Infineum

Additive components

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Outline

1

Overview of Additives

Why are additives needed?

Functions of engine oil

2

Engine Processes and Additives

Oxidation and Antioxidants

Acids and Detergents

Deposits and Dispersants

Wear and Anti-Wear

Friction and Friction Modifiers

3

Formulation

Putting it all together

What's in the bottle*?

=

Base Stock	Ensures fluidity and adds performance
Viscosity Modifier	Changes temperature response
Detergent	Neutralizes acids and prevents deposits
Dispersant	Keeps everything soluble
Anti-Oxidant	Reduces and delays oxidation
Anti-Wear	Reduces abrasive wear
Friction Modifiers	Reduces (or increases) friction
Others	As needed for specialized products

ADDITIVE PACKAGE

Many other, more specialized additives

*Not all oils have all components

Functions of additives

Make "oil" work

Base stock by itself is not good enough for most applications

Tailor base oils for different applications

The same base stock can become PCEO, HDDO, ATF, Industrial Oil, *etc*., depending which additives are used

There are some limitations

Perform two critical functions:

1. Minimize destructive processes

Oxidation, wear, friction, corrosion, *etc*.

2. Confer beneficial properties

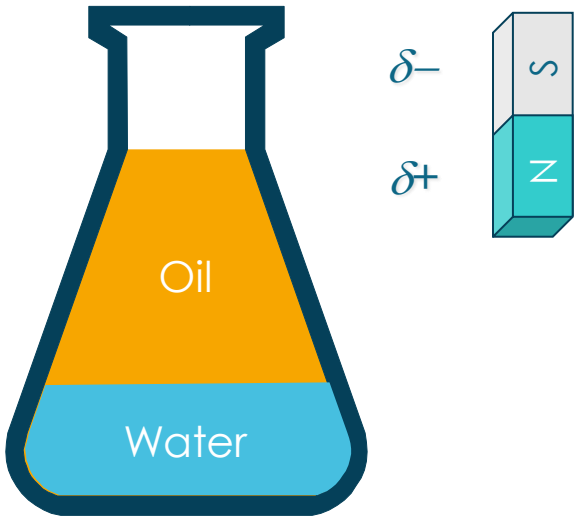
Lubricity, cleaning, *etc*.

Polarity

- **Oil and Water Do Not Mix!**
- Water is a **polar** molecule
  - Oxygen has greater affinity for electrons
    - Becomes partially negative
  - Molecule is neutral, but has separation of charge
    - Hydrogen becomes partially positive
- Oil is a **non-polar** molecule
  - Carbon and hydrogen have roughly same affinity for electrons
  - Molecular symmetry further reduces polarity

More "like water"

More "like oil"



The challenge

Engine lubricating oils are non-polar

- Hydrocarbons

More "like oil"

More "like water"

How to make them mix?

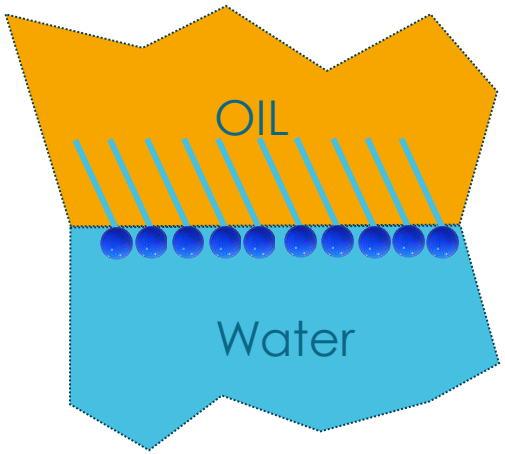
Engines and their contents are polar

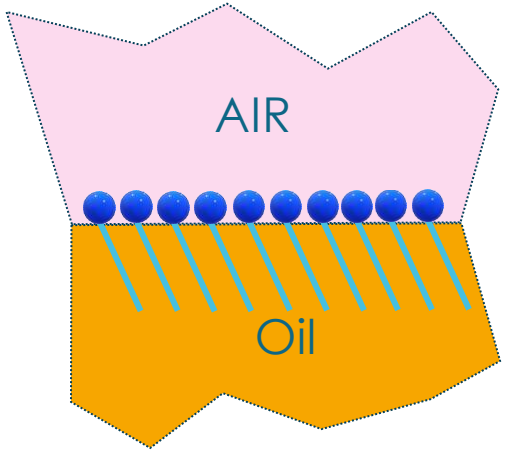
- Metal surfaces
- Oxidation products
- Soot
- Sludge
- Varnish
- *etc.*

Surfactants

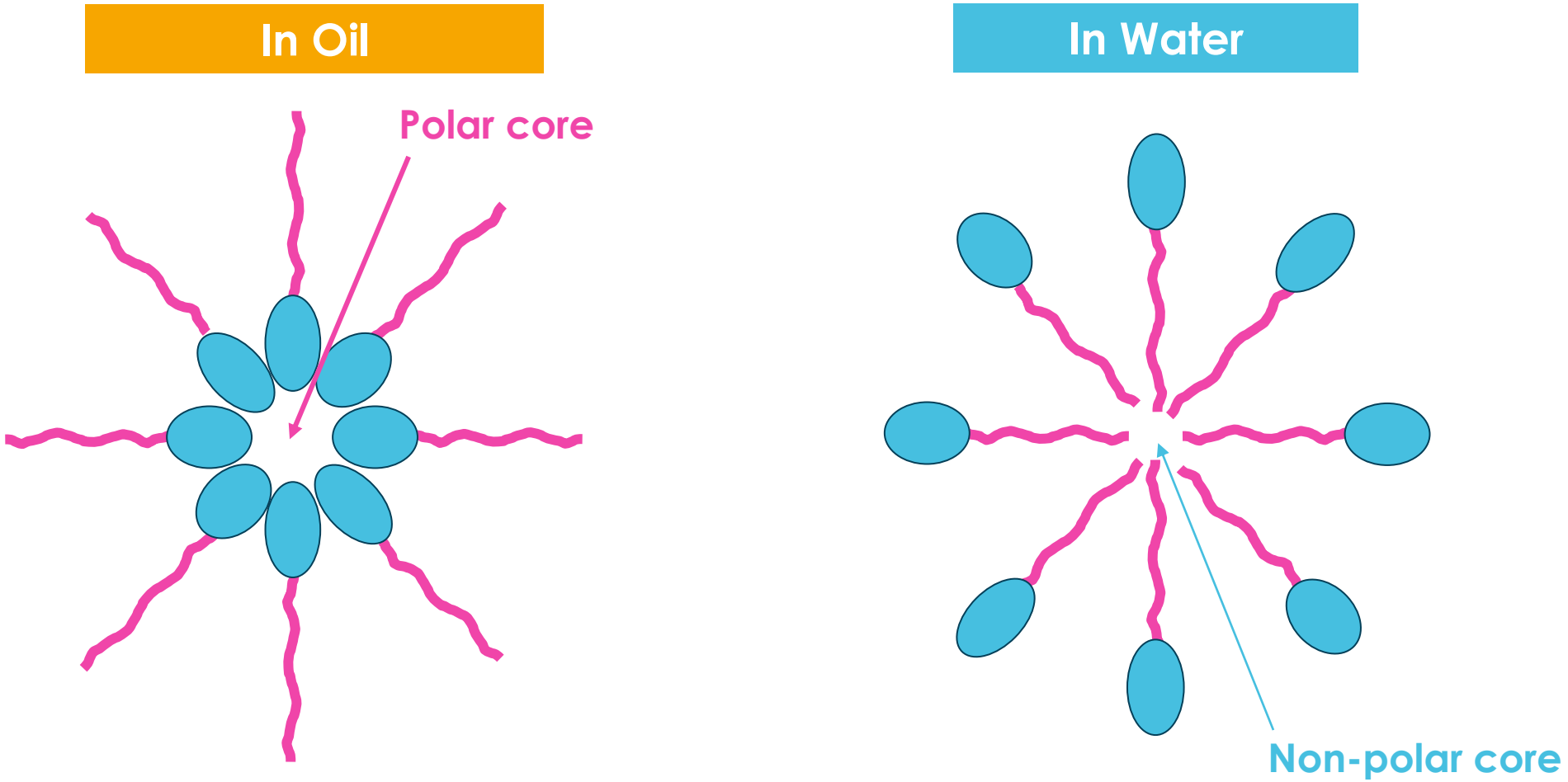
- Molecules with both polar and non-polar sections

- Will orient based on polarity of medium
  - **Interface**
    - Where two phases meet
      - *e.g.*, oil and water
    - Polar ends in water
    - Non-polar ends in oil
  - **In bulk liquid ➔**





Micelles



In three dimensions, these form a spherical environment

Oxidation

What is oxidation?

Destruction of molecules by exposure to oxygen at elevated temperatures

- Technically, oxidation can occur without oxygen,
  but we don't need to consider those cases

Initiated by Radicals

- Molecular fragments with an unpaired electron
- Very unstable and reactive

Radicals attack and "pull apart" the base stock and other molecules

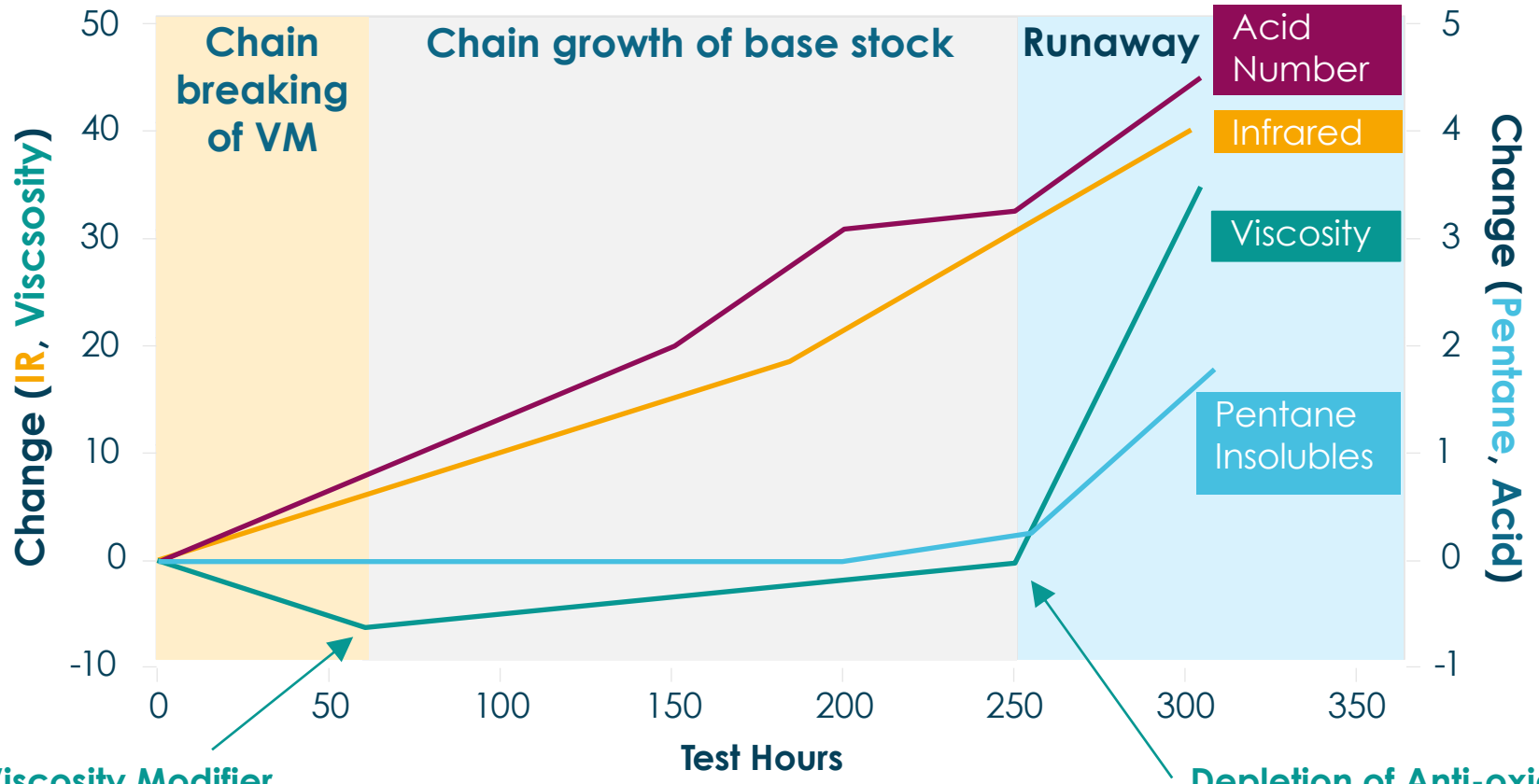
- To pair their lone electron

The process can be catalyzed by metals

- Catalyzed = Accelerated

Indicators of oxidation

Aluminum Beaker Oxidation Test (ABOT)



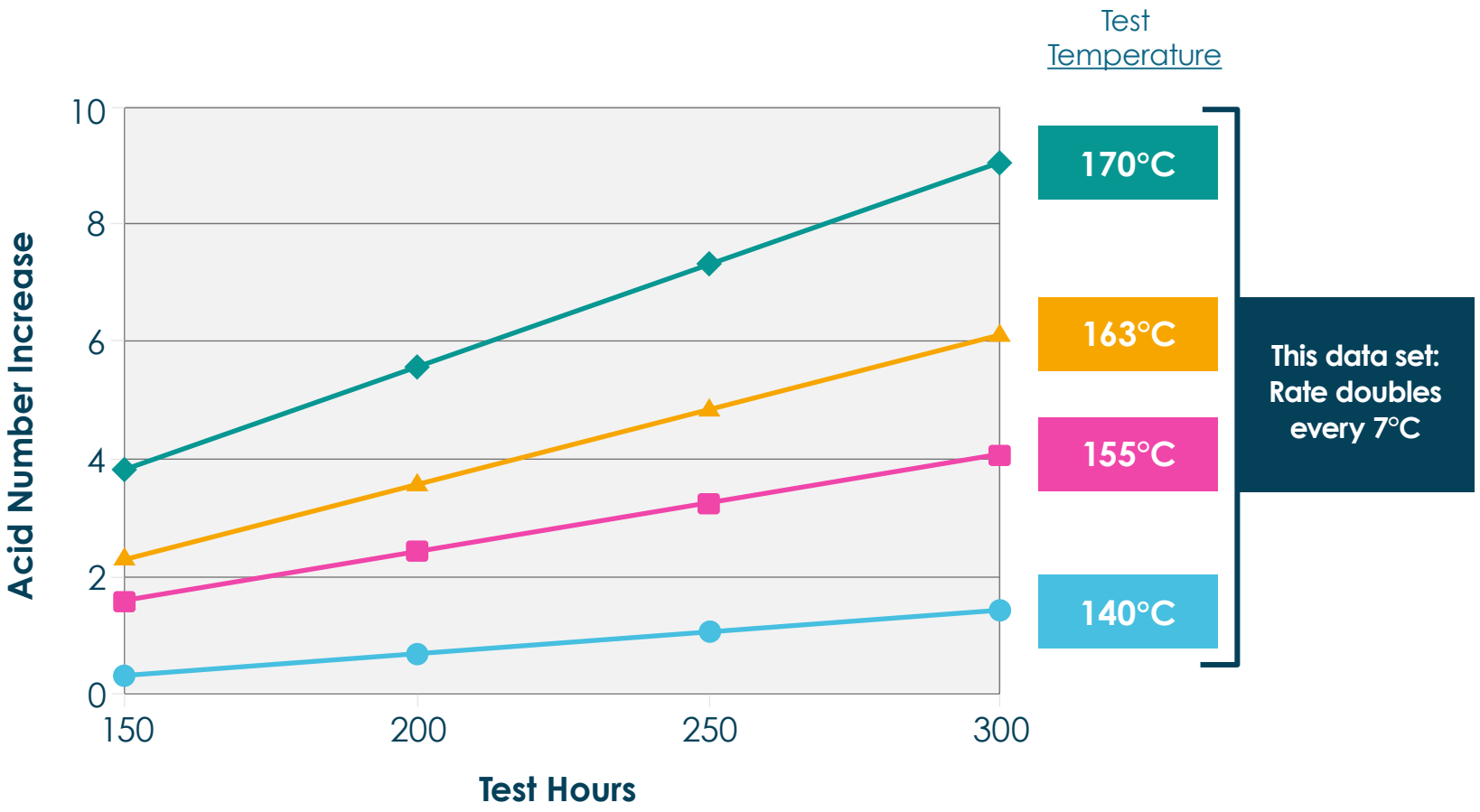
NOT TO SCALE
Relative sizes and timings of decrease and increase will vary

Breaking of Viscosity Modifier
Followed by normal oxidation

Depletion of Anti-oxidant
Followed by runaway oxidation

Effect of temperature

Aluminum Beaker Oxidation Test (ABOT)



Rule of thumb:
Every 10°C increase in temperature doubles the rate of oxidation

Anti-oxidants
(or oxidation inhibitors)

Anti-oxidant

Oxidation

Destruction of molecules by exposure to oxygen at elevated temperatures

Negative consequences of oxidation

- Viscosity increase
- Acid formation
  - Attack engine surfaces
  - Particularly copper-lead bearings
- Insolubles
  - Form deposits
  - Sludge and varnish
- Additive depletion

Function of anti-oxidants

Reduce and control oxidation

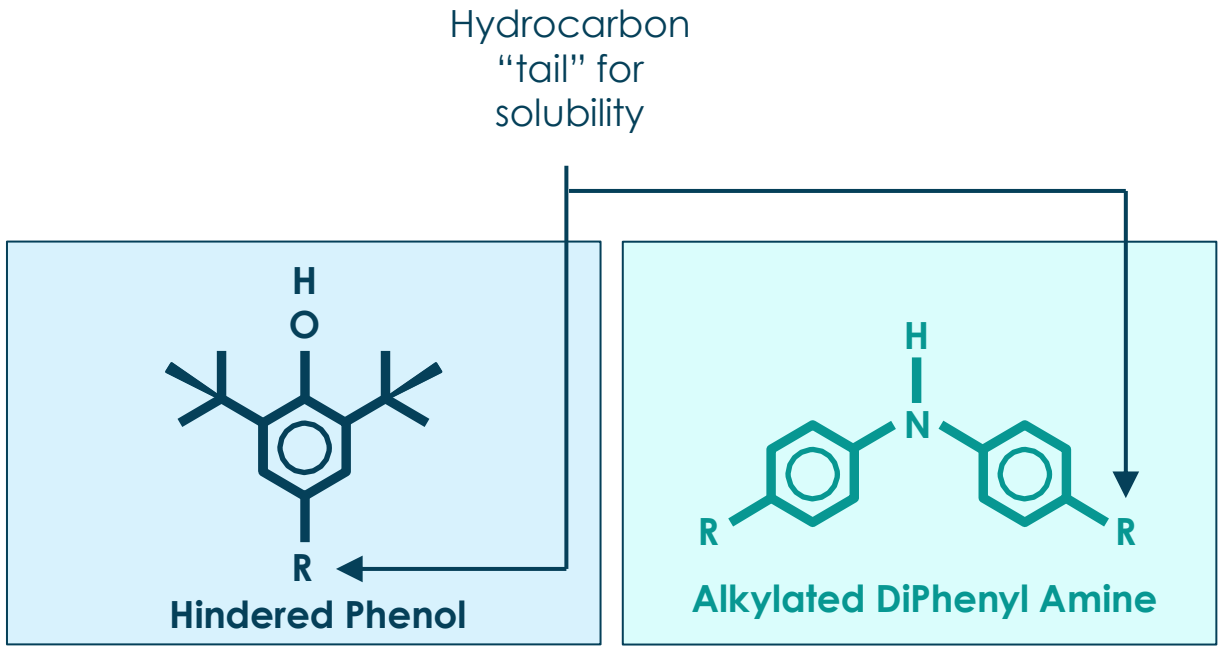
Compositions

Hindered Phenol

Alkylated DiPhenyl Amine (ADPA)

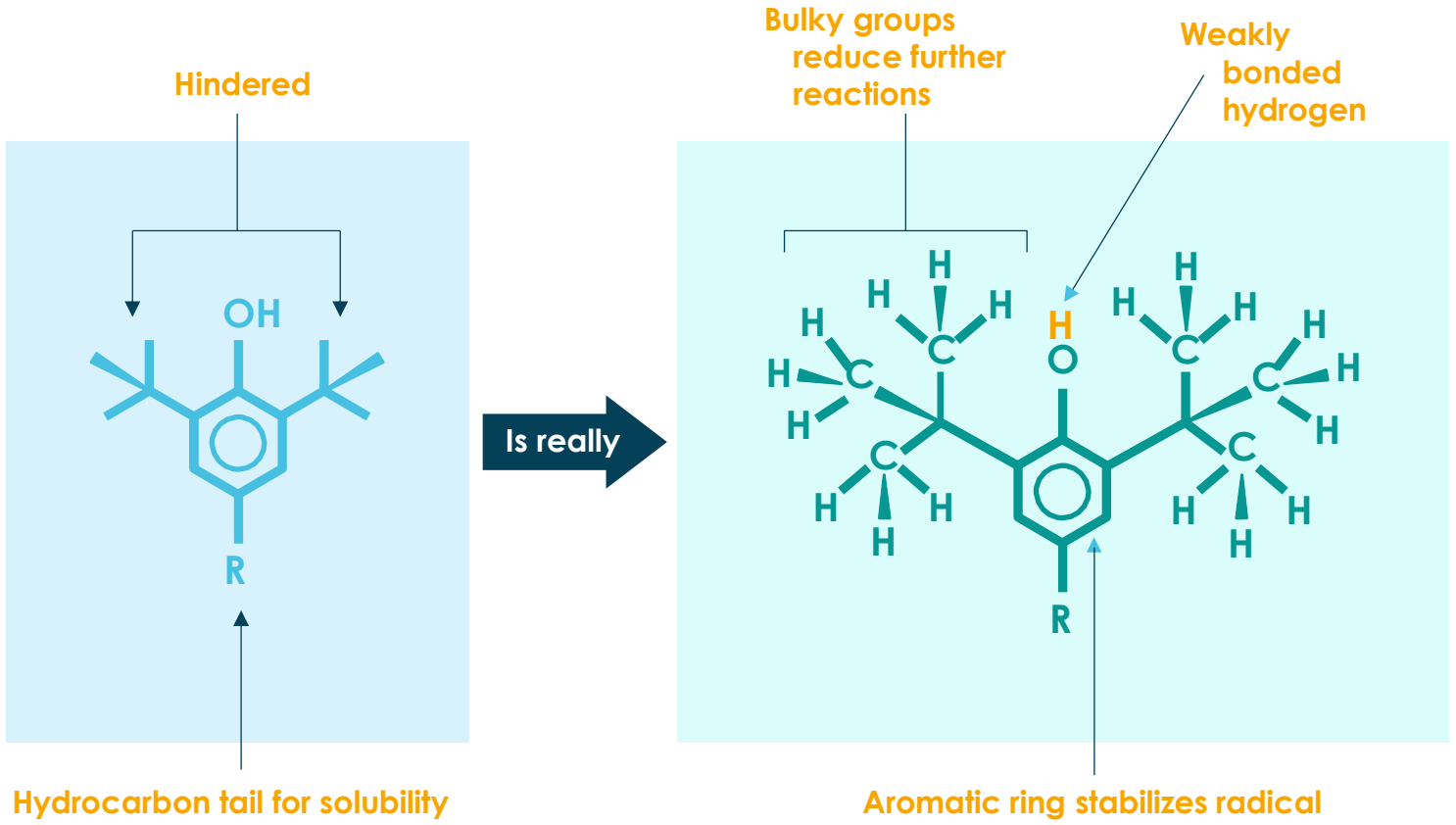
Some sulfur compounds

Certain metal compounds (*e.g.*, Molybdenum)



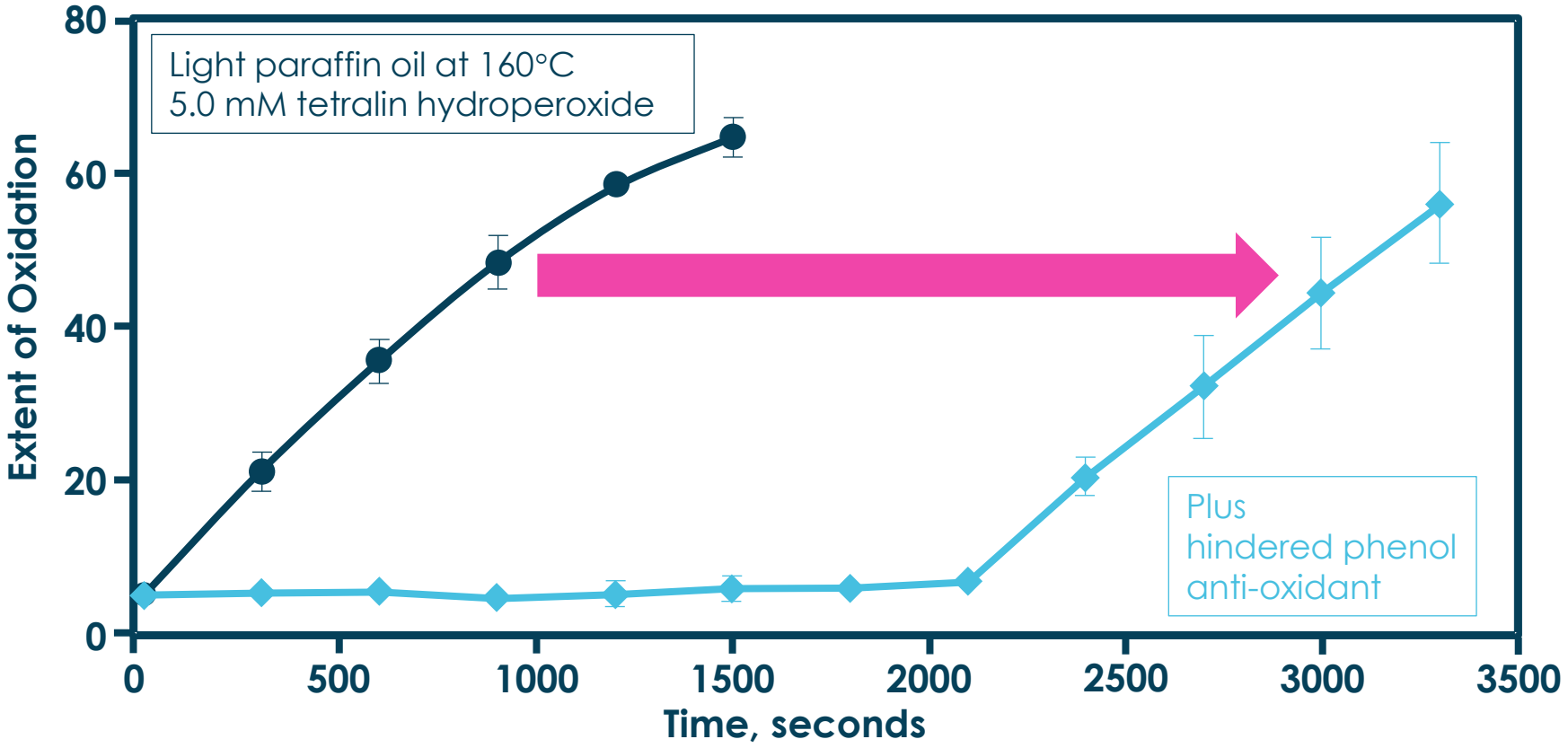
How do hindered phenols work?

- Easily lose a hydrogen to form a **stable** radical
  - Stabilized by aromatic ring
- Further reaction inhibited by molecular structure



Anti-oxidant example

Antioxidant displays "Induction Time" to delay onset of oxidation
Followed by "Break-Point" and resumption of oxidation



Source: E. A. Haidasz, *et. al*. (University of Ottawa), J. Am. Chem. Soc. 2016, 138 (16), pp. 5290-5298

Detergents

Detergents

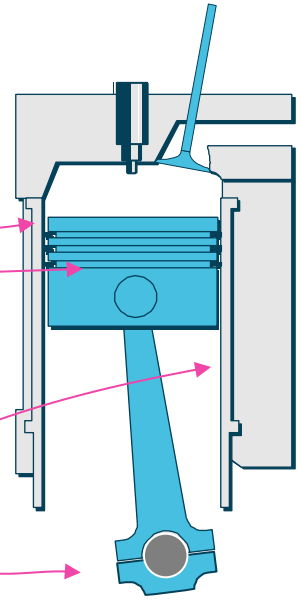
Functions

Neutralize acids

- Combustion products: Sulfur and Nitrogen (strong) acids
- Oxidation products: organic (weak) acids

Reduce high-temperature deposits

- Prevent piston ring sticking
- Prevent lacquer, varnish, and carbon
- Prevent bore polish (abrasive or corrosive liner wear)



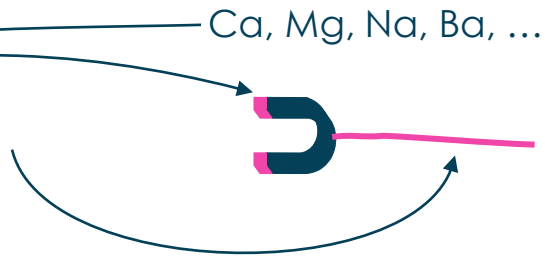
Mechanisms

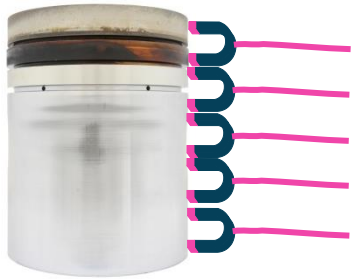
- Basic (alkaline) to neutralize acids
- Surface-active to reduce deposits

Composition

Basic metal with organic "tail"

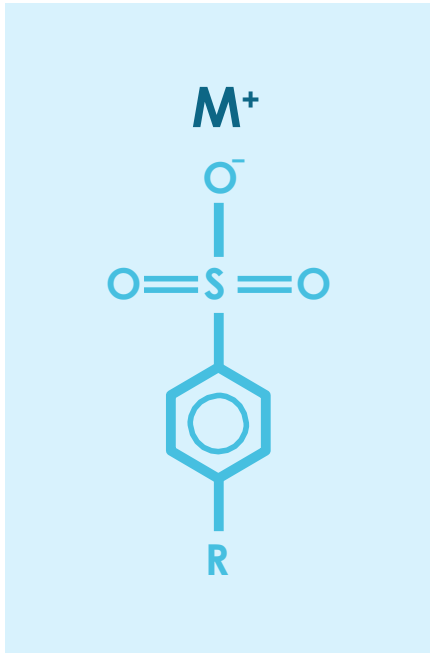
- Sulfonate
- Phenate
- Salicylate



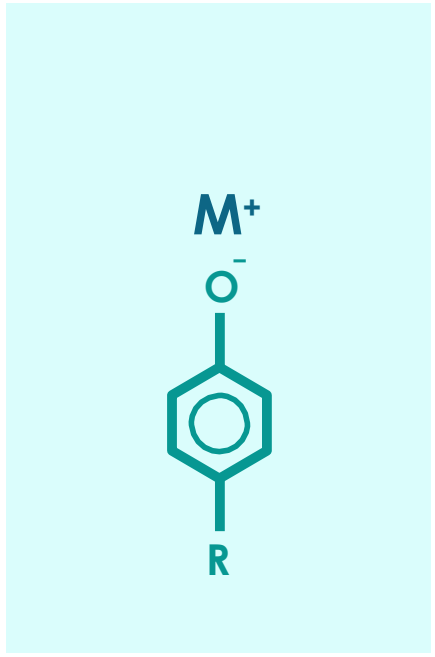


Deposit prevention

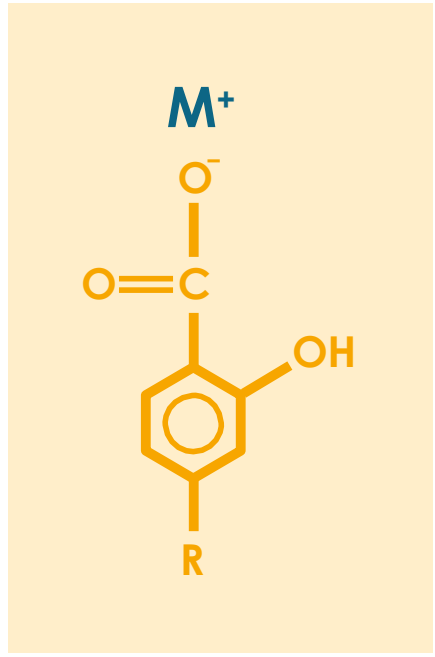
Typical lubricant detergents



Sulfonate



Phenate



Salicylate

"M" is a metal, such as calcium, magnesium, sodium, *etc*.
"R" is a hydrocarbon "tail" for solubility

Sash and ash

Detergents contain metal

Calcium, magnesium, sodium, *etc*.

When burned,
they leave a residue

Called "Ash"

Typically measured as
"sulfated ash"

React the oil with sulfuric acid and burn it

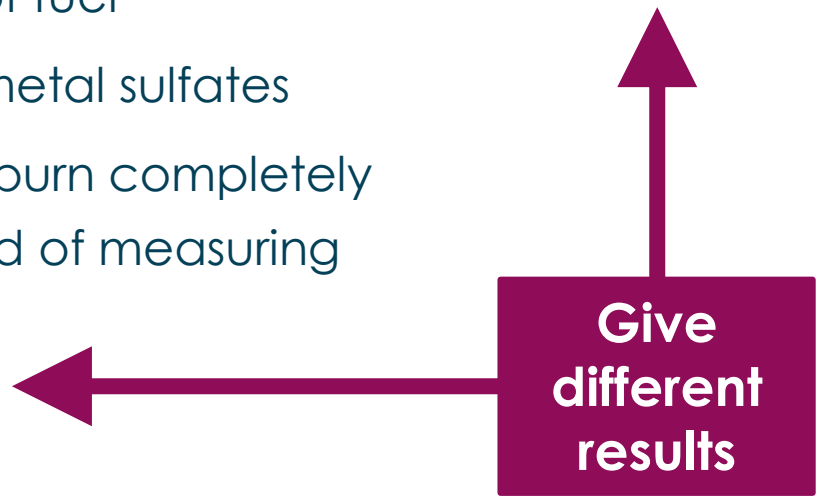
- Simulates burning in the presence of fuel

Metals become metal sulfates

- Hydrocarbons burn completely
- Indirect method of measuring metal content
  - **ASTM D874**

Note:
There is also a test for
"ash"

- Without sulfuric acid
  - **ASTM D482**



Base number

Base Number (BN) is a quantitative measure of alkalinity

Formally called Total Base Number (TBN)

Concentration of base

Expressed as equivalent KOH neutralizing ability (mg KOH/g units)

Add acid until solution is neutralized

A titration

Two test methods

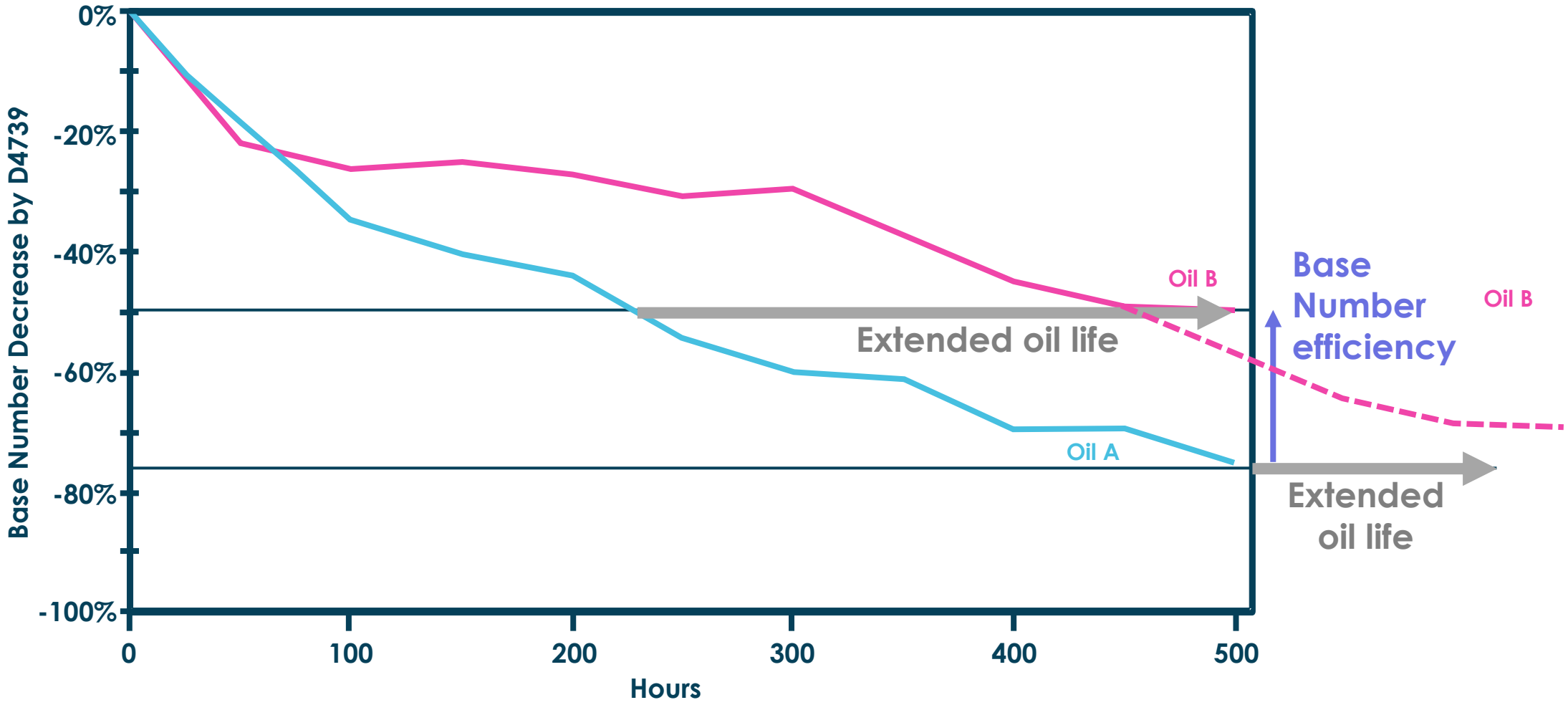
$HClO_4$
pka = – 10

- ASTM D2896
  - Uses perchloric acid, an extremely strong acid
  - Measures "everything"
    - Strong bases, weak bases, some salts, *etc*.
  - Used for fresh oils
  - Gives higher numbers

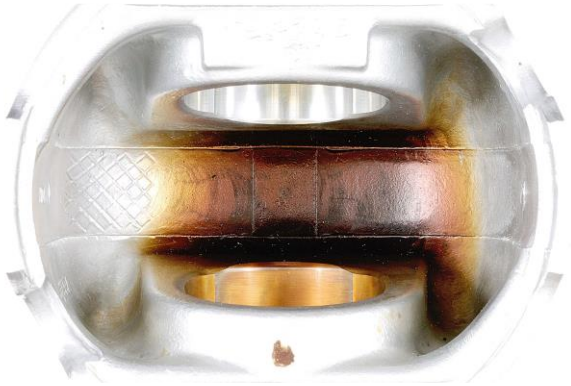
HCl
pka = –7

- ASTM D4739
  - Uses hydrochloric acid, a strong acid
  - Measures "effective"
    - Strong bases
  - Used for in-service oils
  - Gives lower numbers

Detergent example – Acid neutralization



Detergent example – piston cleanliness



Bad Results

Good Results

Dispersants

Dispersants

Definition

- Also called "Ashless Dispersants"
- "Ash" ("SASH") means "contains a metal"
  - Sodium, calcium, magnesium, zinc, *etc*.
- Dispersants don't contain metals
  - Only carbon, hydrogen, nitrogen, oxygen, boron, *etc*.

Fuel additives call these "detergents"

Functions

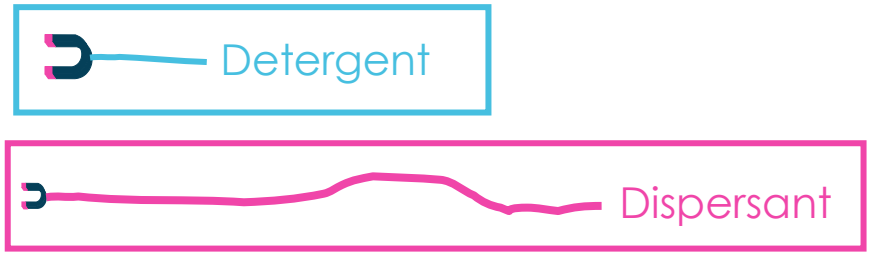
- Suspend (dissolve) soot
- Inhibit and suspend sludge
  - Sludge = oil + water + oxidation + dirt = "black mayonnaise"
- Reduce formation of deposits
- **Maintain cleanliness**
  - Engine oil is a trash collector
  - Oil change is "taking out the garbage"

Diesel engine oils

Gasoline engine oils

Composition

- Long chain hydrocarbon for solubility
- Small (non-metal) polar "head group" to stick to soot and deposits

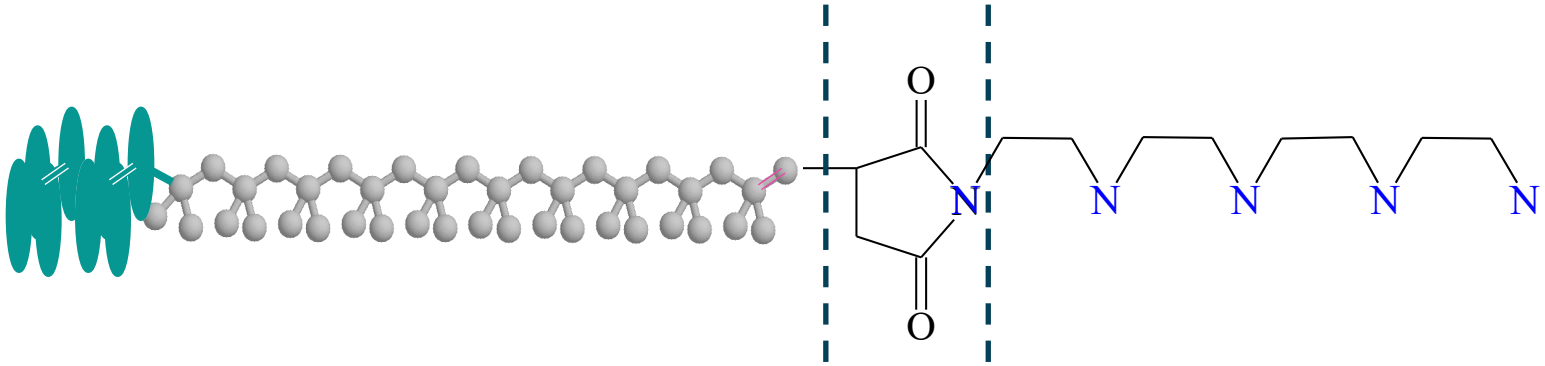


Common Dispersant

PolyIsoButylene Succinic Anhydride/PolyAMine

PIBSA/PAM

Dispersant composition



Non-Polar tail

Bridging Group

Polar head

Example:

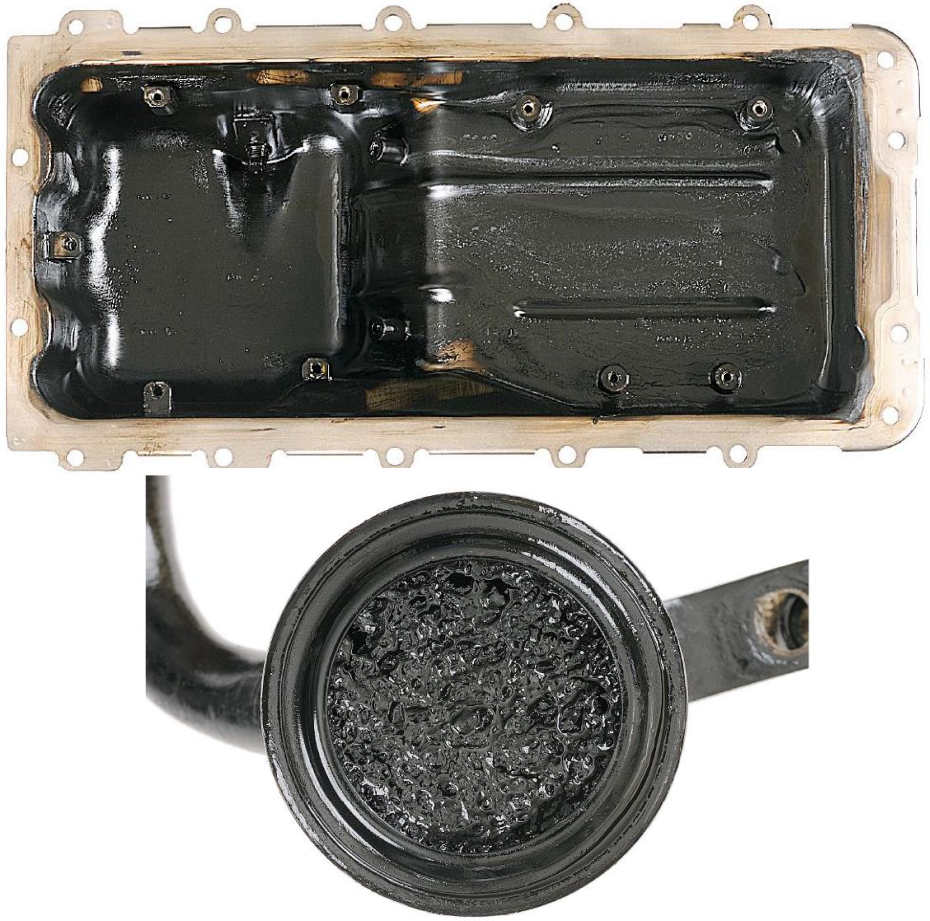
Poly IsoButylene

Succinic Anhydride

PolyAMine

= PIBSA/PAM

Dispersant example



Bad Results

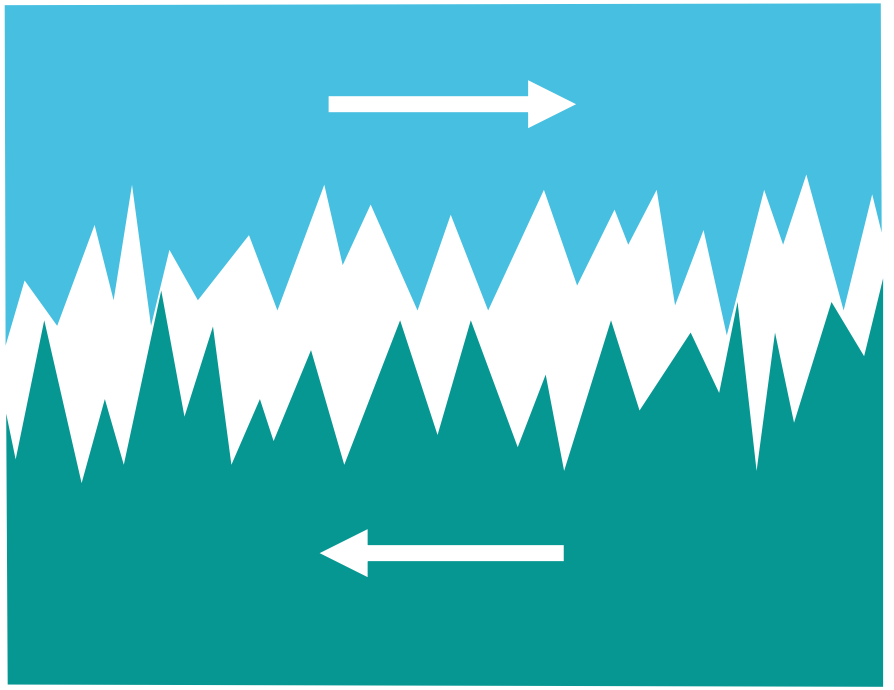
Good Results

Friction and wear

Friction and wear

Both are caused by relative motion between surfaces

- Friction is a loss of ***energy***
  - Dissipated as heat
  - Heat can be damaging
    - Increased rate of oxidation
    - Weakened engine parts
- Wear is a loss of ***material***
  - Changes geometry of contacts
  - Changes equipment performance
  - Introduces metal oxidation catalysts
- Often appear together, but they are different things



Antiwear agents

Antiwear agents

Function

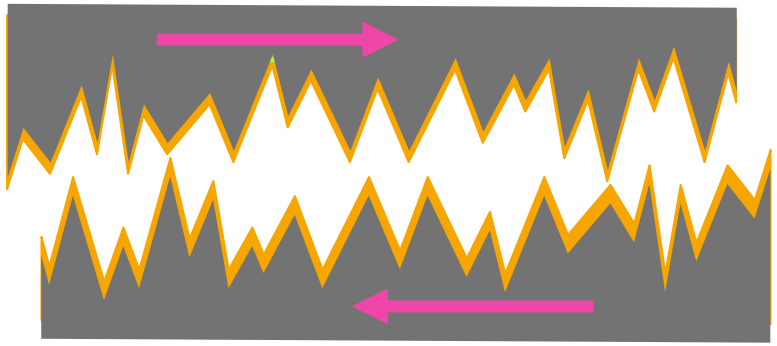
- Reduce surface-on-surface wear

Mechanism

- Decompose on the surface to form protective film
- Heat caused by friction
- "Anti-flux" – dirty surface prevents adhesion

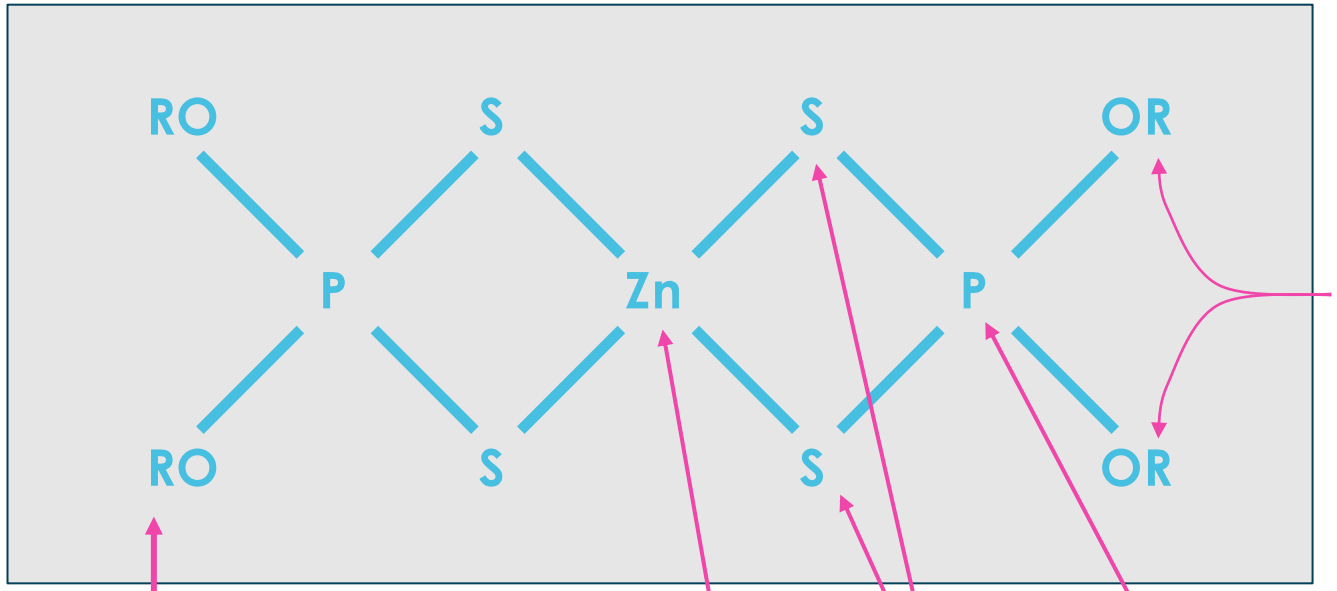
Composition

- Zinc-containing (ZDDP) ➔
  - Engine oils
- Ashless phosphorus based ➔
  - ATF, gear, aviation
- Ashless non-phosphorus
  - Railroad and other special cases
- Extreme pressure
  - Gear oils



Consequence:

Zinc dialkyl dithiophosphate (ZDDP)



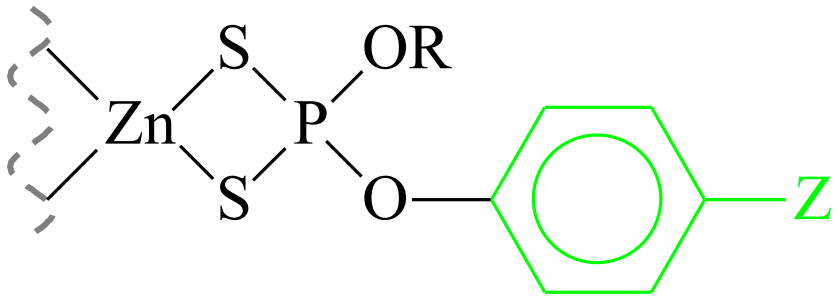
Glossary
Thio = sulfur in Greek

Glossary
Alkyl group =
hydrocarbon missing one hydrogen
Can attach to other structures

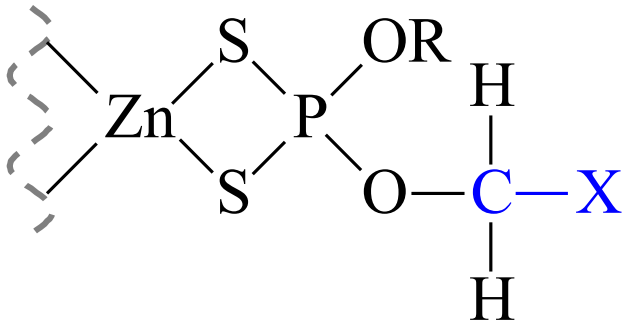
NOTE: Not exact chemical structure; for illustration only

ZDDP alkyl structures

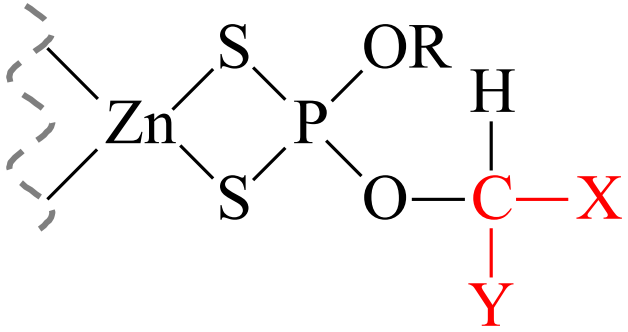
Alkyl type, length, and branching affect ZDDP performance



Aryl ZDDP – aromatic group



Primary ZDDP – one ‘alkyl’ group

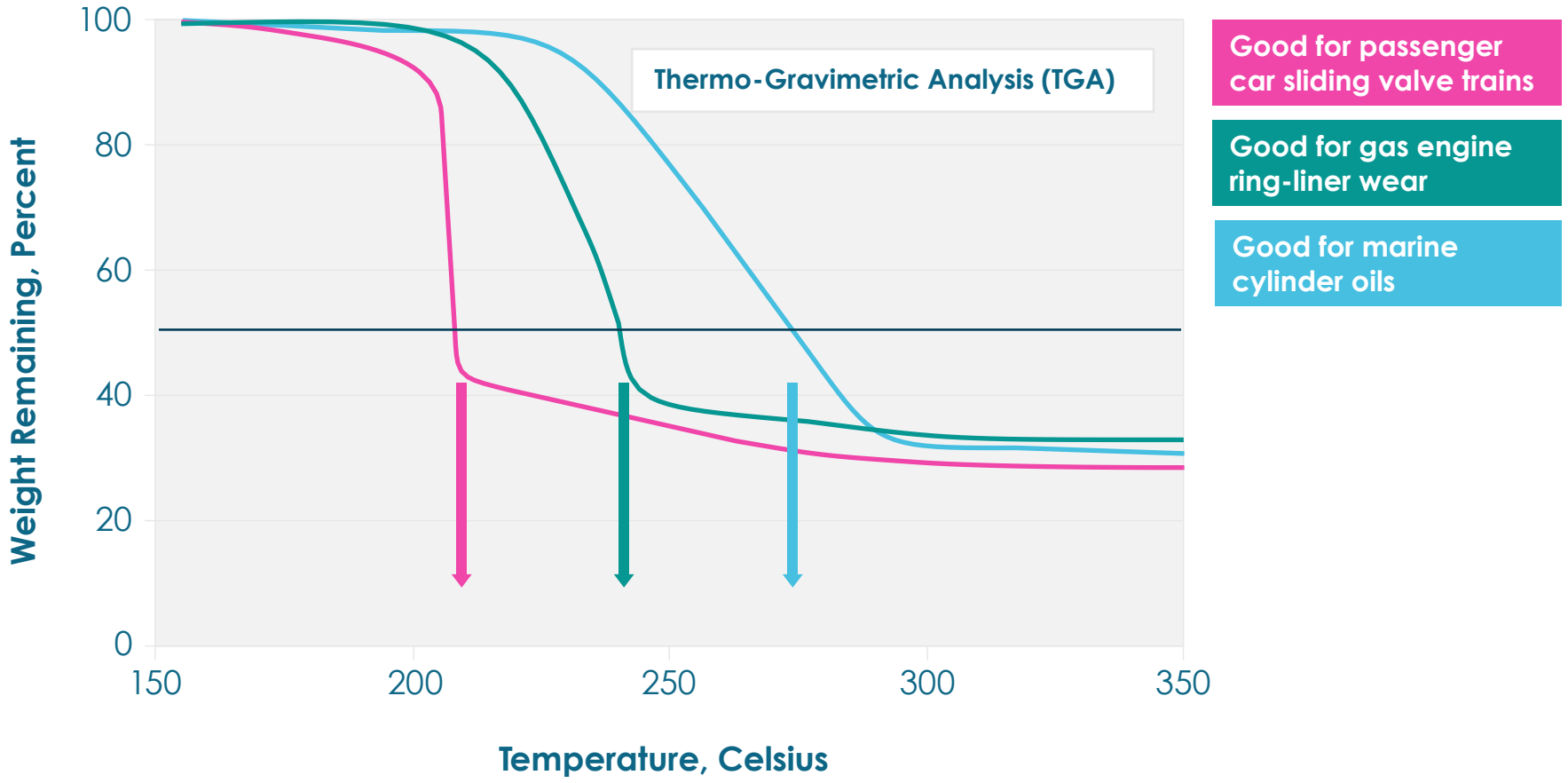


Secondary ZDDP – two ‘alkyl’ groups

Decreasing Decomposition Temperature

ZDDP decomposition

ZDDP decomposition temperatures highly dependent on method and conditions



Friction modifiers

What are organic friction modifiers?

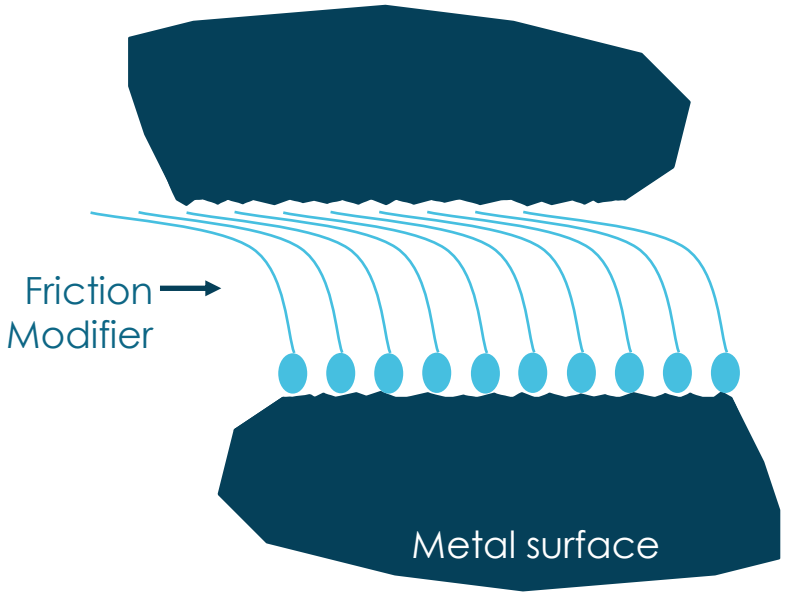
Function
- Reduce friction between moving surfaces

Mechanism
- Form a "springy" layer
- "Plush carpet" effect

Composition
- Straight chain hydrocarbons with polar ends
  - Stiff backbones
- Bond to metal surfaces
  - Rather than soot, for example

Consequence:

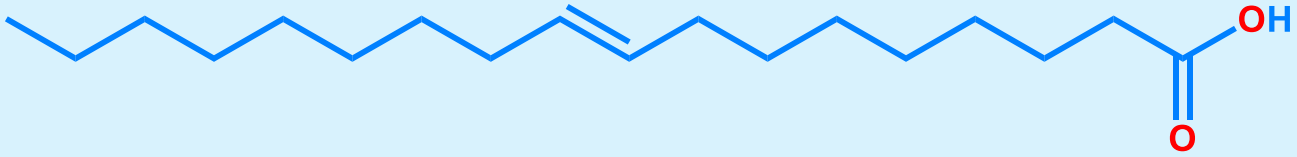
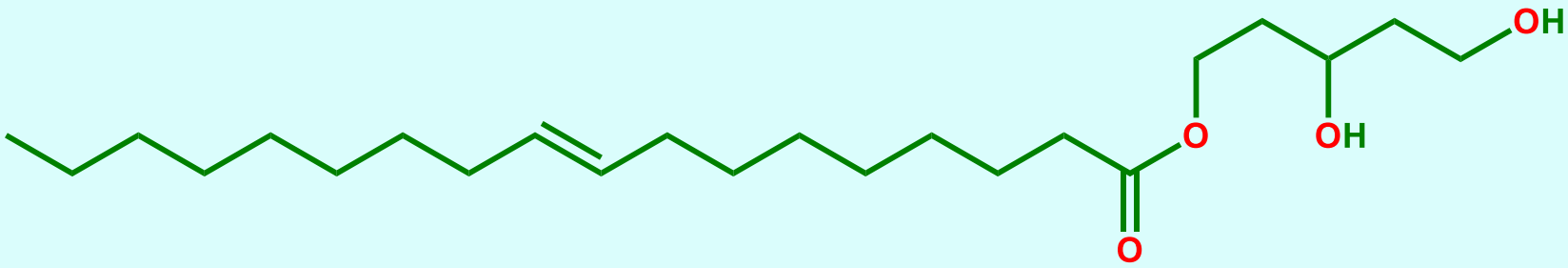
Fuel economy



Not to scale!

Friction modifier

Typical organic friction modifiers

Oleic acid	
Glycerol mono-oleate	
Oleylamide	

Solid friction modifiers

Structure

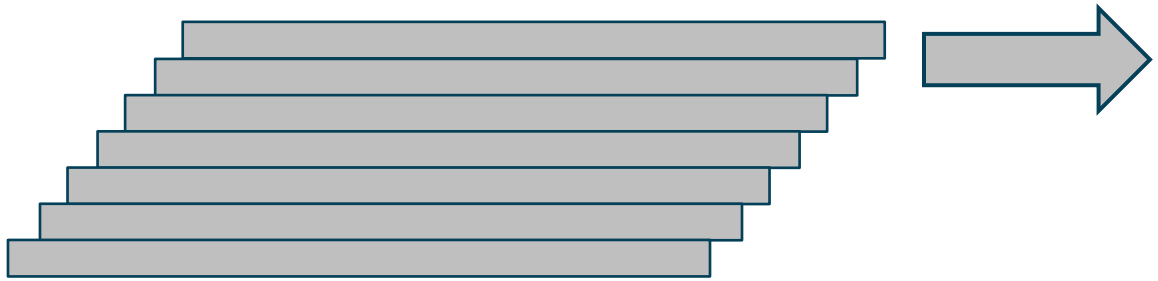
- Flat-plate molecular geometry
- Planes glide over each other

Examples

- Graphite
- Molybdenum disulfide

Alternative technology

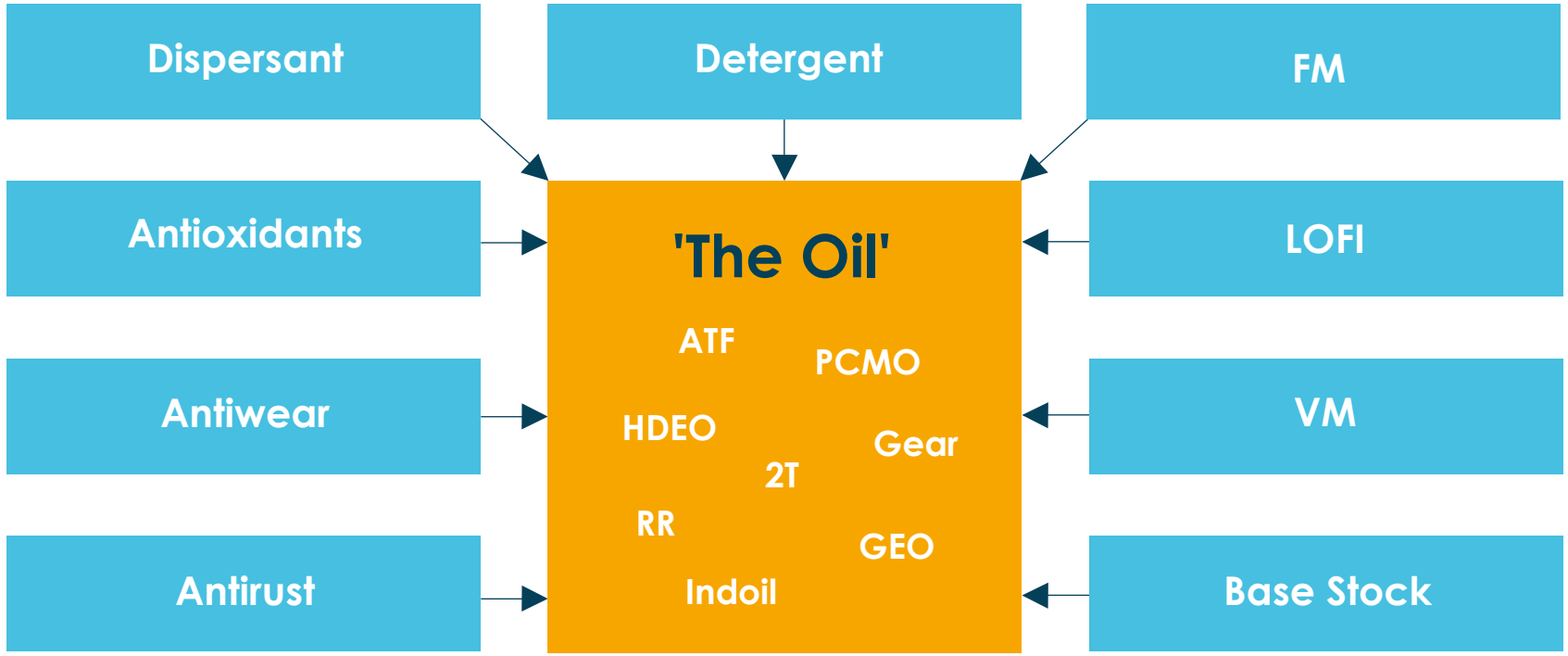
- Polytetrafluoroethylene
- PTFE
  - Teflon®
- Strong terminal bonds don't stick to other things



Formulation
(putting it all together)

Formulation science

The key is **balancing the additives for the application**:



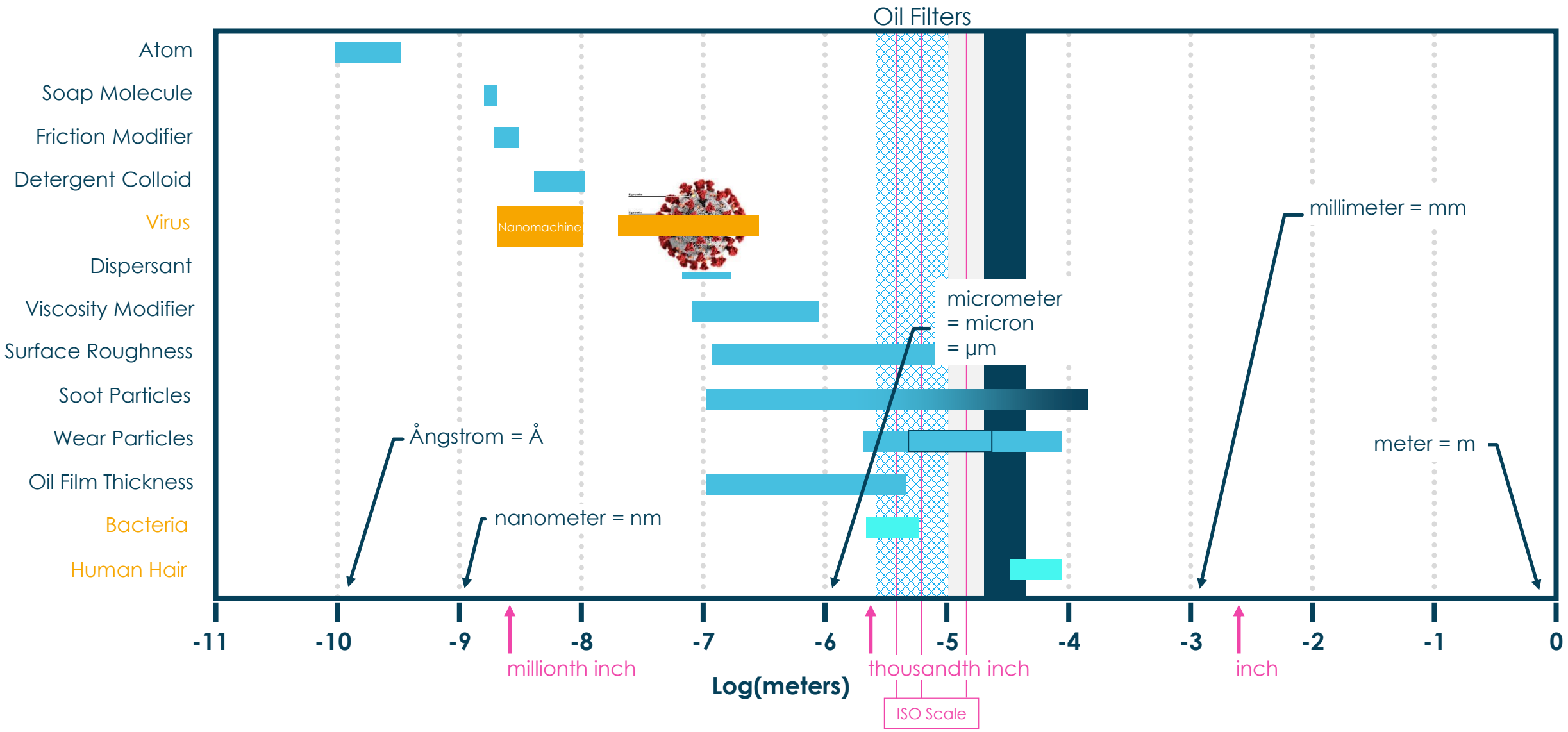
For more information:

"Lubricant Additives, Chemistry and Applications," L. R. Rudnick (ed.), Marcel Dekker, Inc., 2003
"Lubricant Chemistry, Technology, Selection, and Design," S.Q.A. Rizvi, ASTM MNL59, 2009
"Automotive Lubricants Reference Book (2e)," R.F. Haycock and J.E. Hillier, SAE PT-111, 2004

Thank you

Appendix

Comparison of additives



Formulating tomorrow together

Permissions