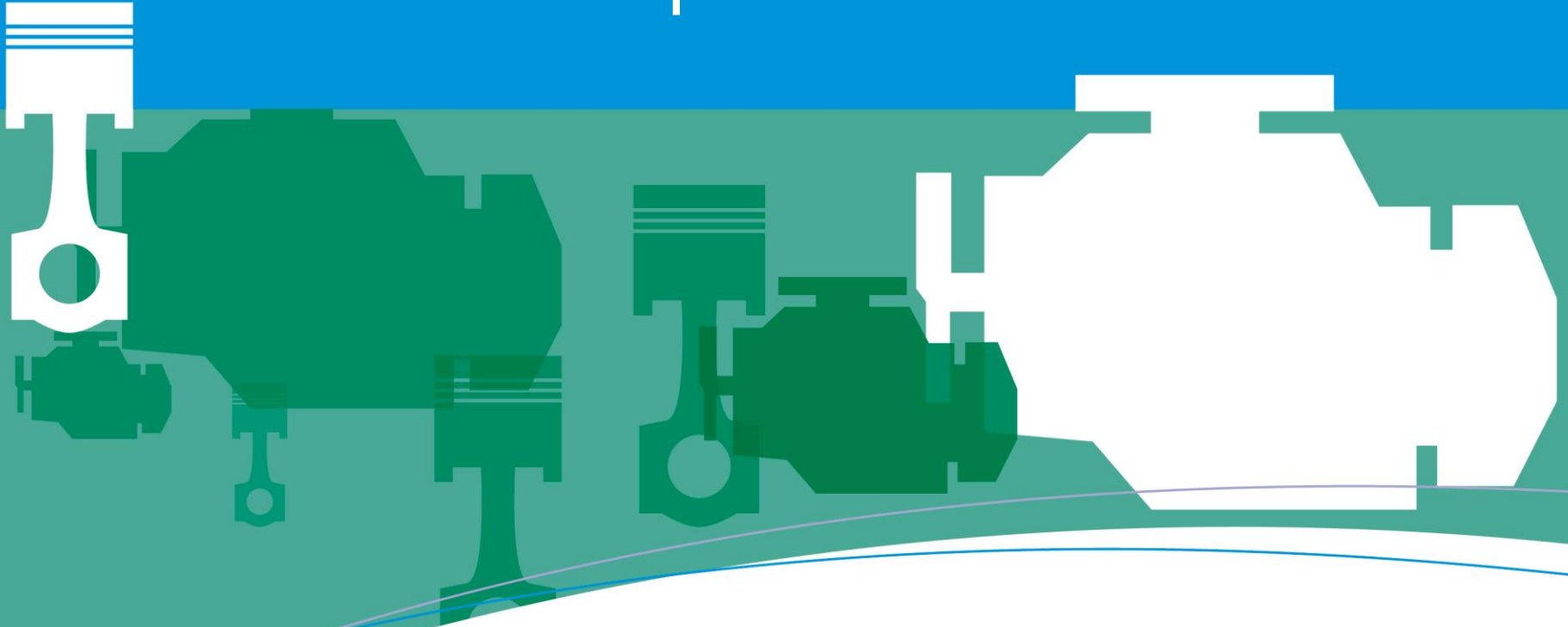


Performance you can rely on.

Additive components



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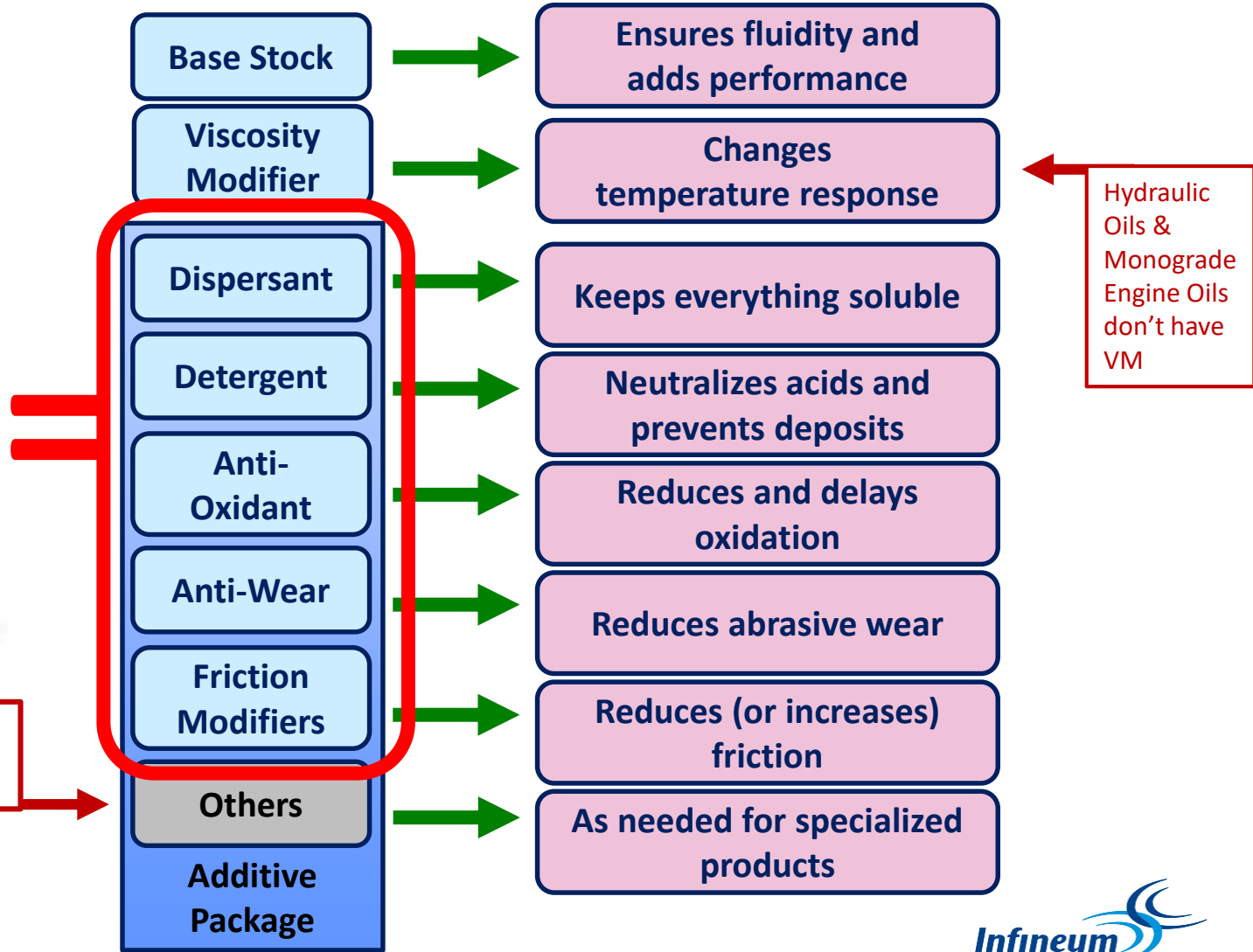


Outline

- Overview of Additives
 - Why they're used
 - Functions of engine oil
 - The Challenge
- Basic Concepts
 - Polarity, Surfactants, and Micelles
 - Colloids and Emulsions
 - Radicals and Reactions
- Engine Processes and Additives
 - Oxidation and Antioxidants
 - Acids and Detergents
 - Deposits and Dispersants
 - Wear and Anti-Wear
 - Friction and Friction Modifiers
- Formulation
 - Putting it all together



What's in the bottle*?



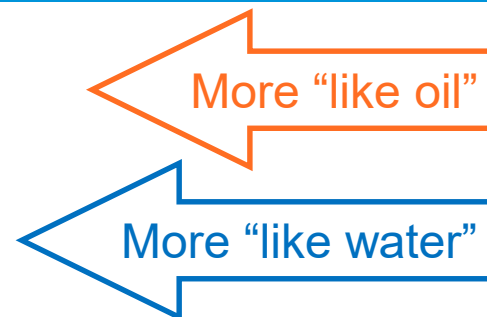
Functions of additives

- 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:
 - Minimize destructive processes
 - Oxidation, wear, friction, corrosion, *etc.*
 - Confer beneficial properties
 - Lubricity, cleaning, *etc.*



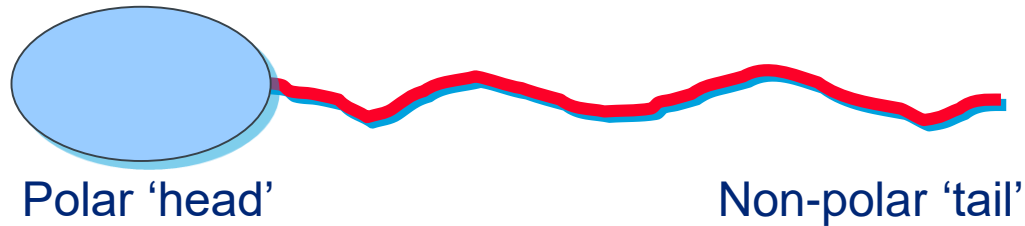
The challenge

- Engine lubricating oils are **non-polar**
 - Hydrocarbons
- Engines and their contents are **polar**
 - Metal surfaces
 - Oxidation products
 - Soot
 - Sludge
 - Varnish
 - *etc.*
- **How to make them mix?**

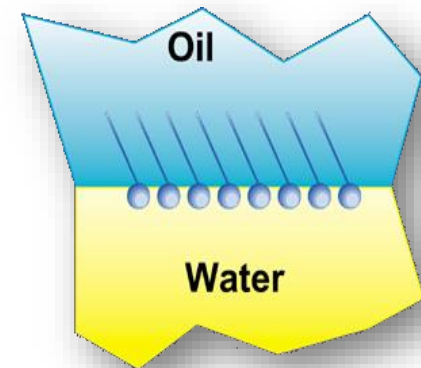


Surfactants

- Molecules with both polar and non-polar sections

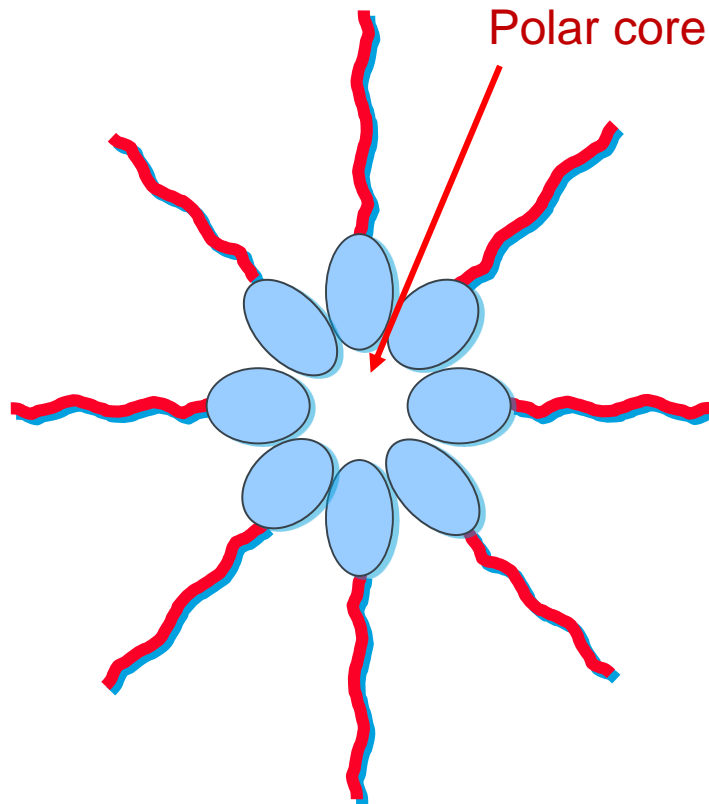


- Will orient based on polarity of medium
 - **Interface**
 - Where two phases meet
 - e.g., oil and water
 - Polar ends in water
 - Non-polar ends in oil
 - **In bulk liquid** →

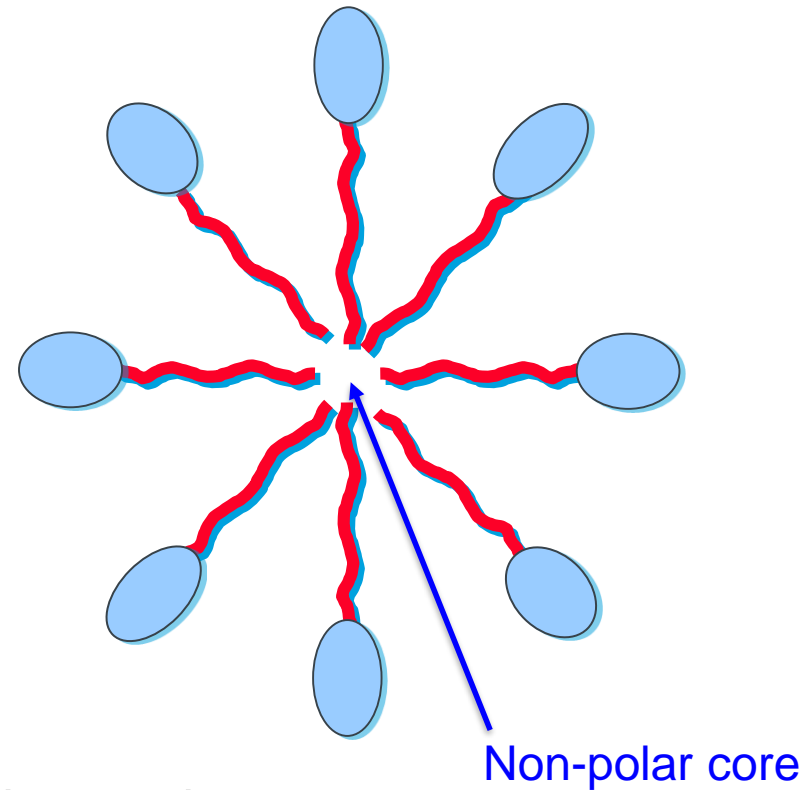


Micelles

In Oil

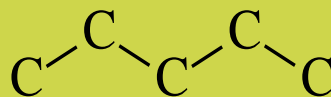
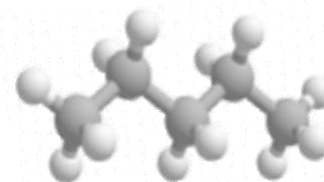
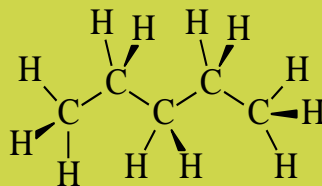
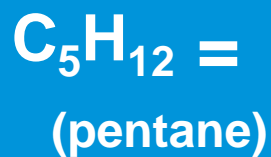


In Water



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

Chemistry shorthand

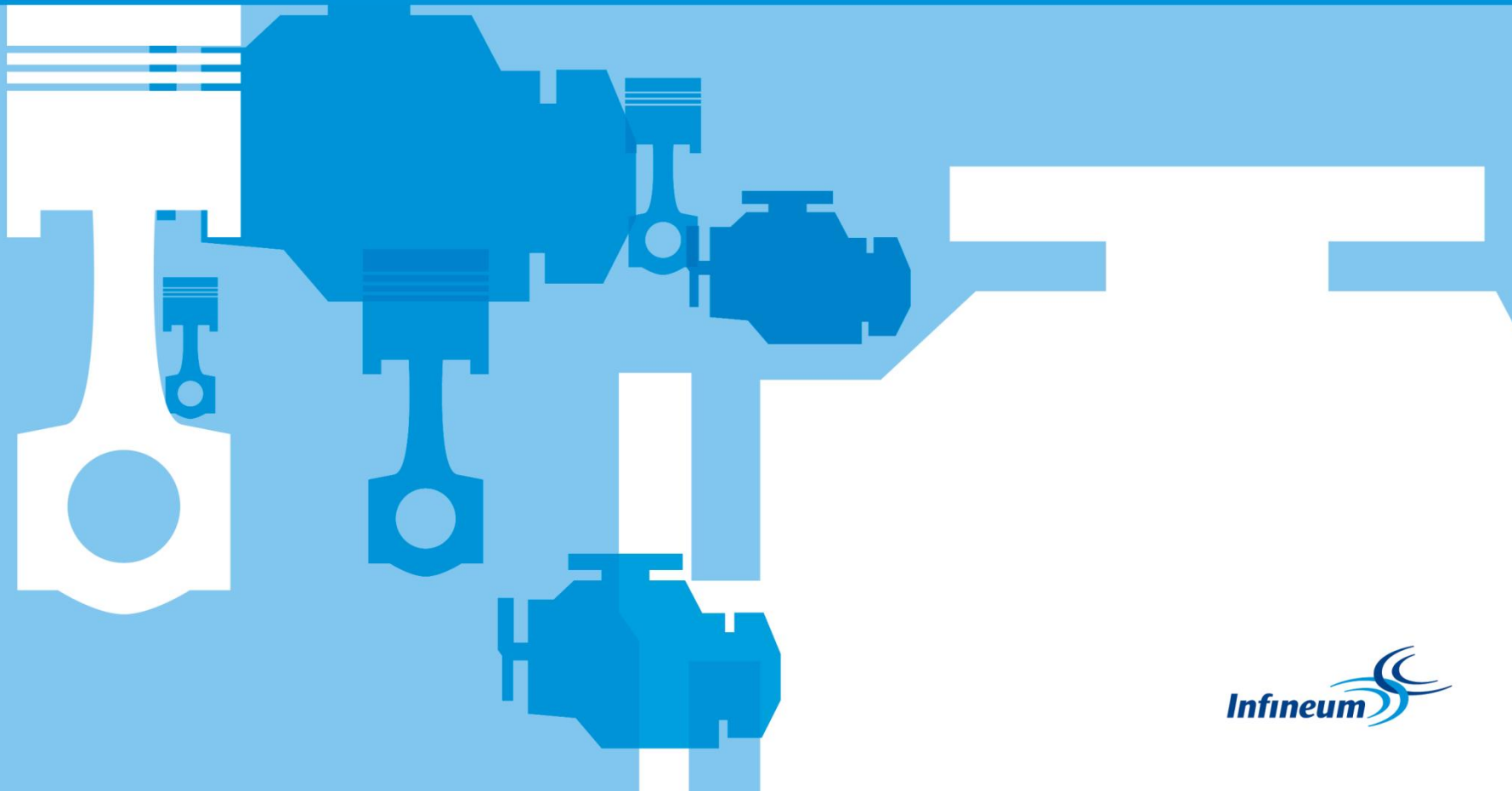


RH is really R:H



Unpaired electron = **Radical**

Oxidation

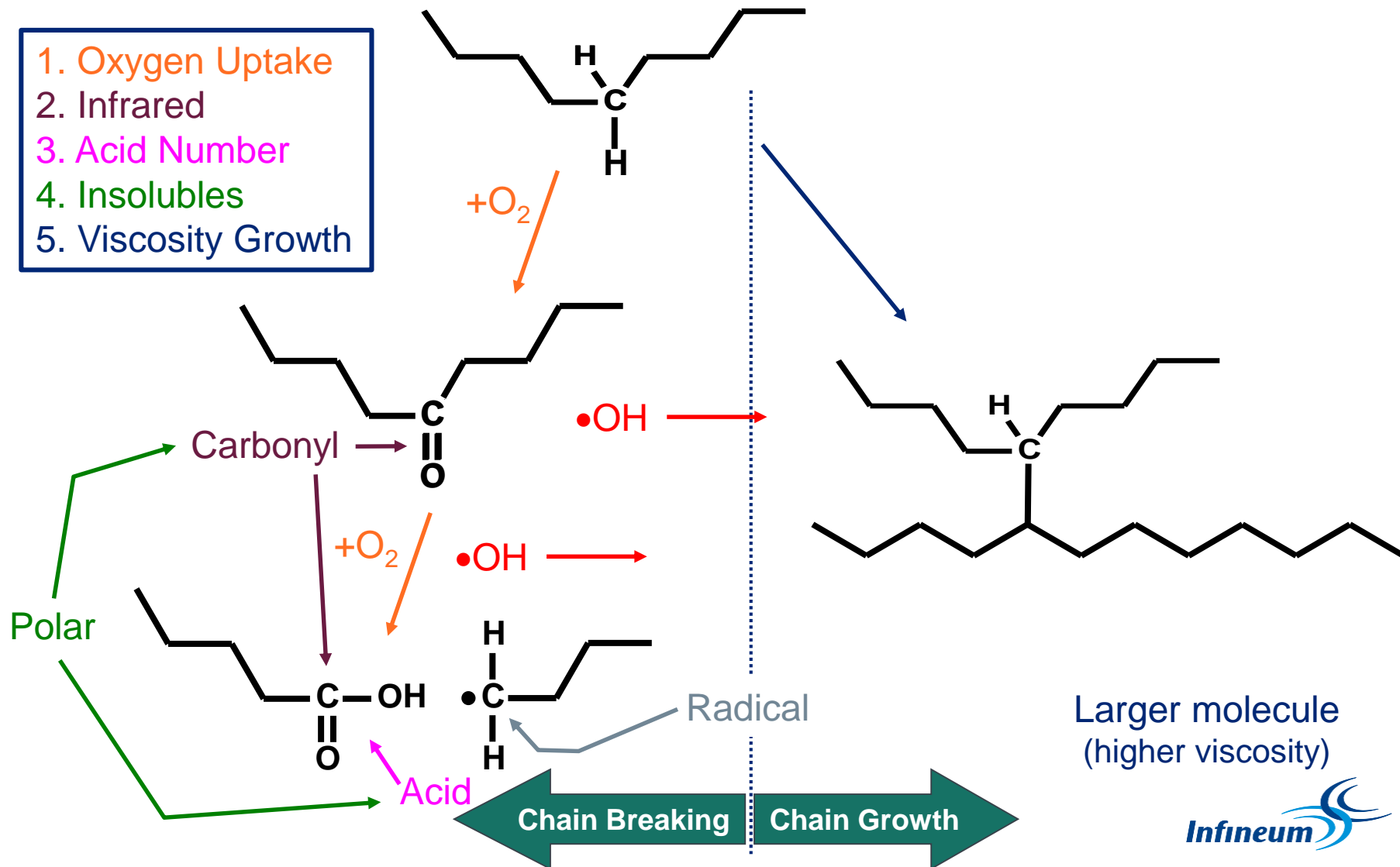


What is oxidation?

- 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 molecules
 - To pair their lone electron
- The process can be **catalyzed** by metals
 - Catalyzed = Accelerated

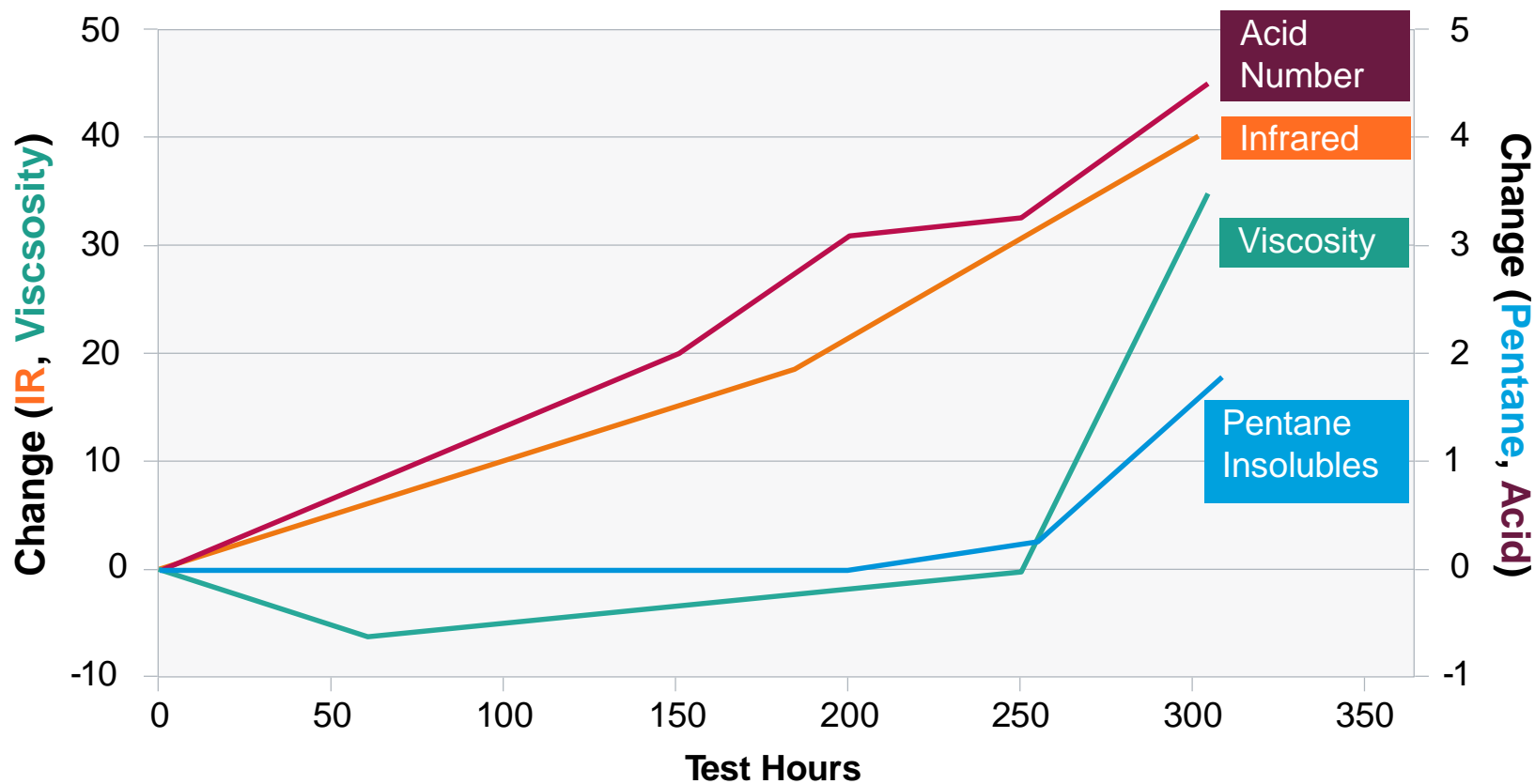


How to measure oxidation

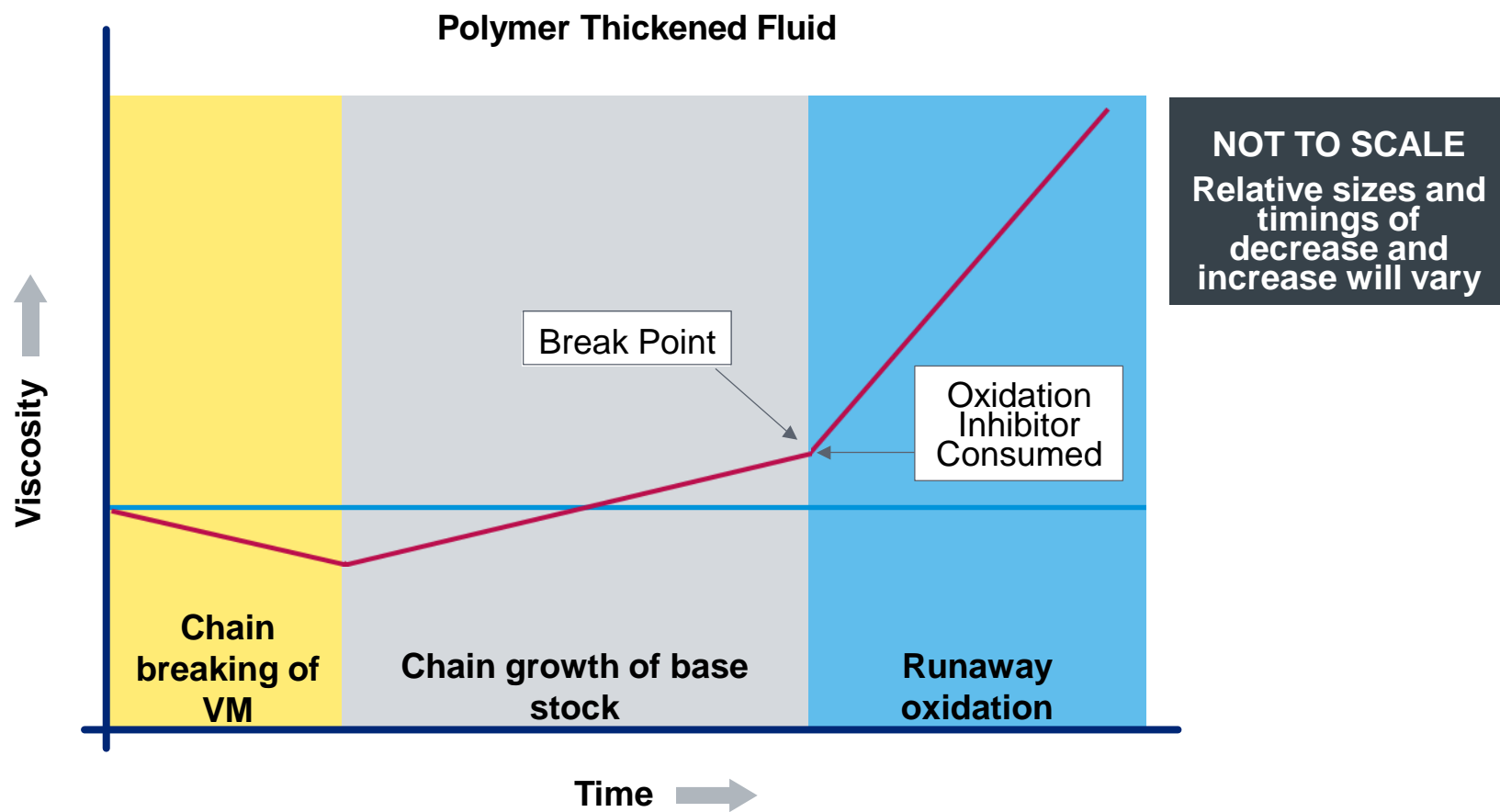


Indicators of oxidation

Aluminum Beaker Oxidation Test (ABOT)

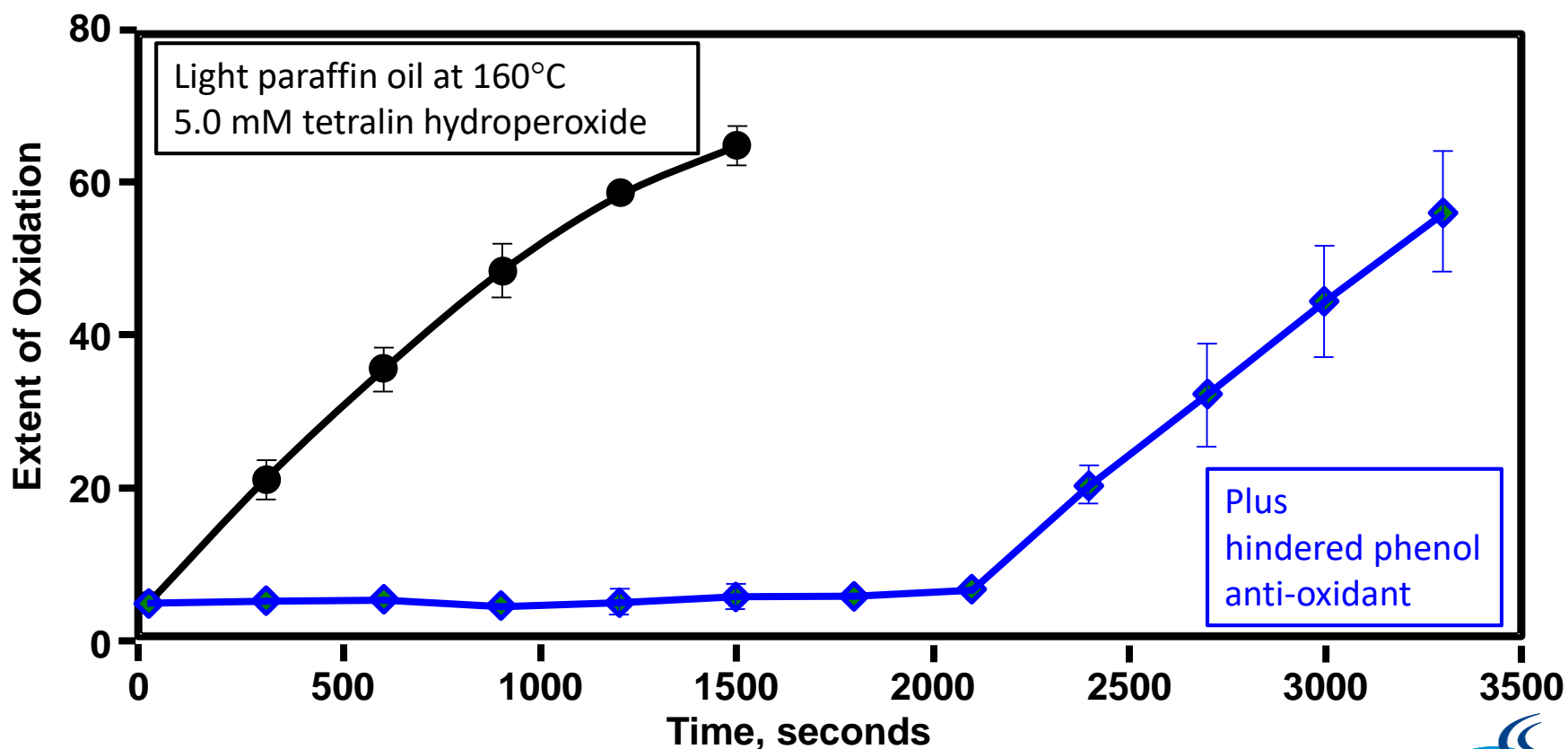


Viscosity changes due to oxidation



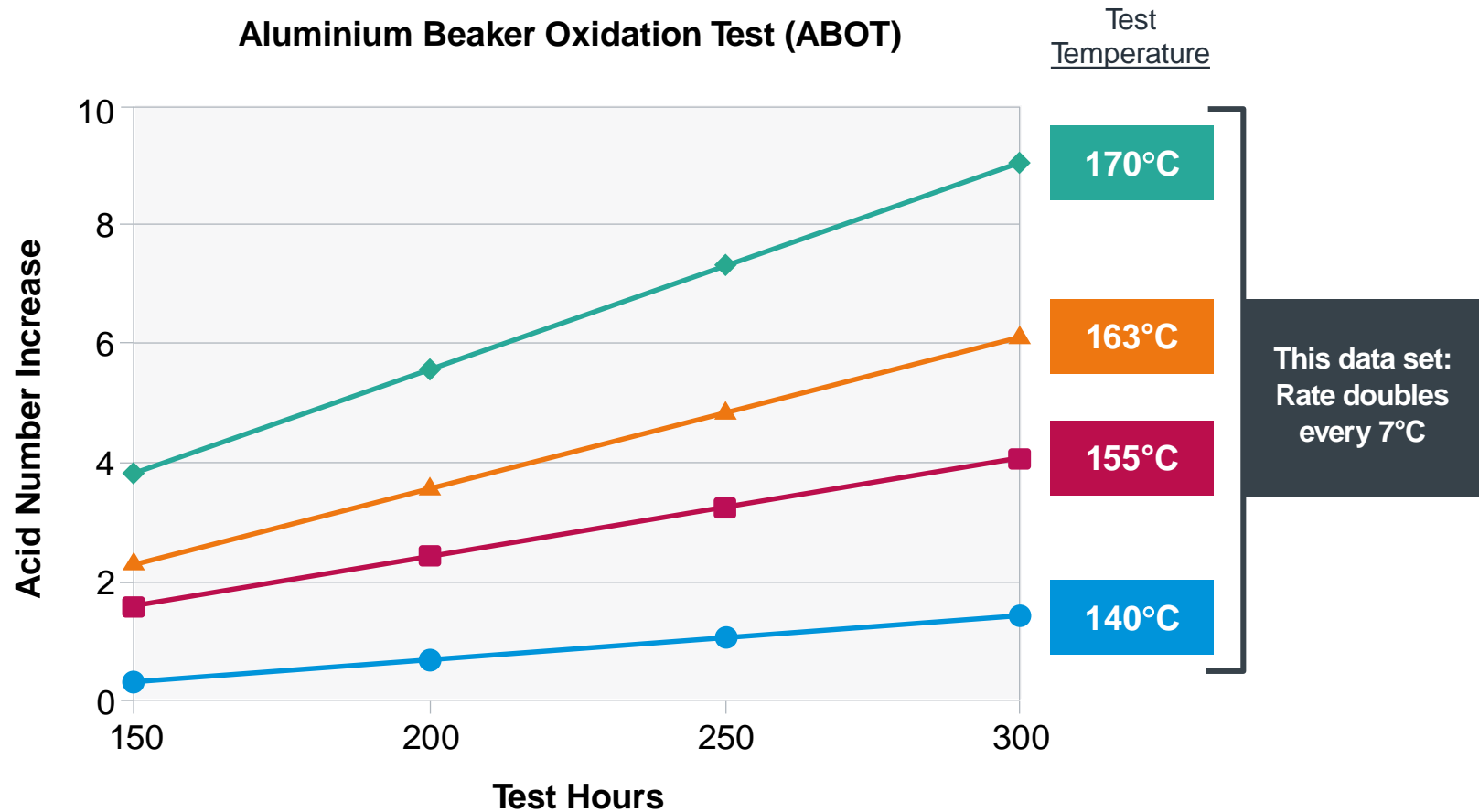
Anti-oxidant example

- Anti-oxidant displays “Induction Time” to delay onset of oxidation
 - Followed by “Break Point” and resumption of oxidation



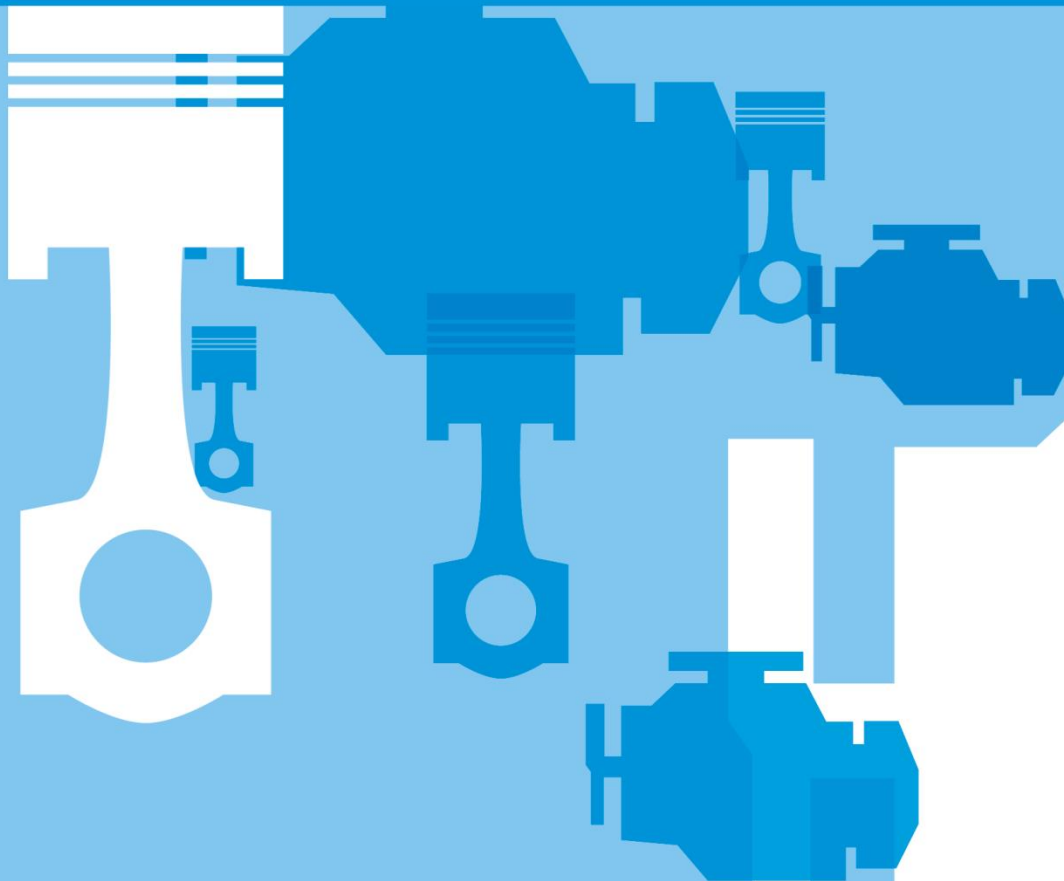
Source: E. A. Haidasz, *et. al.*, *J. Am. Chem. Soc.* 2016, 138 (16), pp. 5290-5298

Effect of temperature



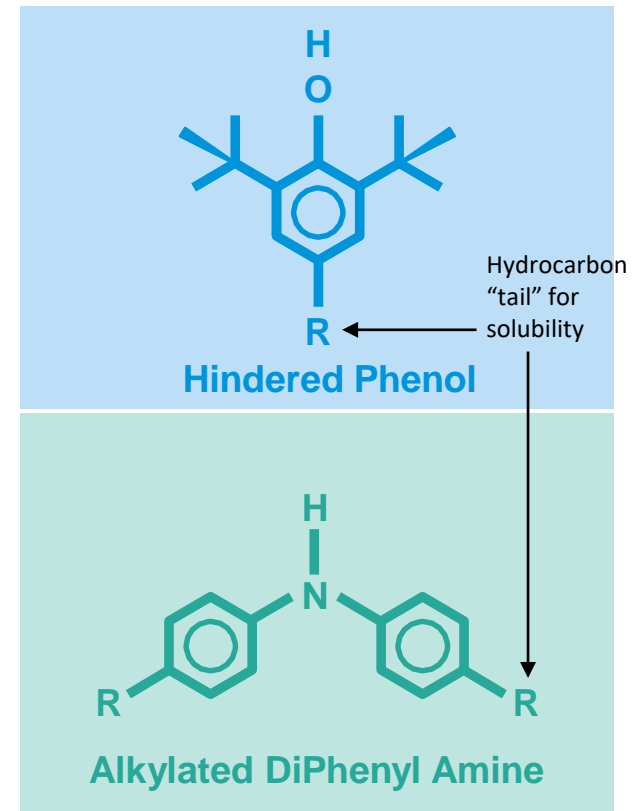
Rule of thumb - every 10°C increase in temperature doubles the rate of oxidation

Oxidation inhibitors (or anti-oxidants)



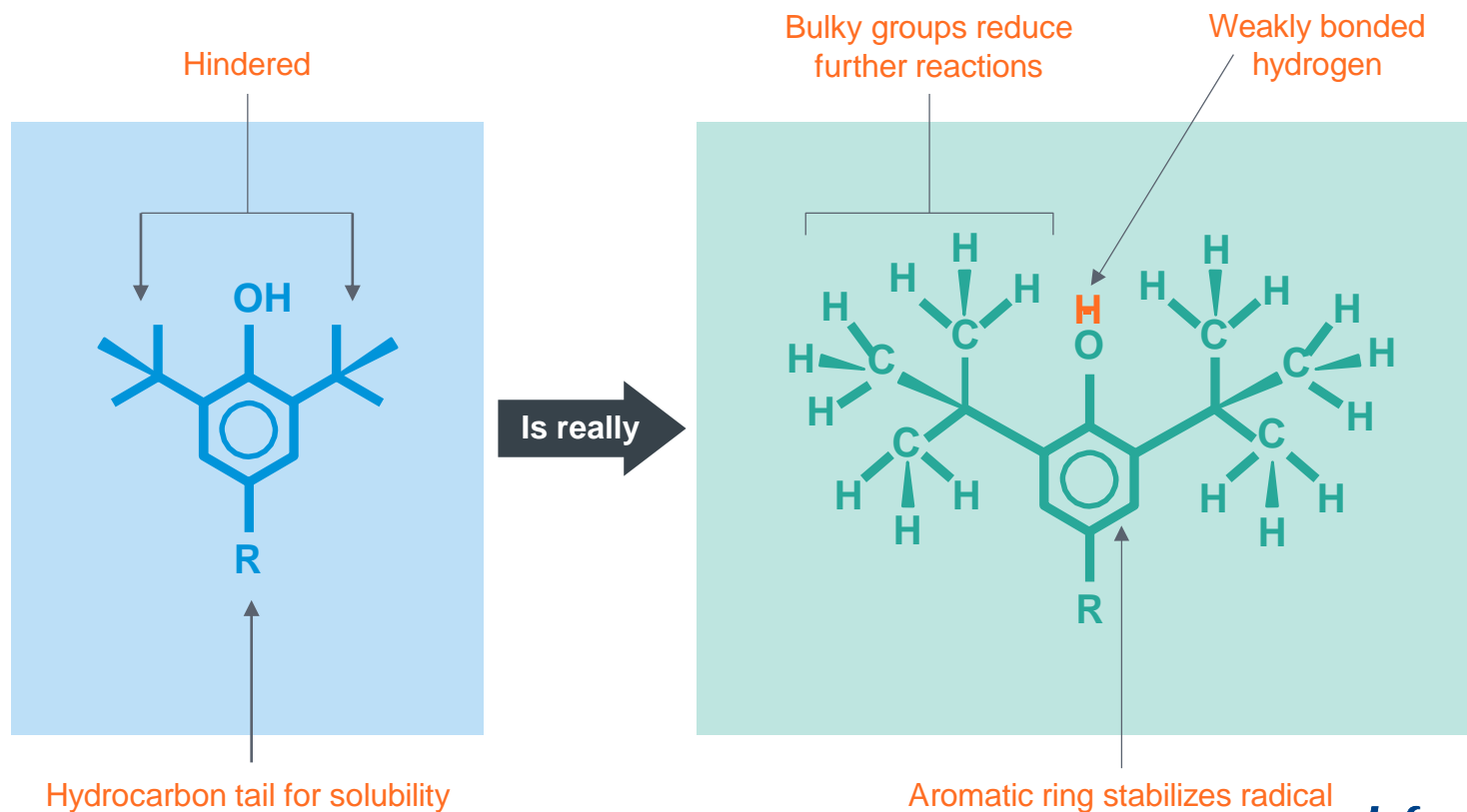
Anti-oxidant

- 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
 - Some sulfur compounds
 - Certain metal compounds (e.g., Molybdenum)

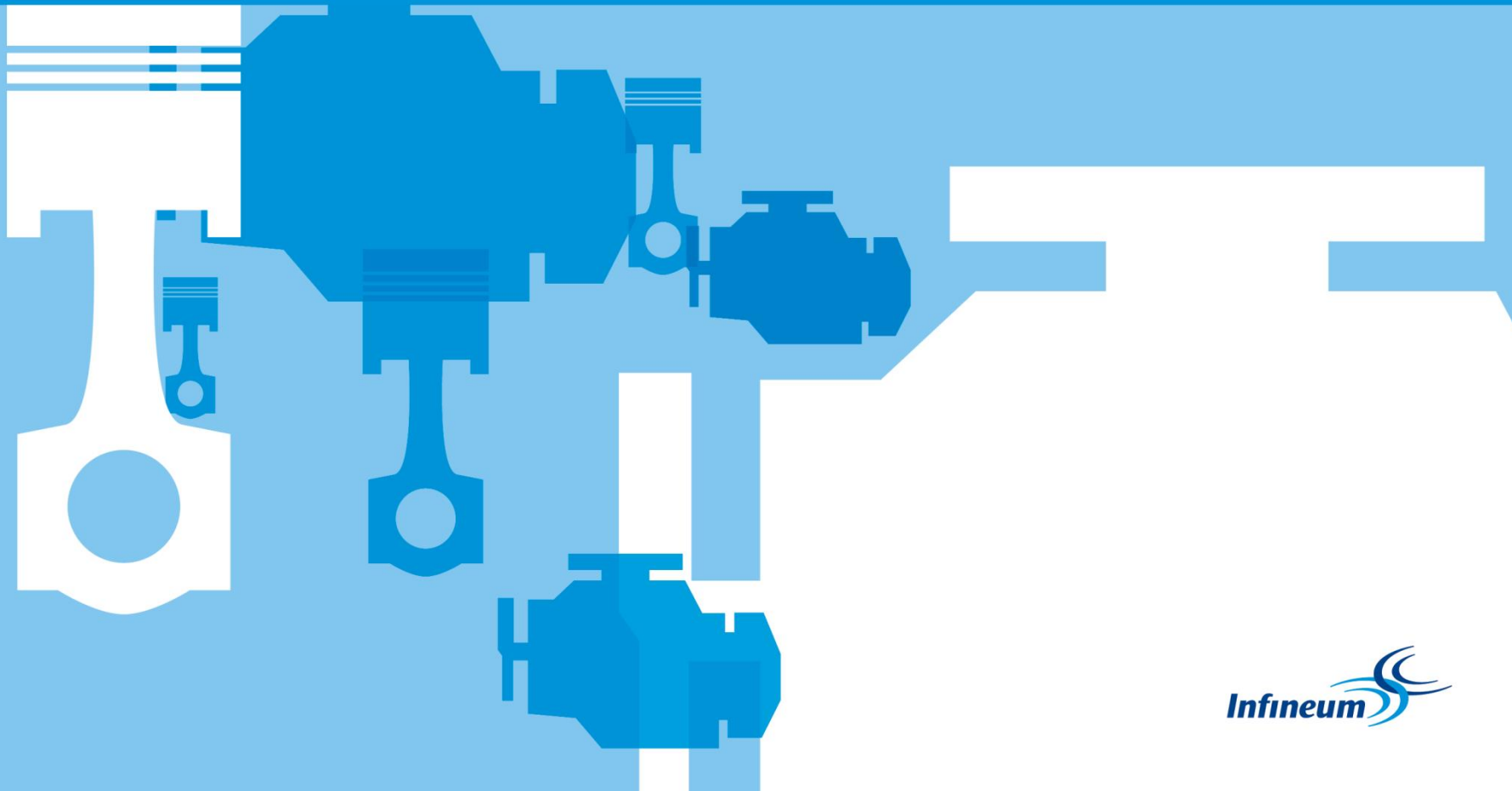


How do hindered phenols work?

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



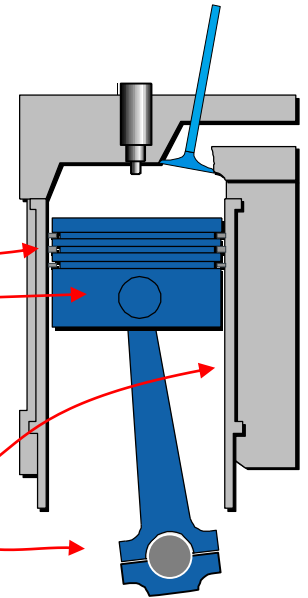
Detergents



Detergents

- Functions

- Neutralize acids
 - Combustion products: Sulfur and Nitrogen (strong) acids
 - Oxidation products: organic (weak) acids
- Reduce high-temperature deposits
 - Prevent piston ring sticking
 - Lacquer, varnish, and carbon
 - Prevent bore polish (abrasive or corrosive liner wear)



- Mechanisms

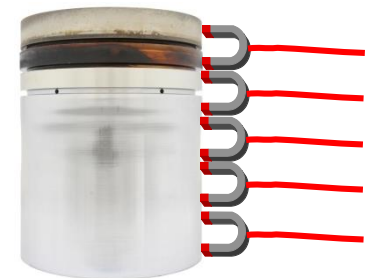
- Basic (alkaline) to neutralize acids
- Surface-active to reduce deposits

- Composition

- Basic metal with organic "tail" 

- Sulfonate
- Phenate
- Salicylate

Ca, Mg, Na, Ba,

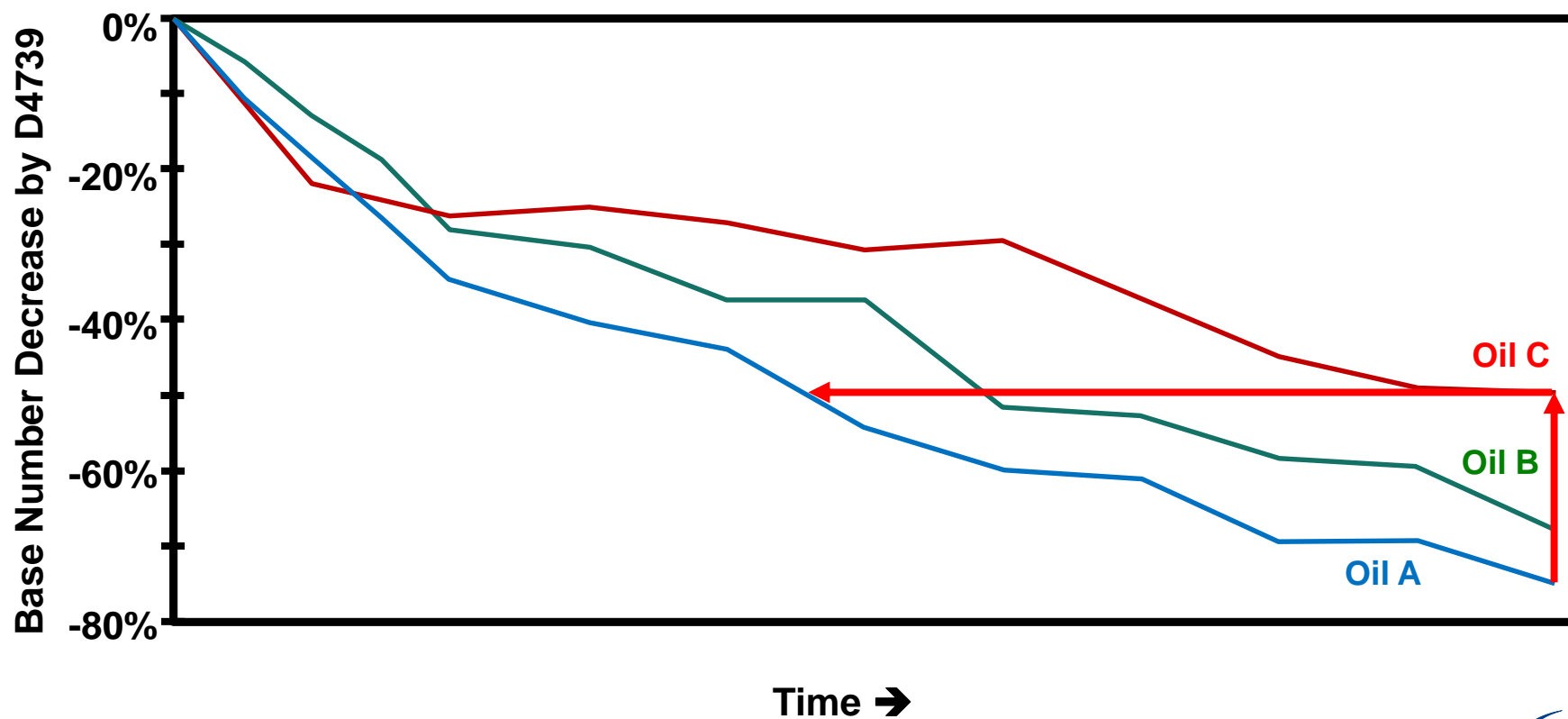


Deposit prevention

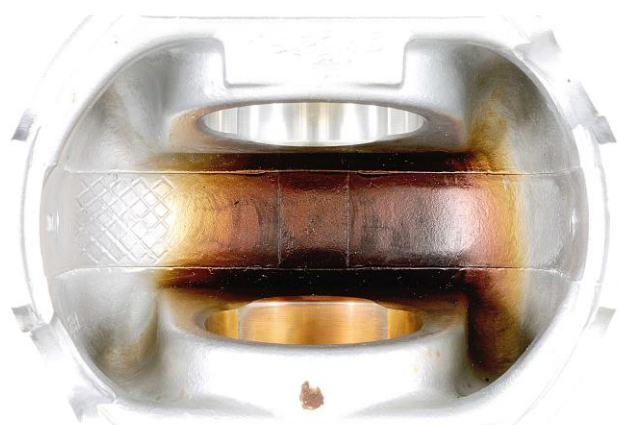


Detergent example

- Acid neutralization



Detergent example

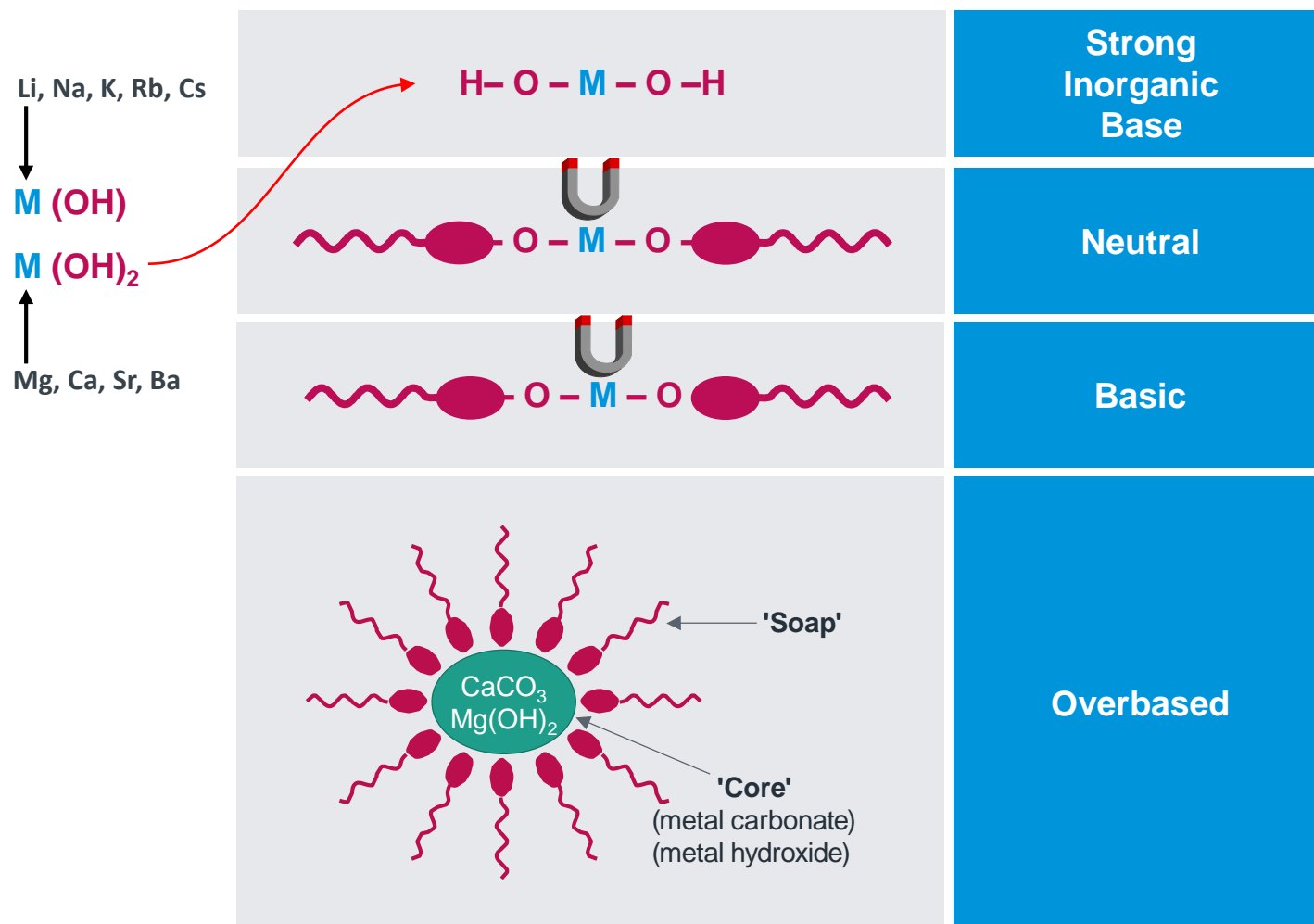


Bad Results



Good Results 

Detergents



“M” is a metal, such as calcium, magnesium, sodium, etc.

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

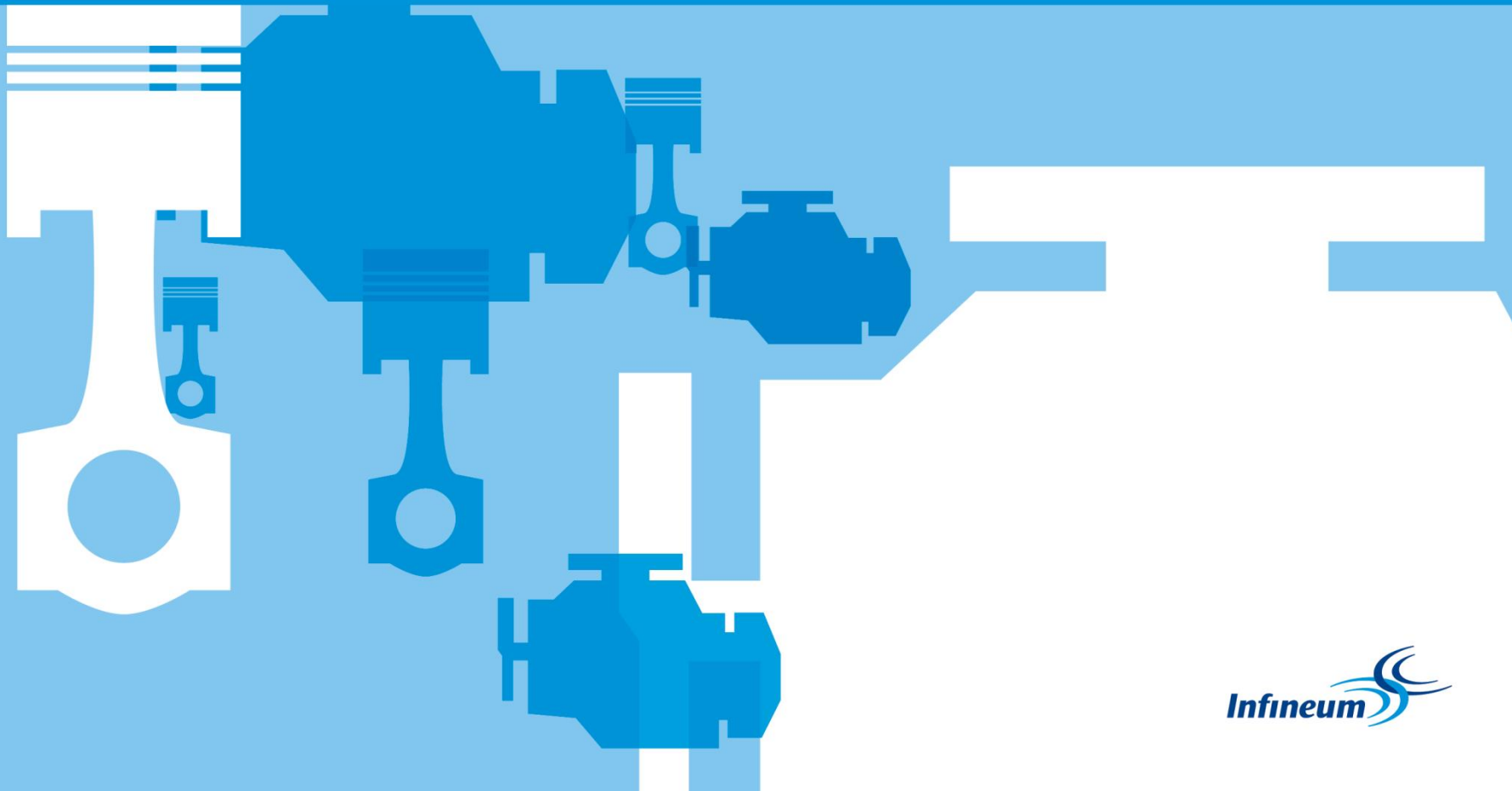


Base number

- Base Number (BN) is a quantitative measure of alkalinity
 - Formerly known as Total Base Number (TBN)
- Concentration of base
 - Expressed as equivalent KOH neutralizing ability (mg KOH/g units)
- Add acid until solution is neutralized
- Two test methods
 - ASTM D2896
 - Uses perchloric acid, an extremely strong acid
 - Measures “everything”
 - Strong bases, weak bases, some salts, *etc.*
 - Gives higher numbers
 - Used for fresh oils
 - ASTM D4739
 - Uses hydrochloric acid, a strong acid
 - Measures “effective”
 - Strong bases
 - Gives lower numbers
 - Used for in-service oils



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.*

Common Dispersant

PolyIsoButylene Succinic Anhydride/PolyAMine

PIBSA/PAM

Fuel additives call these “detergents”

- Functions

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

Diesel engine oils

Gasoline engine oils

 Detergent

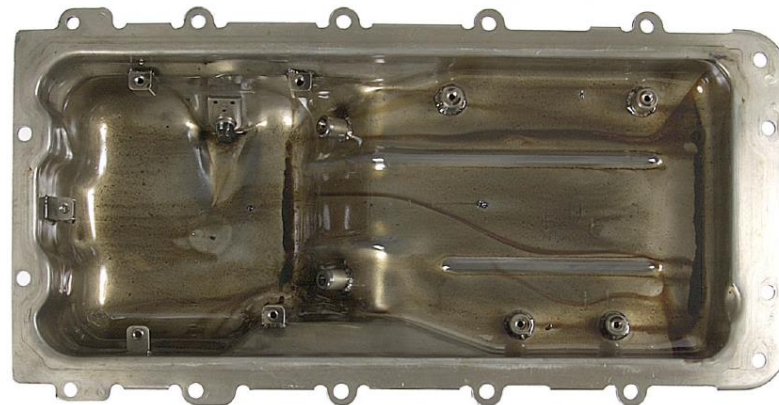
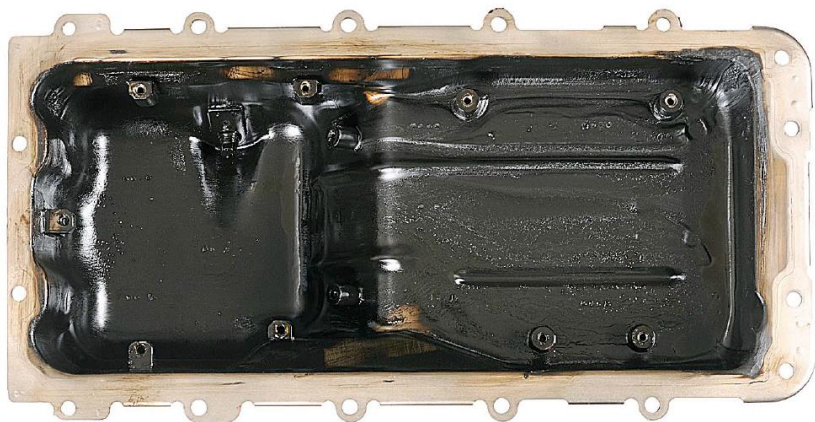
 Dispersant

- Composition

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



Dispersant example

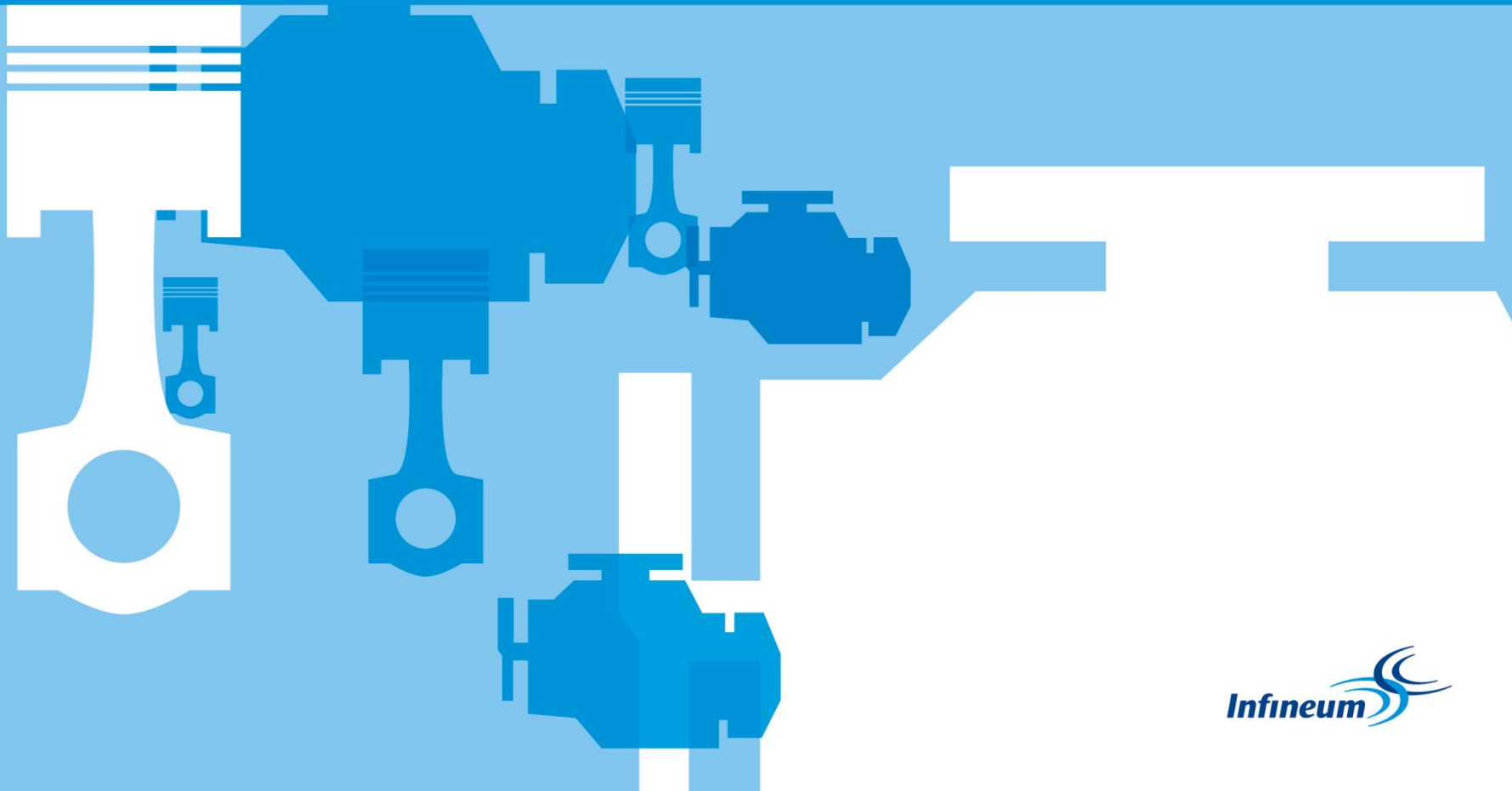


Bad Results



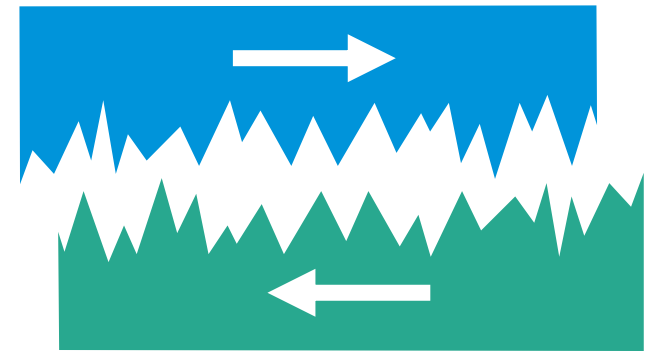
Good Results

Friction and wear

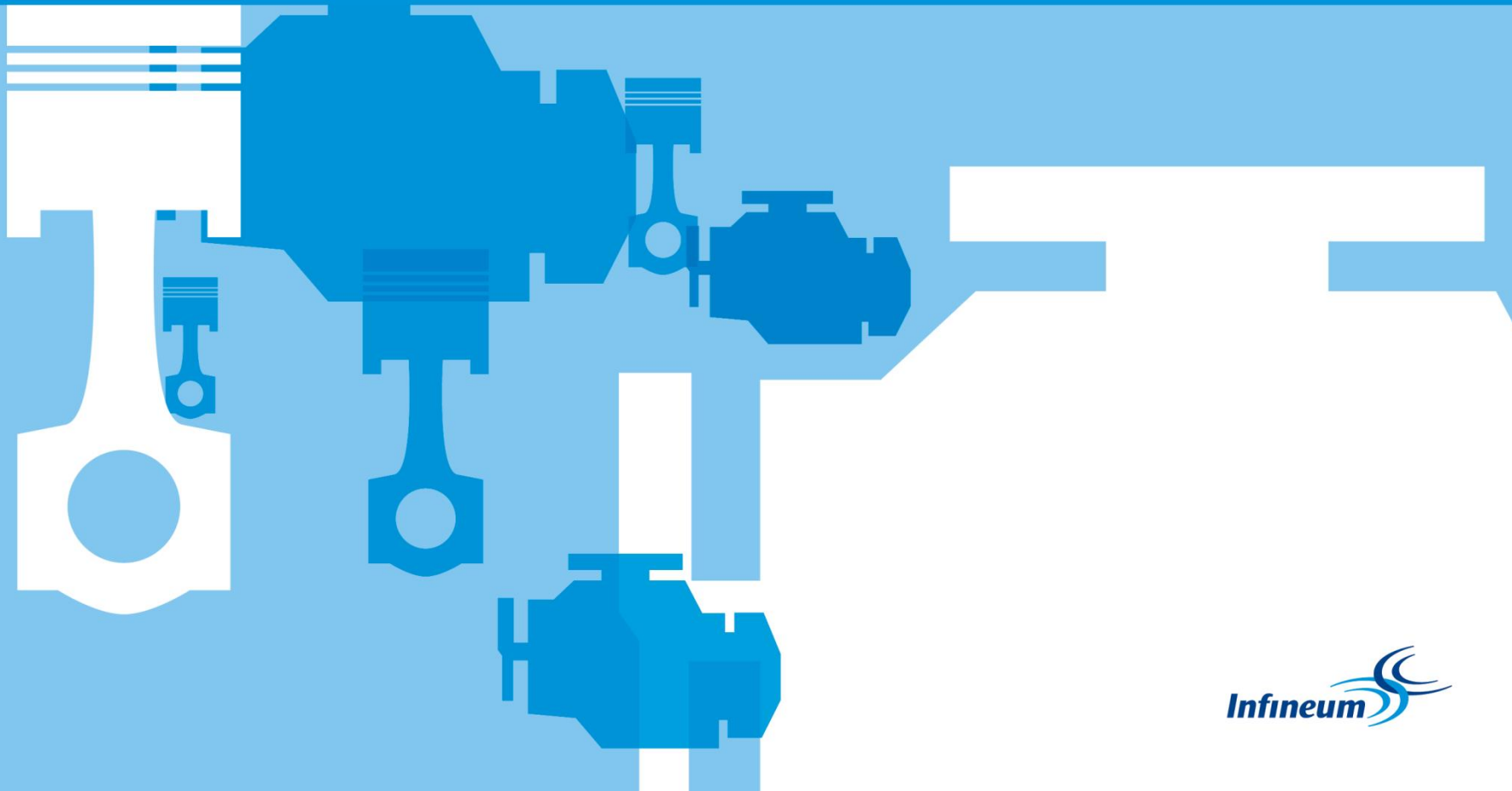


Friction and wear

- Both are caused by relative motion between surfaces
- Friction is a loss of **energy**
 - Dissipated as heat
 - Heat can do damage
- Wear is a loss of **material**
 - Changes geometry of contacts
 - Changes equipment performance
 - Introduces metal oxidation catalysts



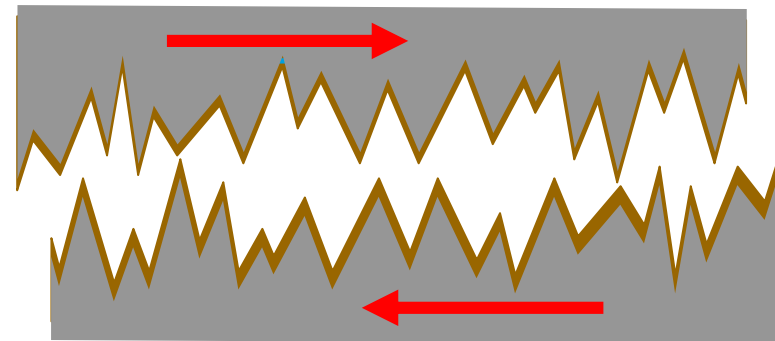
Antiwear agents



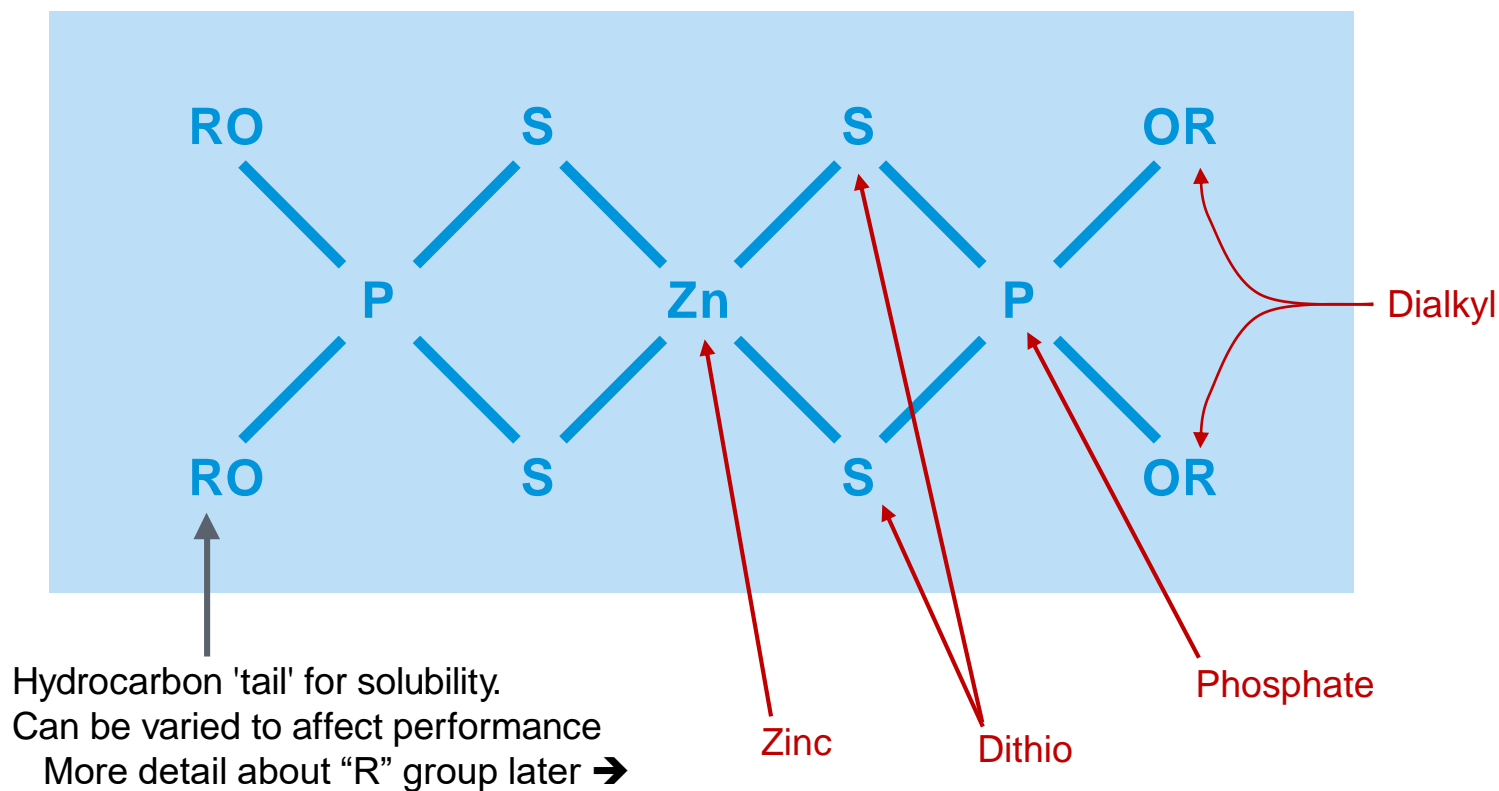
Antiwear agents

- 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:



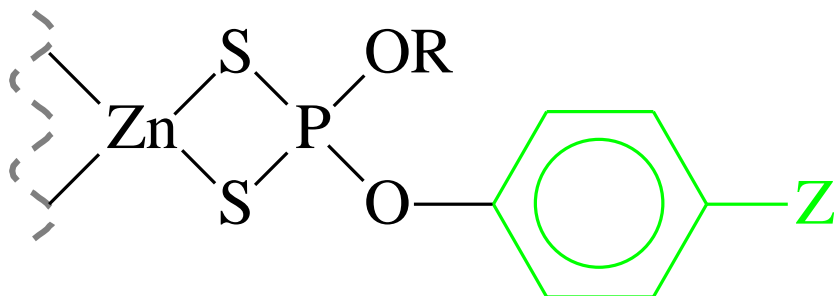
Zinc Dialkyl DithioPhosphate (ZDDP)



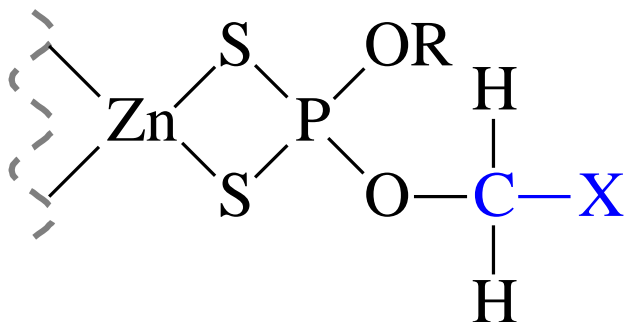
Note: Not exact chemical structure; for illustration only

ZDDP “alkyl” structures

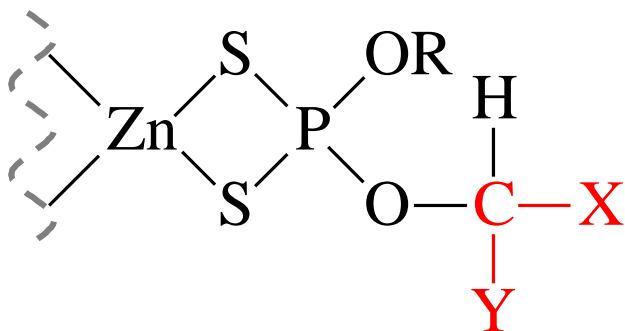
Alkyl type, length, and branching affect ZDDP properties



Aryl ZDDP – aromatic group



Primary ZDDP – one ‘alkyl’ group

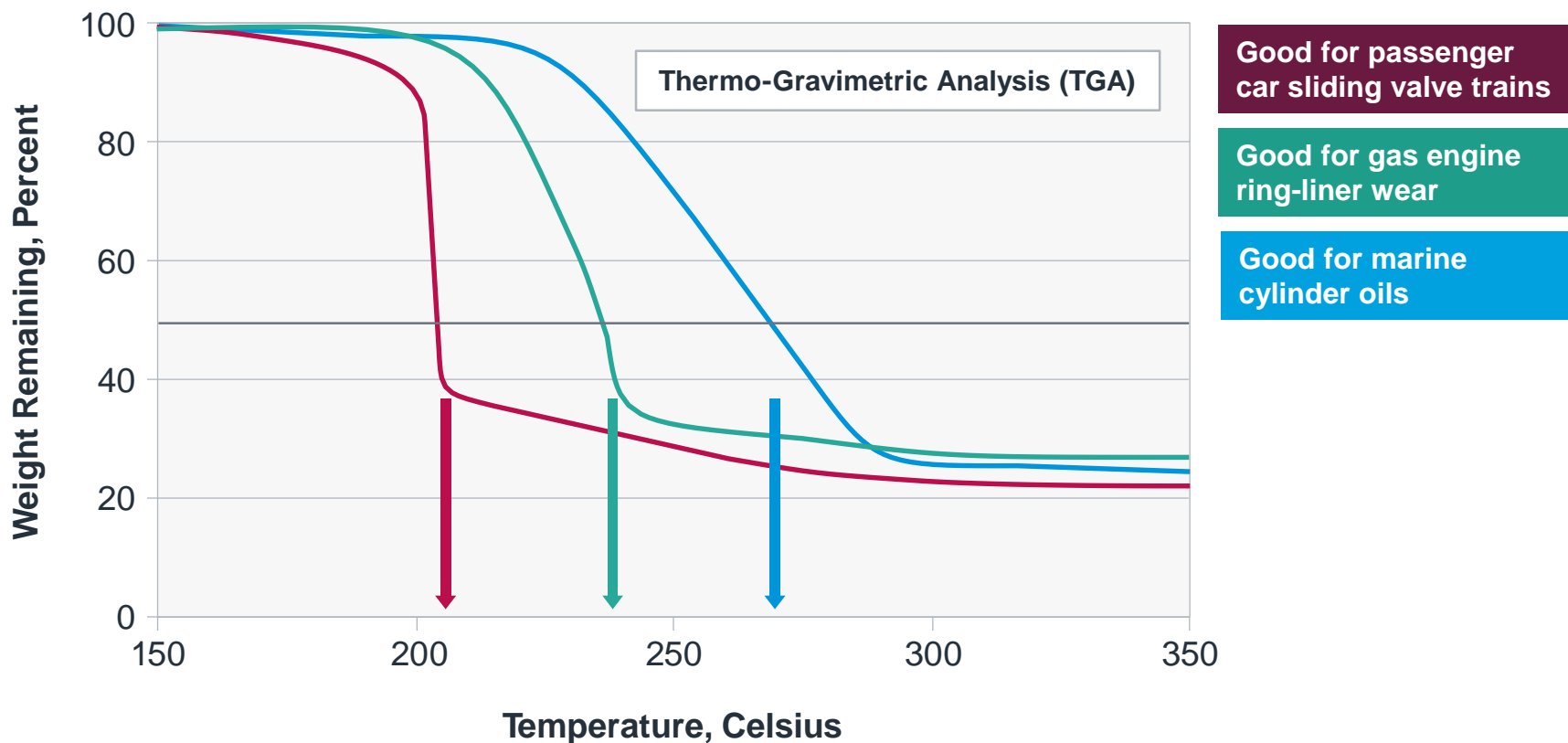


Secondary ZDDP – two ‘alkyl’ groups

Decreasing Decomposition Temperature

ZDDP decomposition

ZDDP decomposition temperatures highly dependent on method and conditions

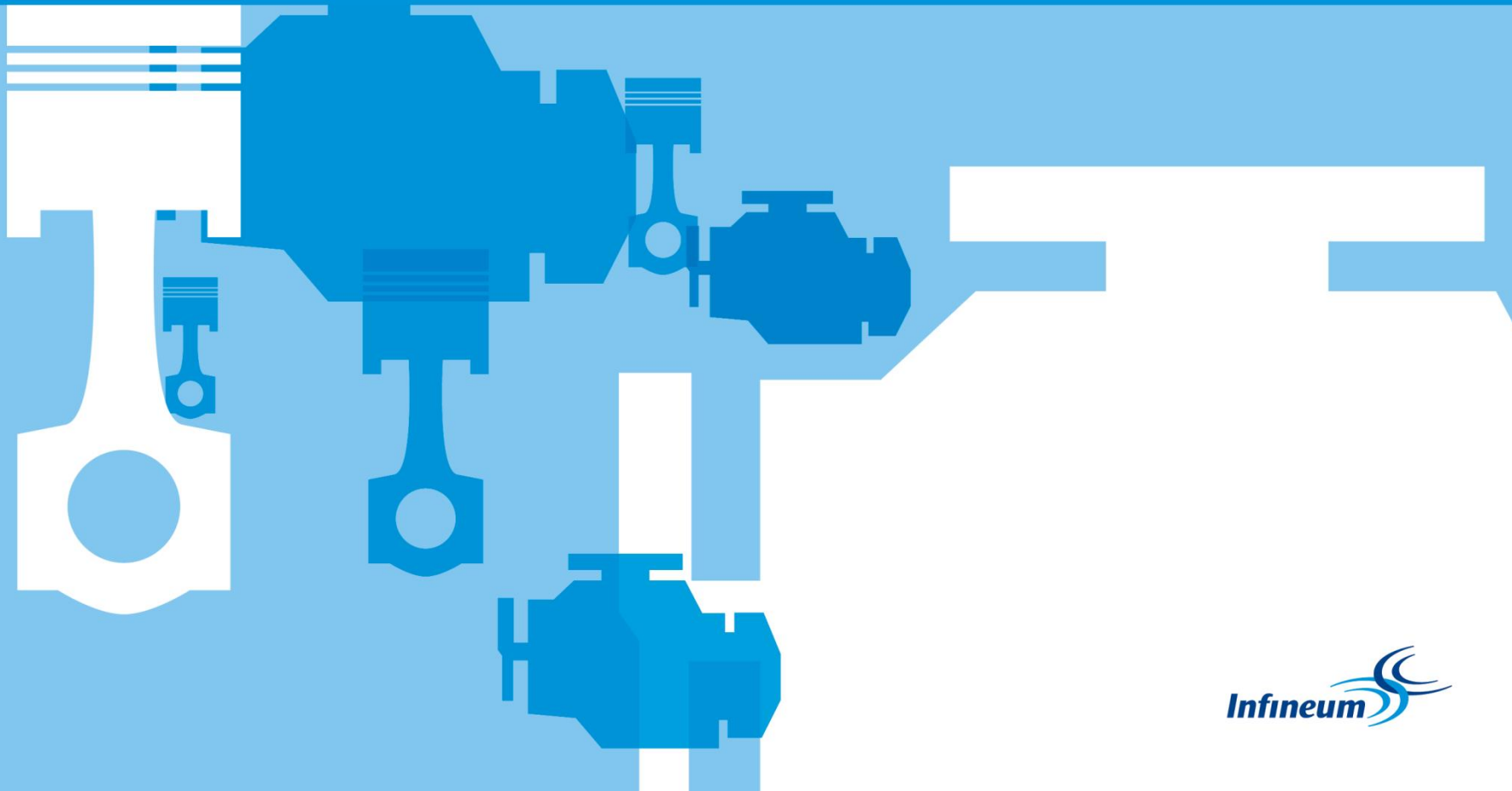


Extreme pressure (EP) additives

- 'Extreme' is a relative term
 - ZDDP sometimes called 'EP'
- EP more commonly refers to
 - Additives for high loads in gear oils
 - Chlorine-containing molecules
 - Highly reactive sulfur or sulfur-phosphorus compounds
- Work similar to ZDDP, but
 - More active
 - More corrosive
- Balance EP protection with corrosion



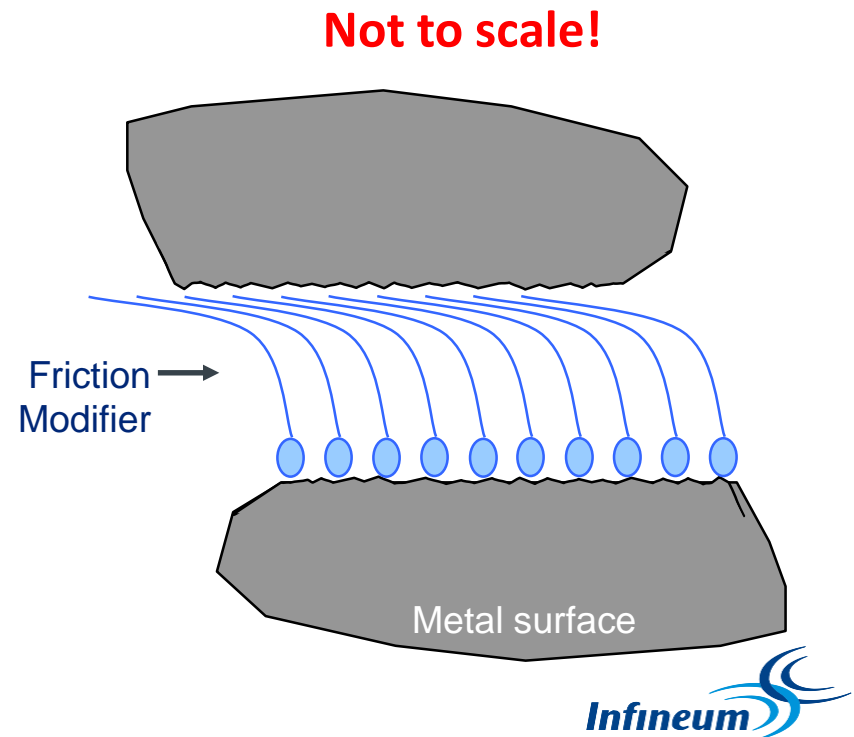
Friction modifiers



What are friction modifiers?

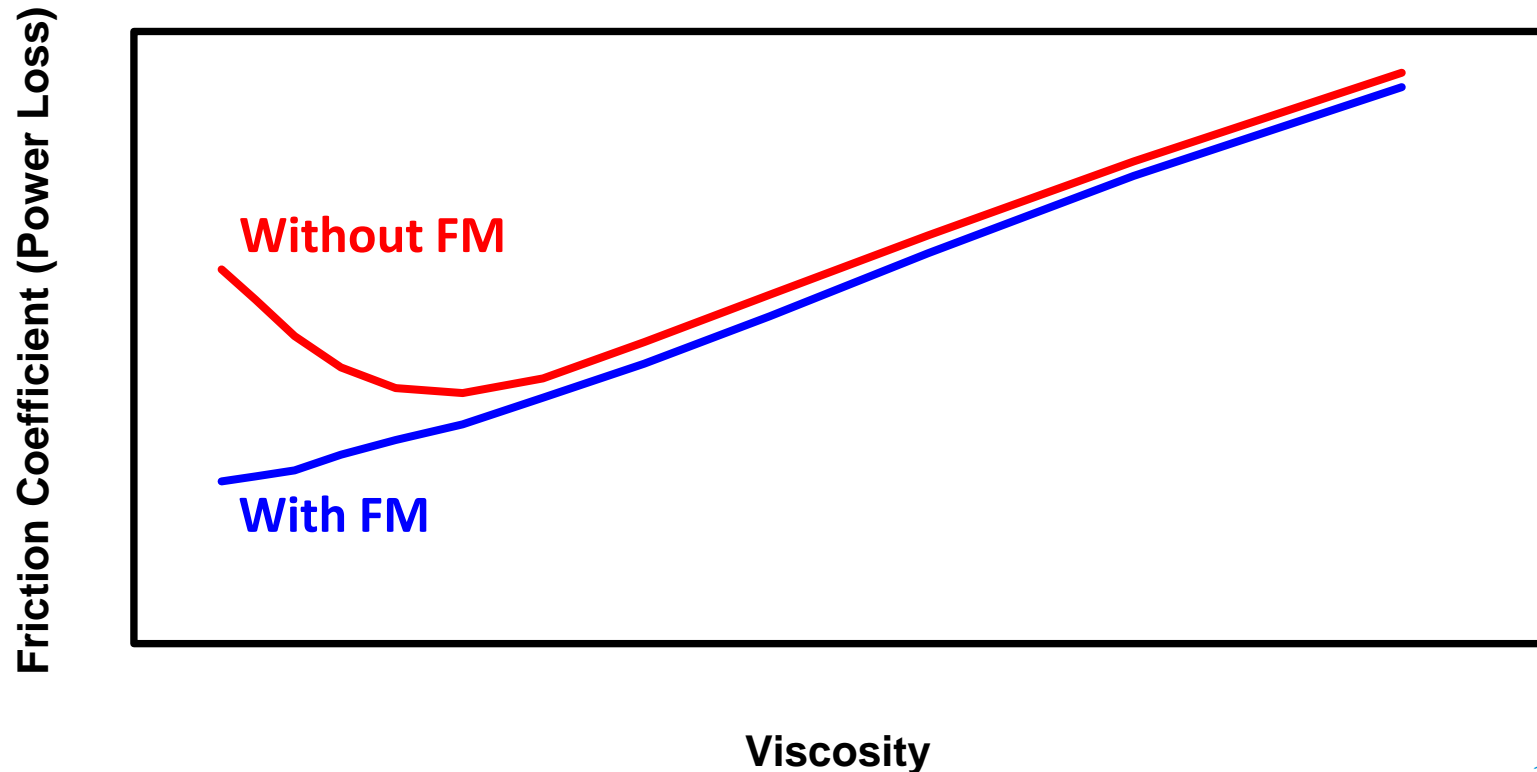
- Function
 - Reduce friction between contacting surfaces in relative motion
- Mechanism
 - Form a “springy” layer
 - “Plush Carpet” effect
- Composition
 - Straight-chain stiff hydrocarbons with polar end groups
 - Bond to metal surfaces
 - Rather than soot, for example

Consequence:



Friction modifier example

- Stribeck curve
 - Friction modifier extends the hydrodynamic region
 - Enabling protection at lower viscosities



Ref: Passut, C.A. and Kollman, R.E., SAE paper 780601

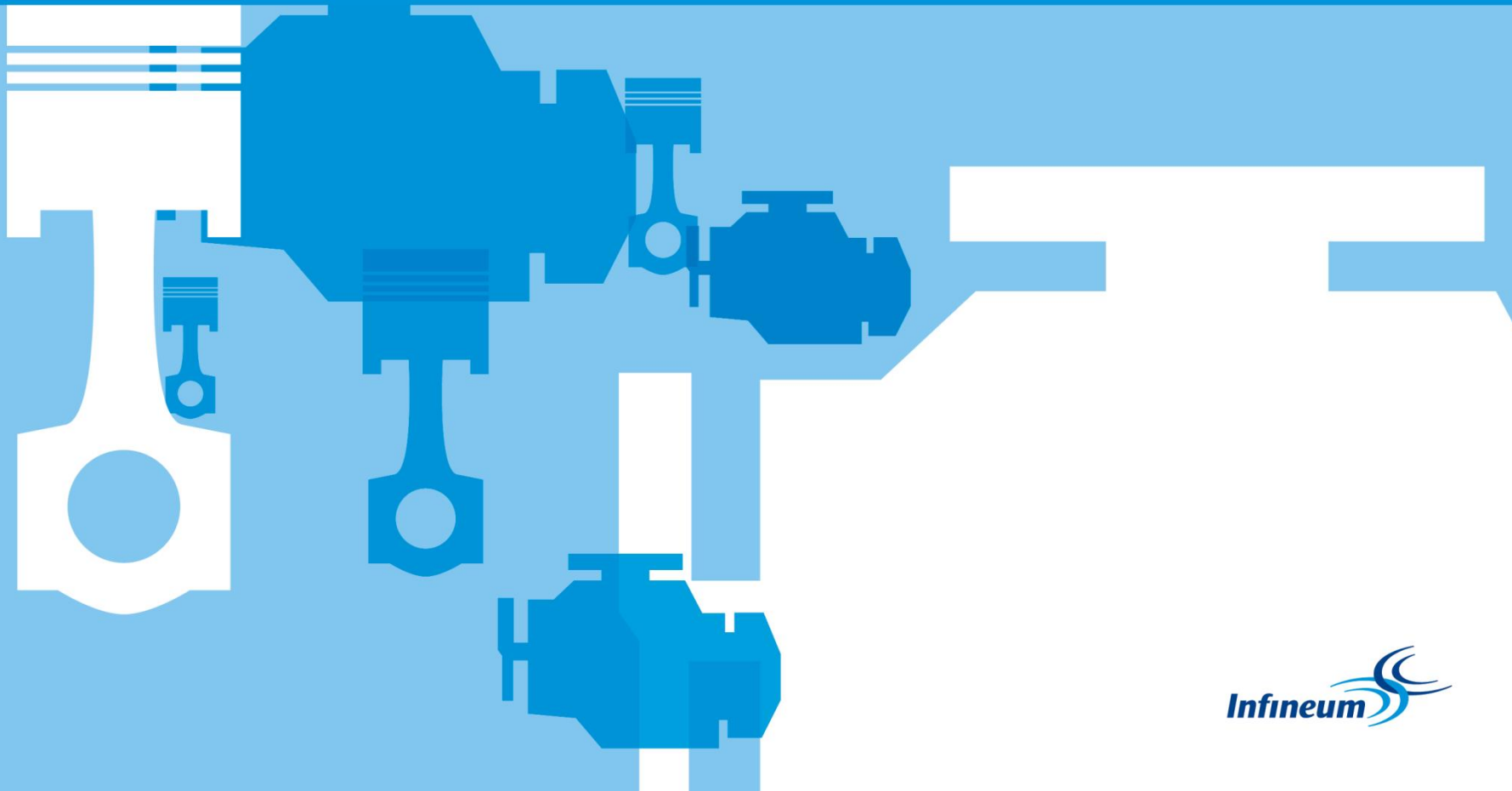
Solid friction modifiers

- 'Flat Plate' molecular geometry
 - Planes glide over each other
 - Graphite (Carbon)
 - Molybdenum DiSulphide (MoS_2)



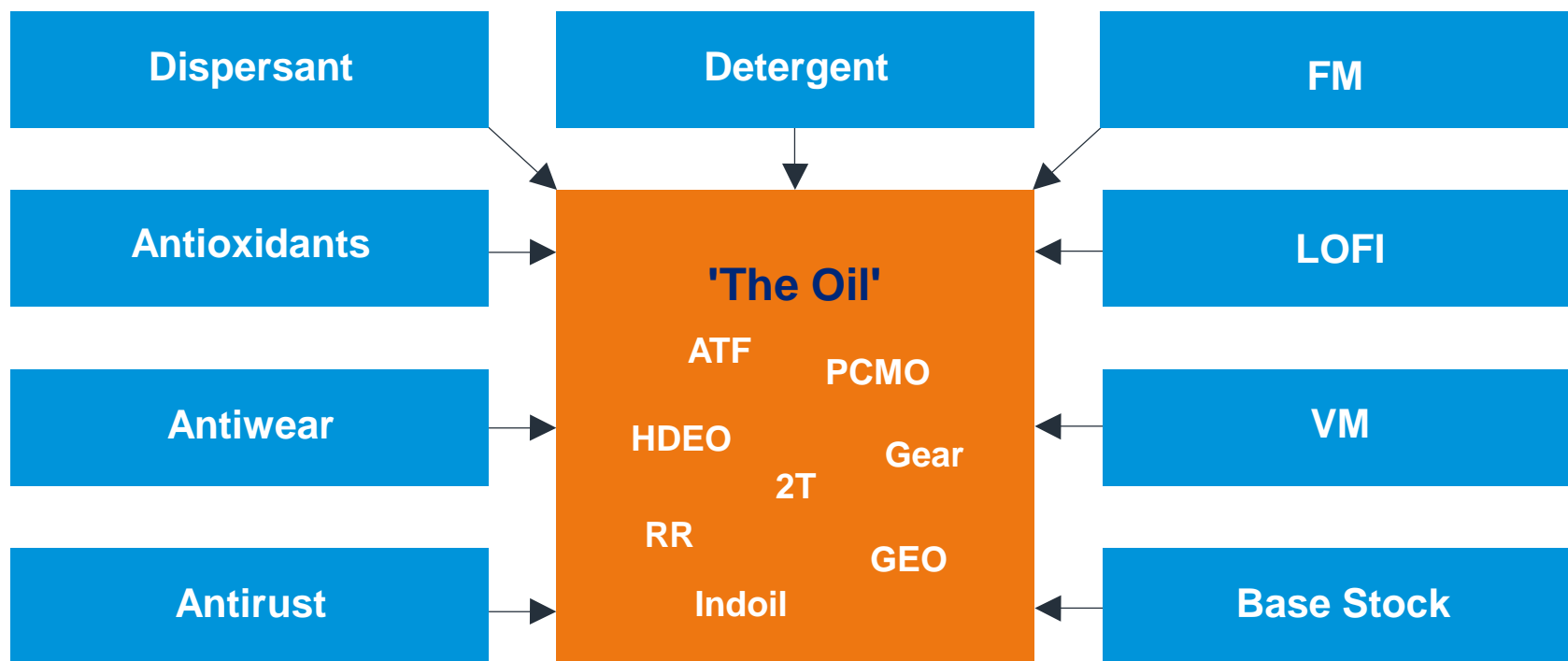
- Polytetrafluoroethylene = PTFE
 - Teflon®
 - Strong terminal bonds don't stick to other things

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



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