidal particles with two discrete sub-sections

Organic Stabilising Surfactant (Soap)



Inorganic Metal Carbonate Core (Base)



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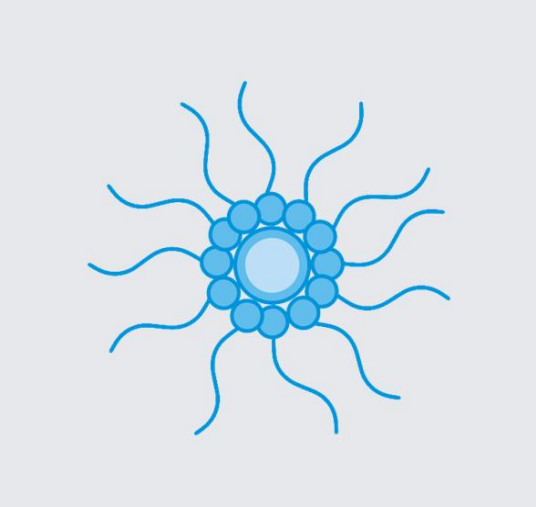
Metal-containing Detergents

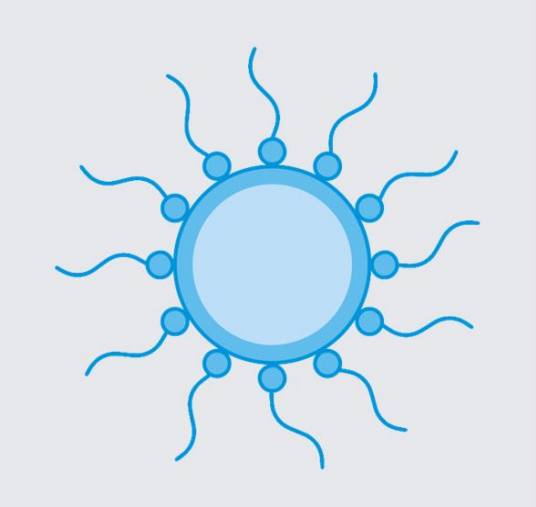
Function	Consequence
Neutralise acidic blow-by gases	Prevent corrosive wear
Solubilise engine combustion products	Reduce lacquer, carbon and varnish deposits on pistons
Inhibit high-temperature deposit formation	Prevent ring sticking under severe operating conditions
Provide supplementary anti-oxidancy	Reduce base oil degradation

Typical compositions – colloidal

- Alkylated metal sulphonates, sulphurised phenates, salicylates
- "Neutral" or "overbased " (*Excess base*)

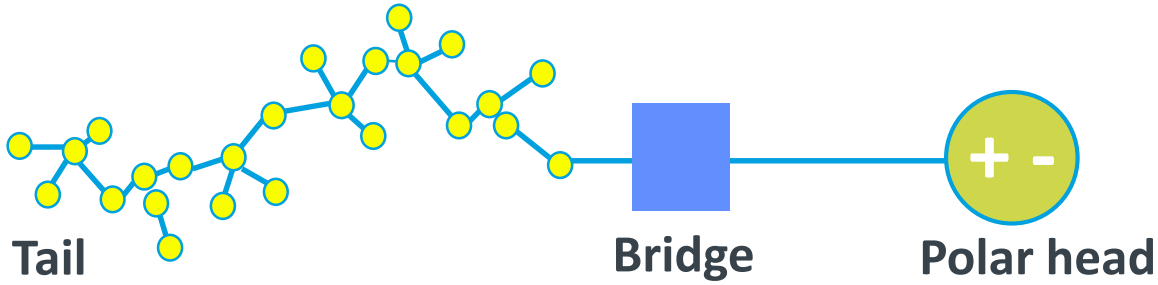


High soap low base



Low soap high base

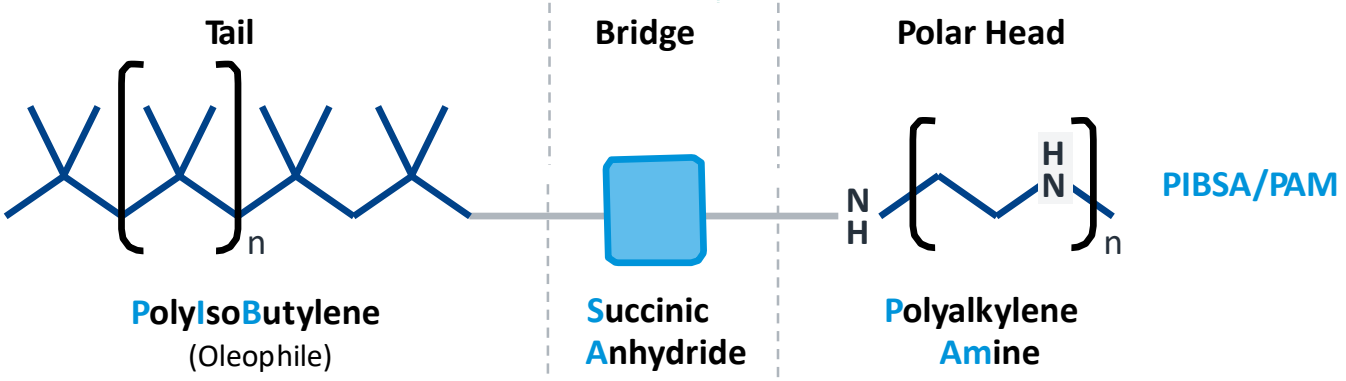
General Dispersant Structure



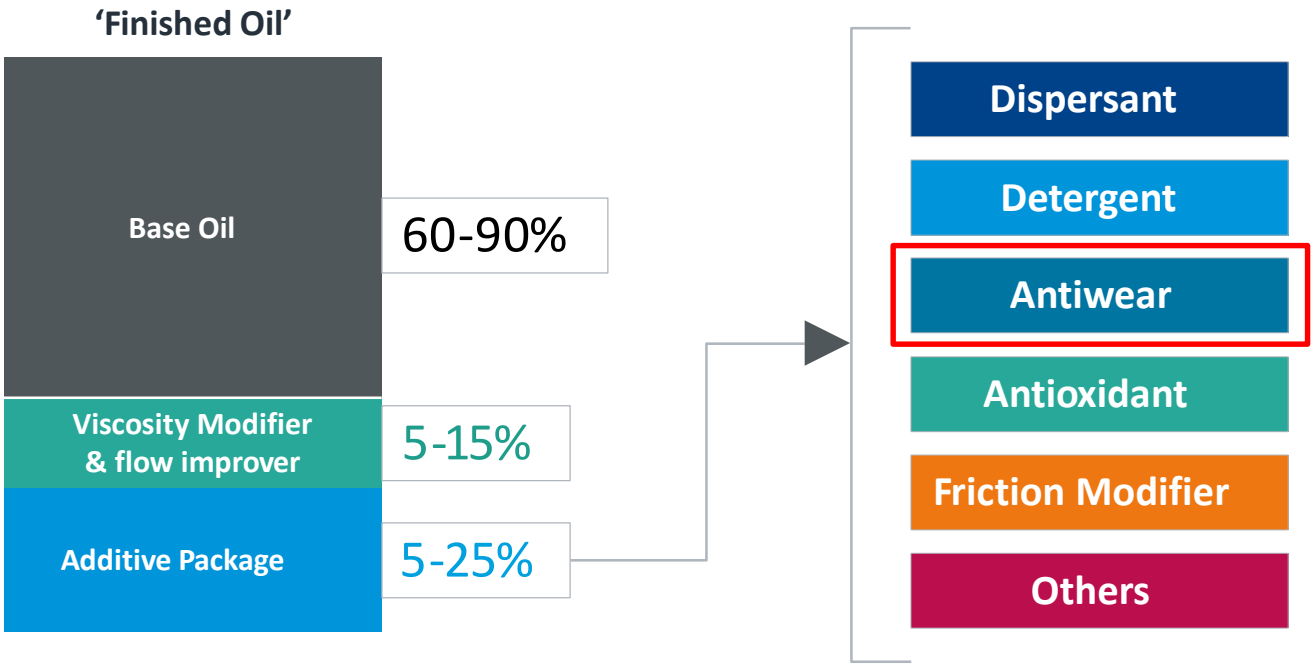
- Oleophilic (hydrophobic) tail and hydrophilic head group
- Sometimes contains a bridge for ease of attachment
- Can have multiple tails or multiple heads or both

Ashless Dispersants

Function	Consequence
Absorbs to particle surfaces preventing agglomeration/ controlling viscosity growth	Rheology control
Surface adsorption	Forms protective layer altering friction/wear properties
Inhibits sludge formation and phase separation	Solubilisation
Inhibits deposit formation/suspends soot	Keep engine parts clean
Delivers other moieties e.g. boron	Enhances overall efficiency of lubricant



Balance of Additives and Base Oil



Wear is the process of physical loss of material from a metal surface

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Wear and Antiwear Agents

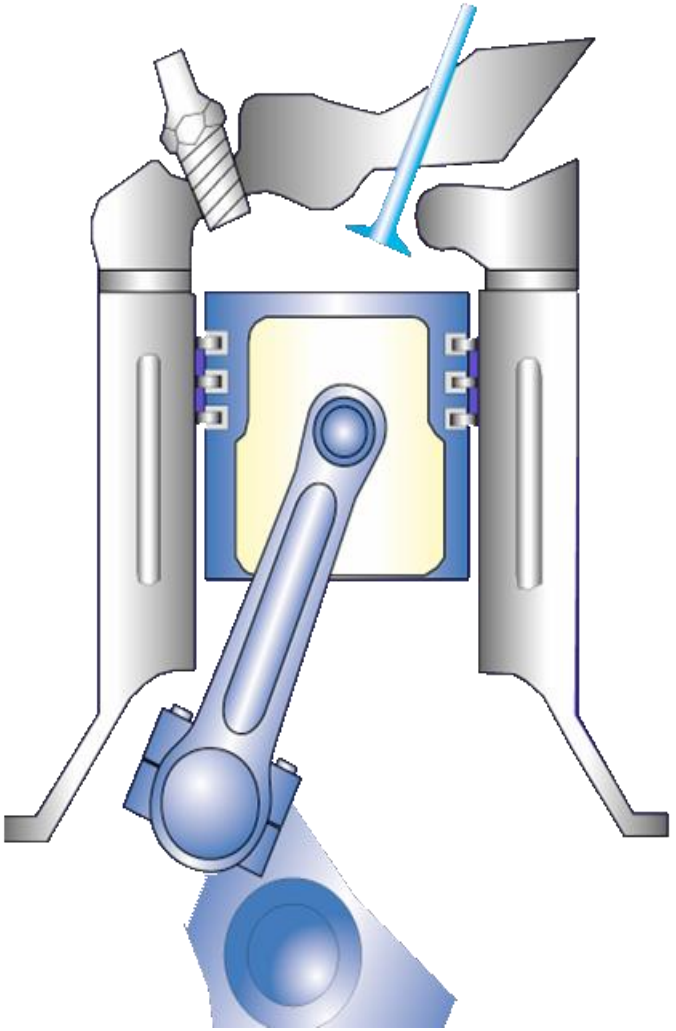
Process of physical loss of material from a metal surface

Adhesive: metal extremities fuse together and motion pulls them apart

Abrasive: hard material in the contact abrades the metal surface

Corrosive: loss of material by chemical reaction; water, combustion acids, excess antiwear or EP additives

Fatigue: high stress deforms the metal structure below the surface



50% of engine friction is between piston rings and liner

Antiwear Agents

Zinc-based: zinc dialkyldithiophosphates (ZDDP)

Engine oils

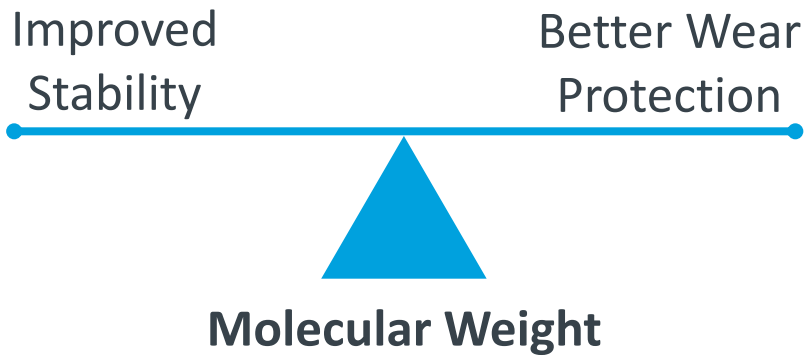
Molybdenum-based: molybdenum dithiocarbamates (MoDTC)

Phosphorus-based: tri-cresyl phosphate

ATF, gear, aviation

Extreme pressure: highly reactive sulphur-phosphorus compounds

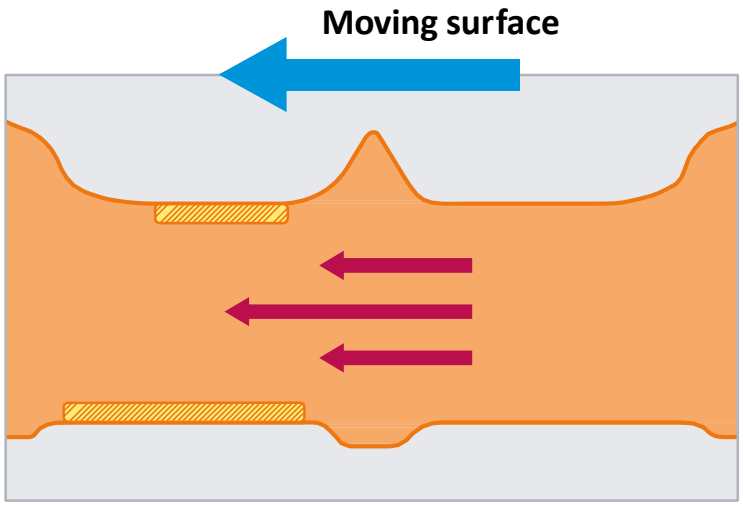
Gear oils



Antiwear Agents

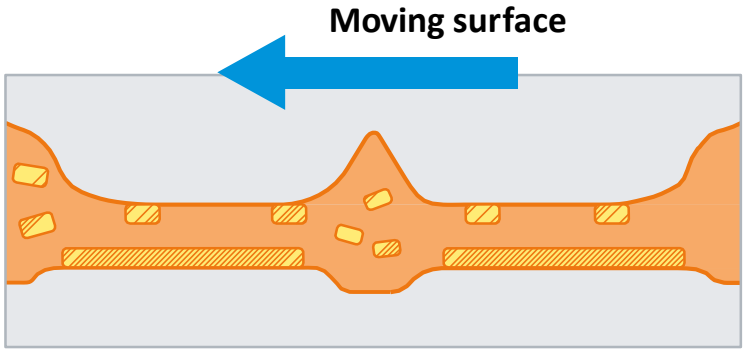
Protection mechanism

Mechanism of antiwear protection by ZDDP



Hydrodynamic contact

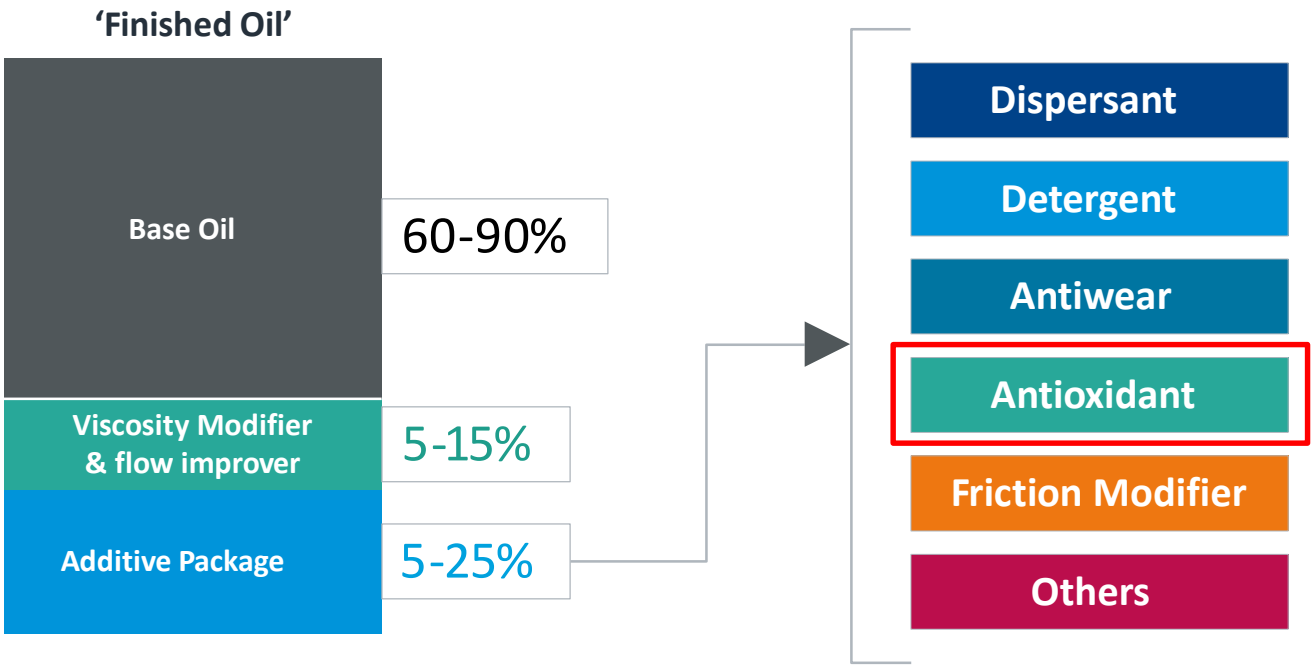
- Thick oil film
- No metal/metal contact
- Phosphate layers will not form but would be maintained if formed previously



Boundary contact

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

Balance of Additives and Base Oil



Oxidation is one of the major destructive processes the lubricant experiences

Oxidation and Consequences

Consequences

- Degradation of base oil and its additives
- Acidification through carboxylic acid generation
- Chain cleavage and volatilisation of light ends
- Increased polarity and viscosity
- Loss of performance - Hardware damage

OXIDATION

Consequences and other parameters

Consequences

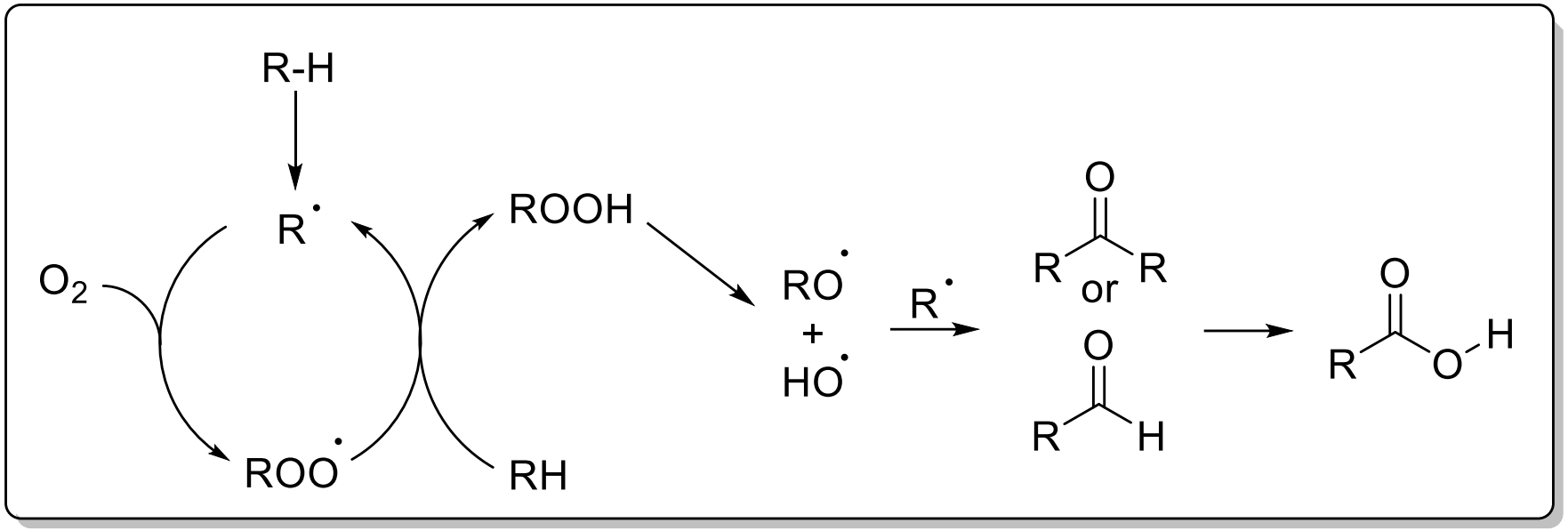
- Degradation of base oil and its additives
- Acidification through carboxylic acid generation
- Chain cleavage and volatilisation of light ends
- Increased polarity and viscosity
- Loss of performance - Hardware damage
- Deposit formation, poor pumpability, oil starvation

Affecting parameters

- Base stock
- Additive package
- Biofuel contamination
- Operating temperature
- Presence of wear metals

OXIDATION

Mechanistic Overview



Decomposition products (carbonyl and hydroxy compounds) are the major oxygenated components of used oils

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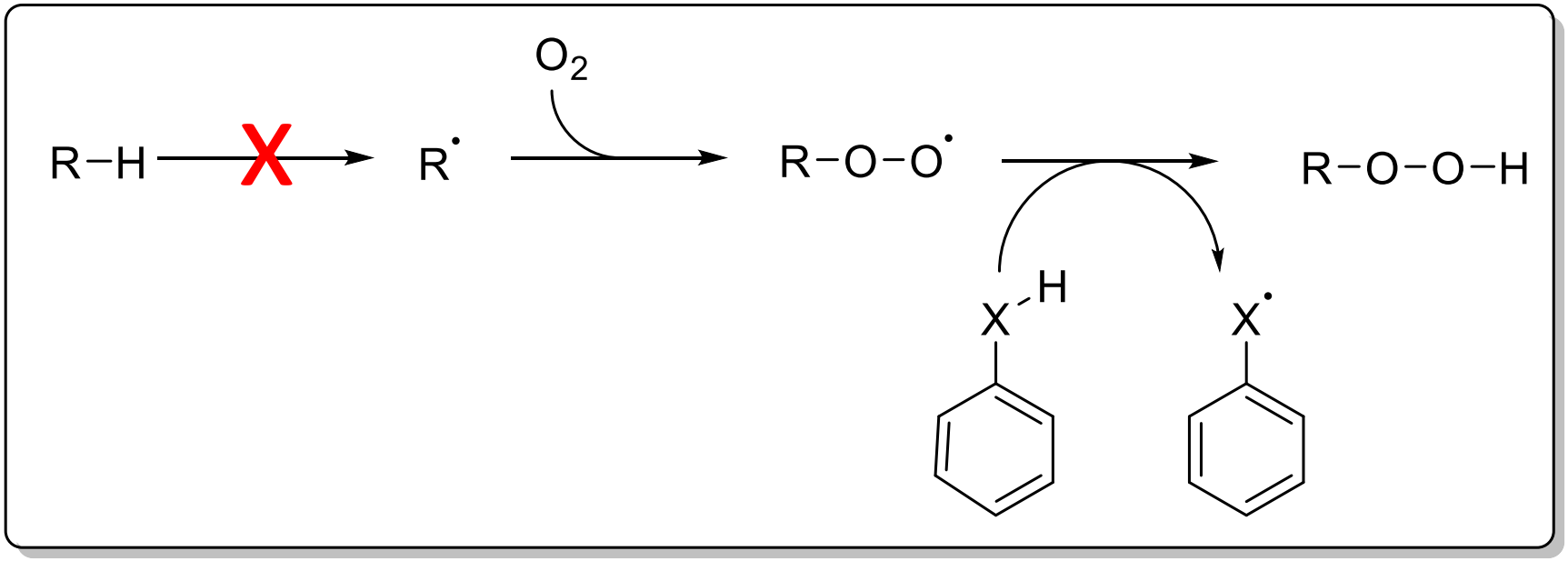
Types of Antioxidants

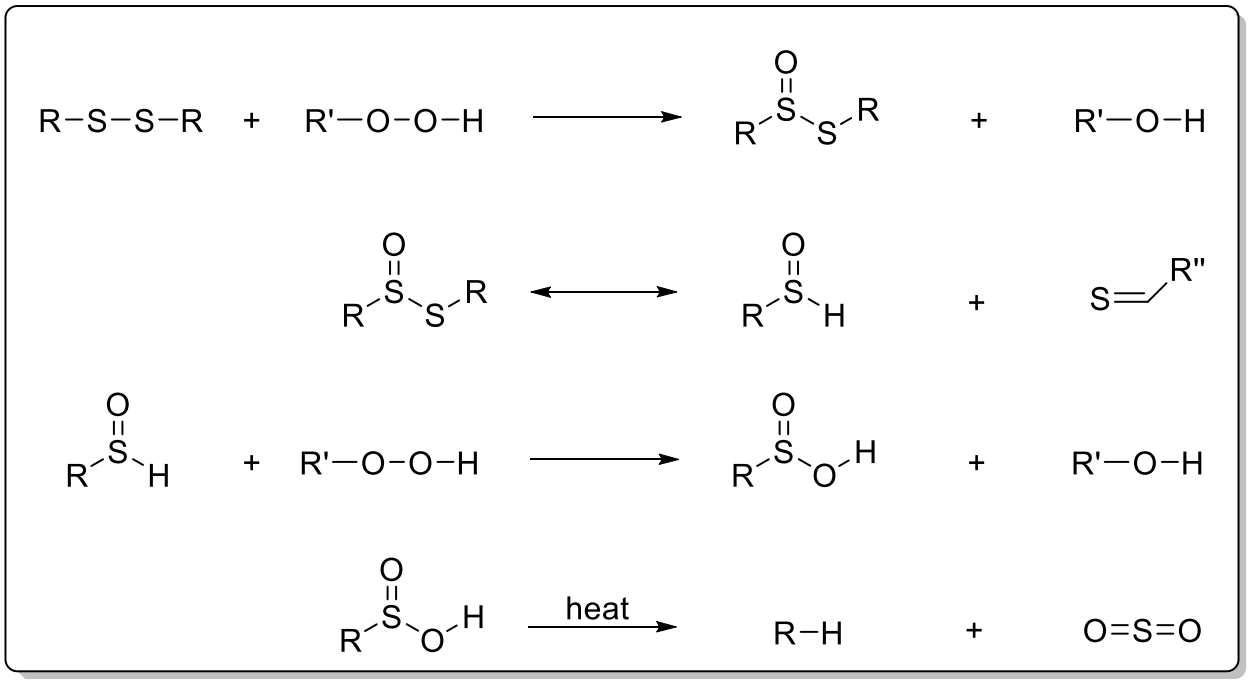
Primary antioxidants: Act as radical traps, interrupting oxidation process



- ✓ Hindered Phenols
- ✓ Alkylated **DiP**henyl **A**mines (DPA)

Types of Antioxidants

Secondary antioxidants: Peroxide/hydroperoxide decomposers



- ✓ Zinc Dialkyl Dithiophosphates
- ✓ Molybdenum Dithiocarbamates
- ✓ Thioethers

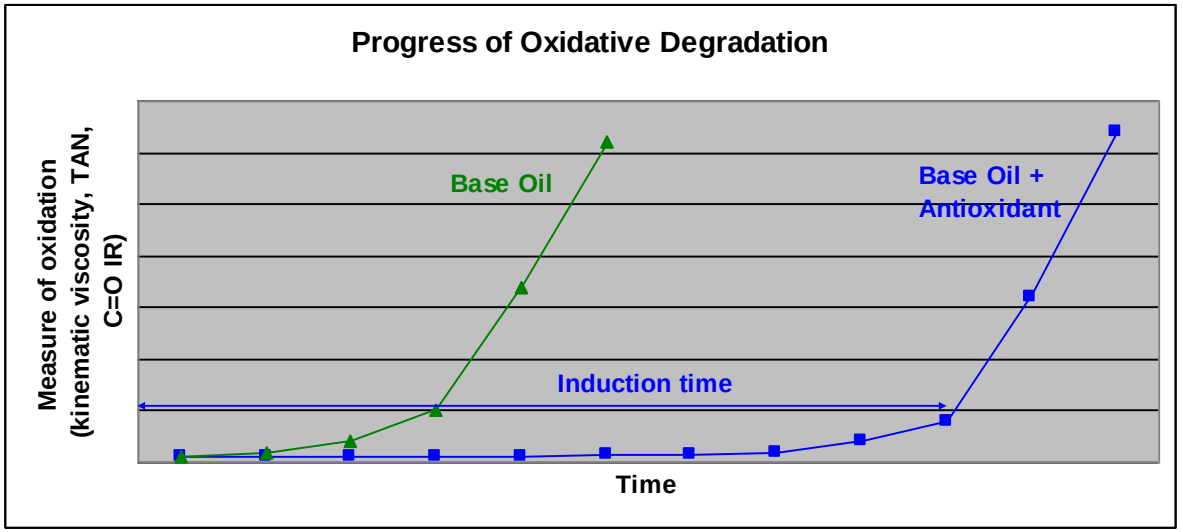
OXIDATION

Synergy and Effects

Synergy is the phenomenon where the performance of two additives is greater than the sum of their individual appearances, common in antioxidants

- **Homosynergism** – two additives working by the same mechanism
- **Heterosynergism** – two different mechanisms operating

Once antioxidant is used up, autoxidation results in rapid lubricant degradation



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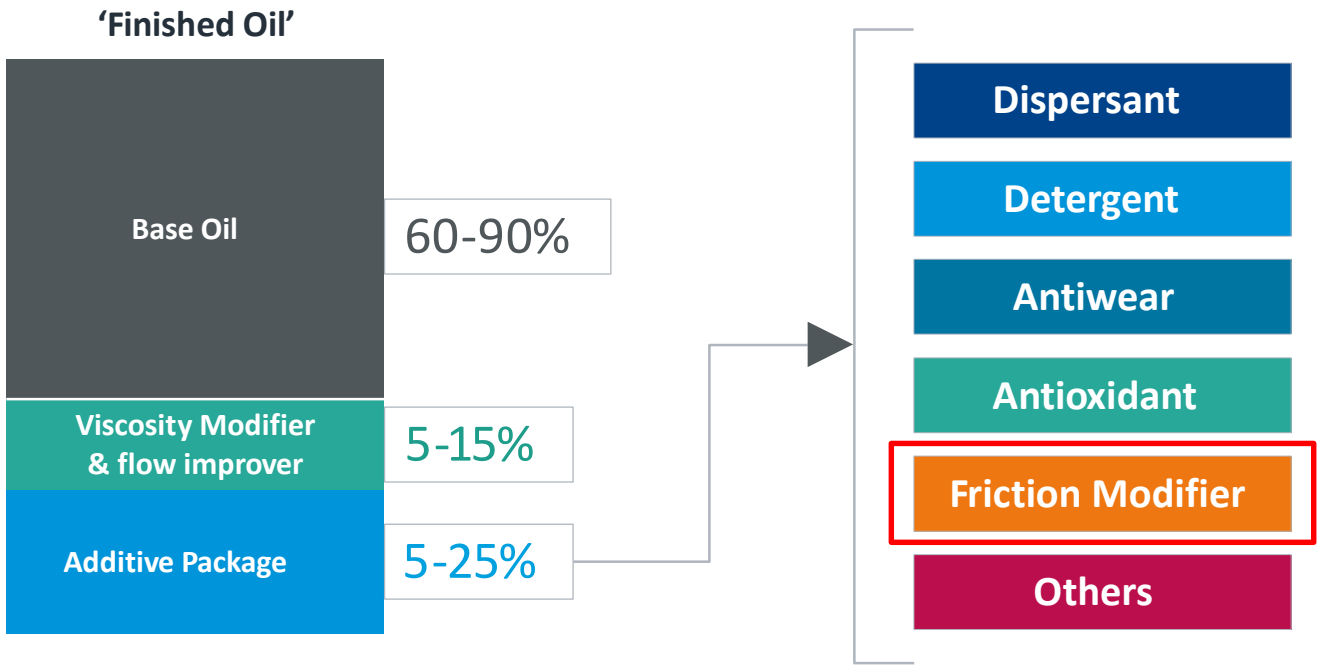
Balance of Additives and Base Oil



Friction coefficient reduction allows **better fuel economy**

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FRICTION MODIFIERS

General Aspects

Give a low coefficient of friction by providing a **low shear surface**

Defined as…

Surface active chemicals that affect friction coefficient

Almost all additive components fit this broad definition!

For our purposes…

Chemicals at less than 1% concentration in lubricating oil significantly affect friction coefficient

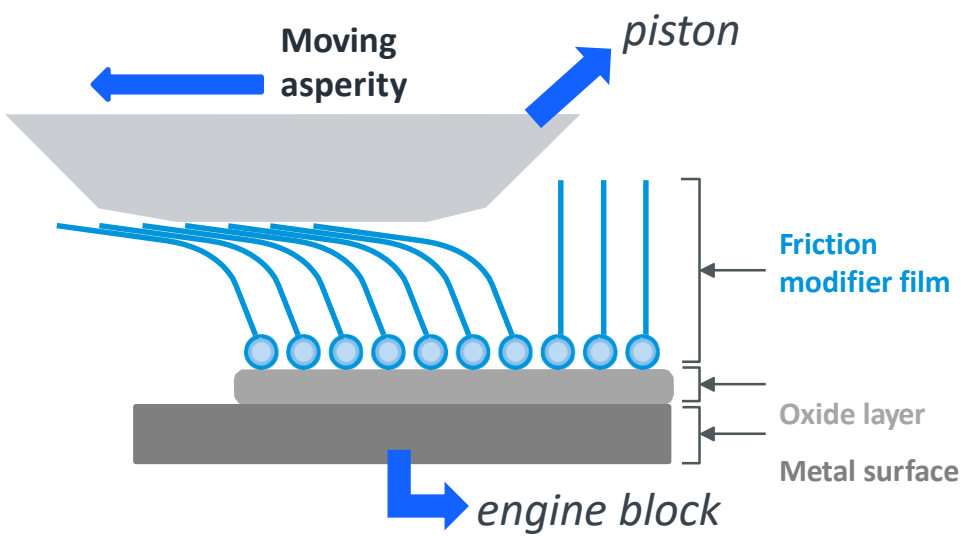
Long chain hydrocarbons with polar end groups (*surfactants*)

Molecules designed to:

- Adhere/adsorb to metal surfaces
- 'Stand' upright into bulk oil

Friction coefficient is affected by:

- Temperature, speed, load



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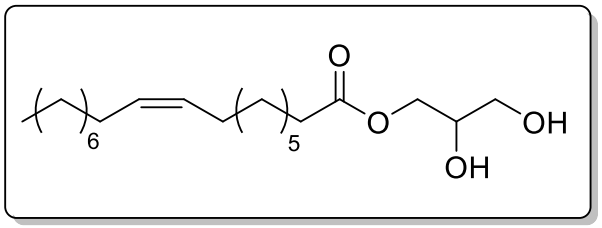
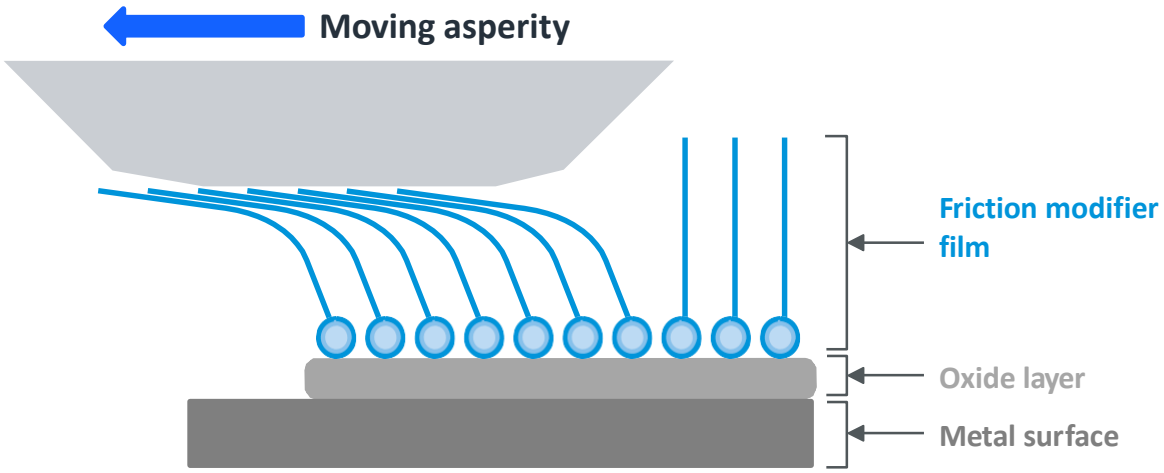
FRICTION MODIFIERS

Organic

- Molecular geometry similar to detergents (surfactant)
- Act “intact” (not chemically transformed at the surface)
- e.g. oleic acid and glycerol monooleate



Glycerol monooleate



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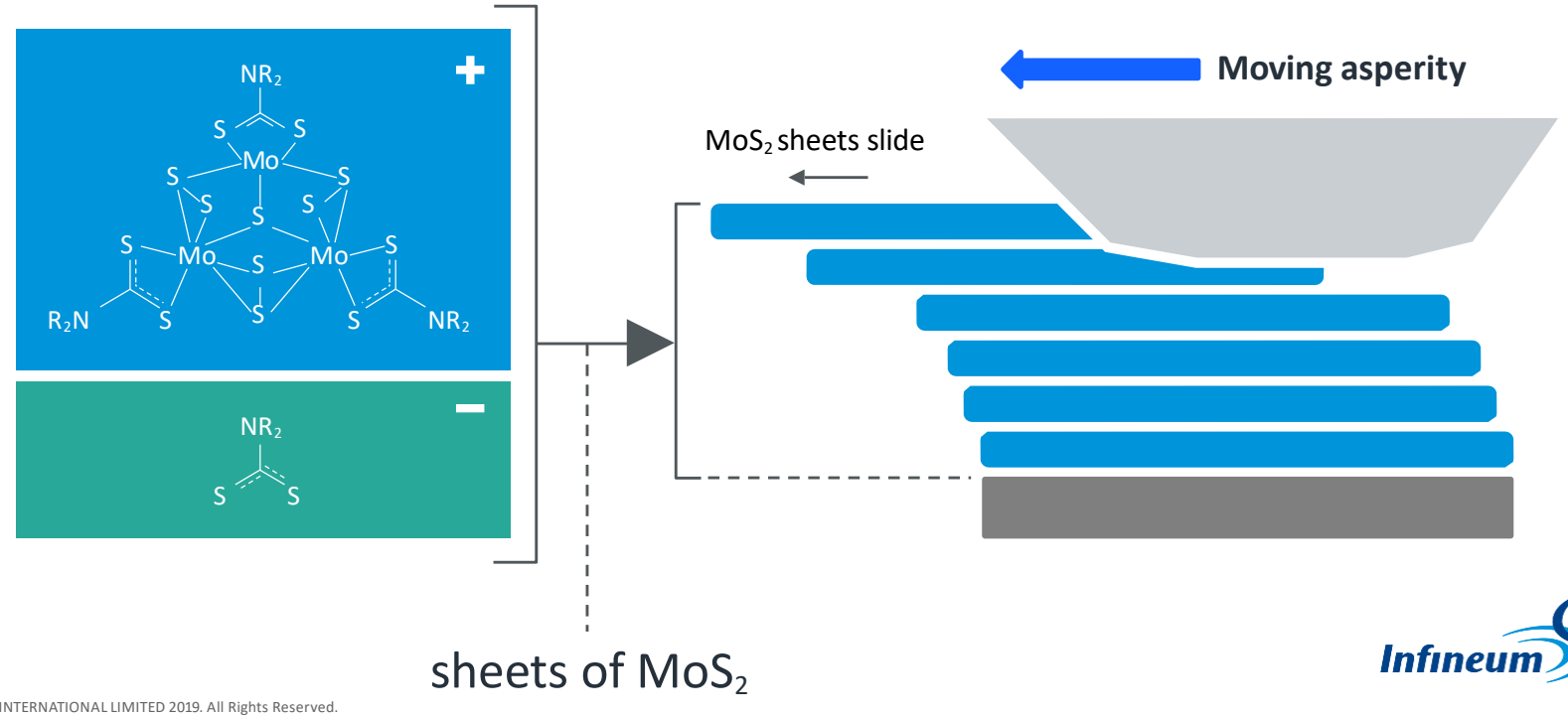
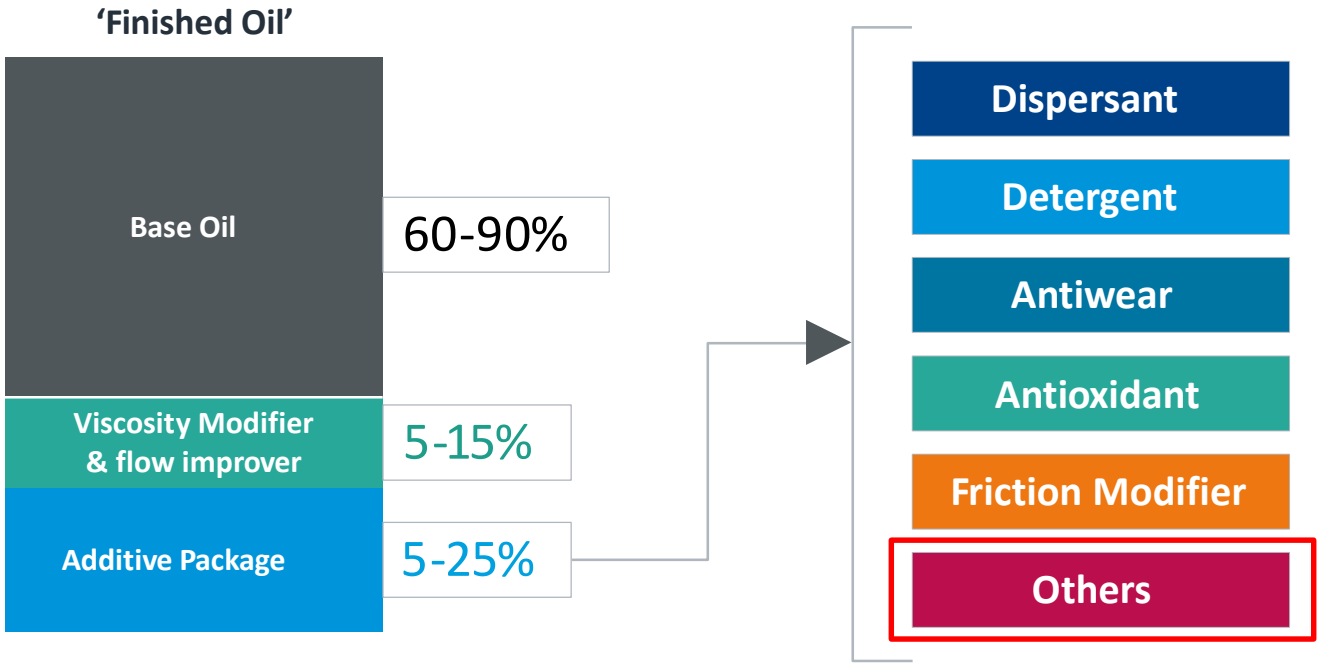
FRICTION MODIFIERS

Solid

- Molecular geometry describes a “flat plate”
- Act after chemical transformation at the surface
- Examples include molybdenum disulphide (MoS_2) from molybdenum trimer (MoDTC)



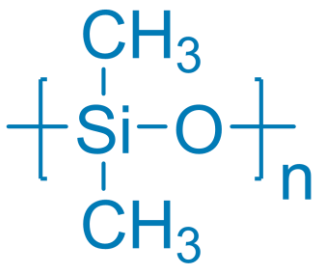
Balance of Additives and Base Oil



Other Additives

Anti-foamant

High viscosity silicone fluid to prevent foaming



Demulsifiers

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

Emulsifiers

Typically used in metal-working applications to form an emulsion

Other Additives

Rust inhibitors

Surface coating or improving acid neutralisation – especially in factory-fill oils

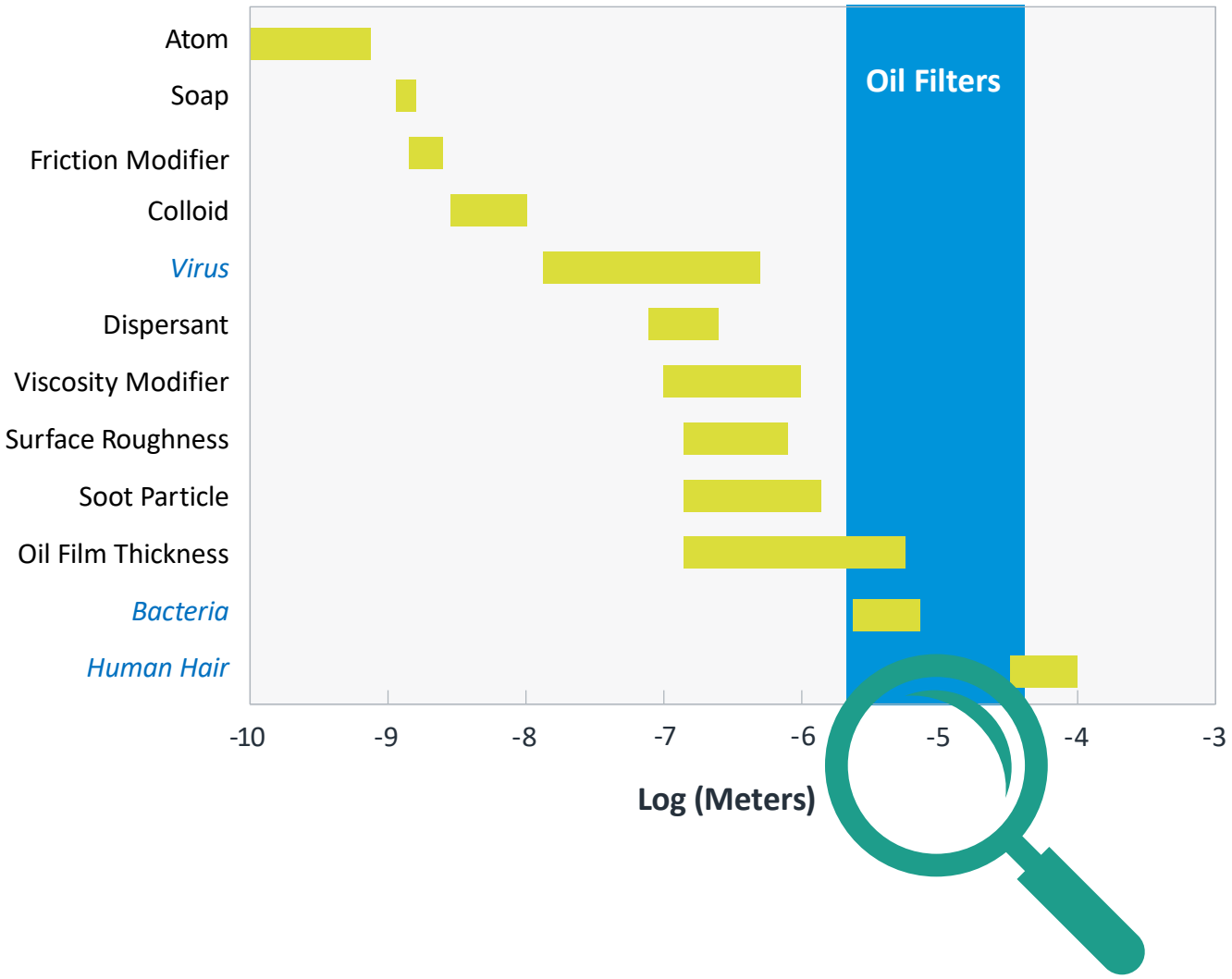
Corrosion inhibitors

Film-forming agents as tolyl triazole

Seal compatibility agents

Control oil polarity

Relative Sizes



Conclusion

Benefits

- ✓ Enhanced lubricant performance
- ✓ Minimisation of destructive processes
- ✓ Extended engine and oil life time

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