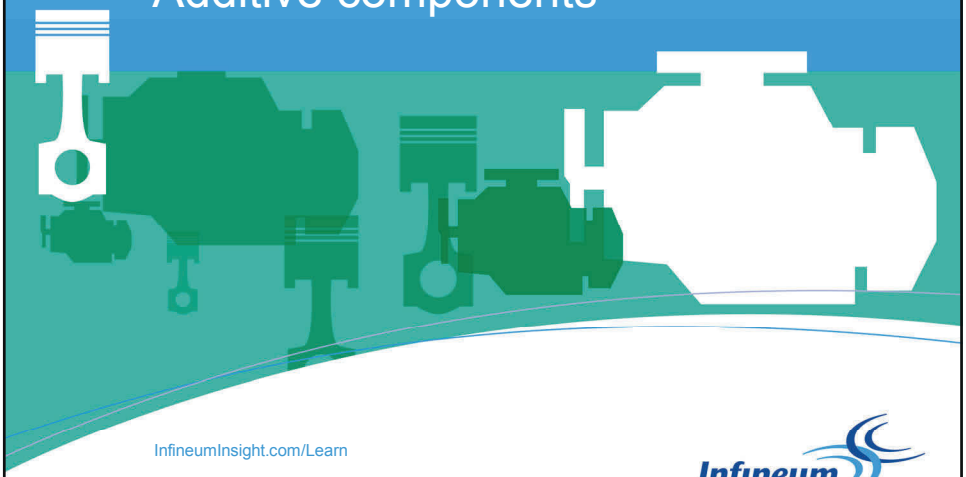
Performance you can rely on.

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

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What's in the bottle*?

Base Stock	Ensures fluidity and adds performance
Viscosity Modifier	Changes temperature response
Dispersant	Keeps everything soluble
Detergent	Neutralizes acids and prevents deposits
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

Hydraulic Oils & Monograde Engine Oils don't have VM

**Many other, more specialized additives

*Not all oils have all components

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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*.

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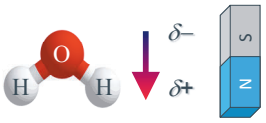
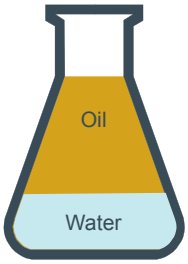
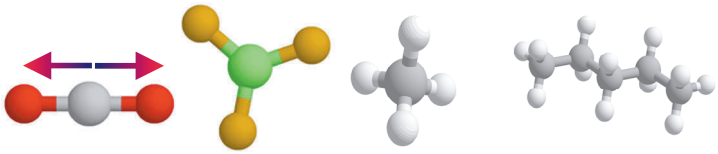
Polarity

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





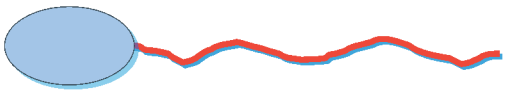


The challenge

- 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?**

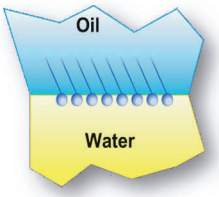
Surfactants

- Molecules with both polar and non-polar sections



Polar 'head' Non-polar 'tail'

- 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 ➔



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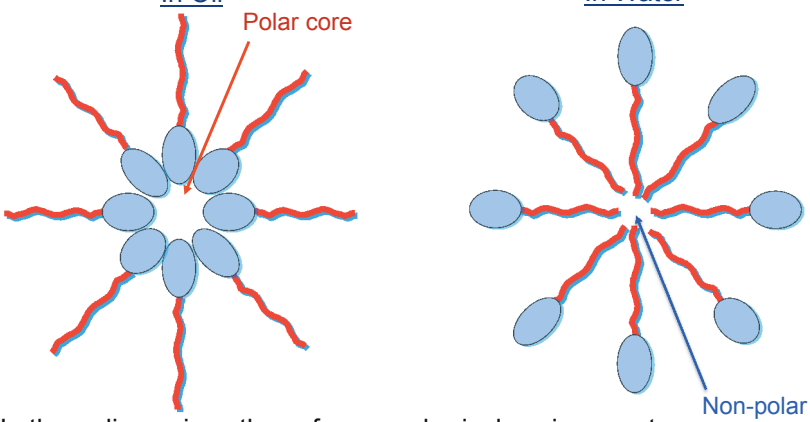
Micelles

In Oil

In Water



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

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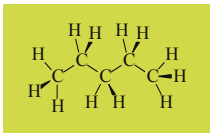
Chemistry shorthand

C_5H_{12} =
(pentane)



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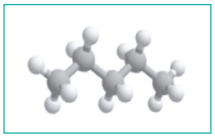

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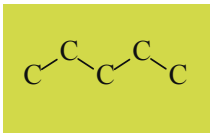

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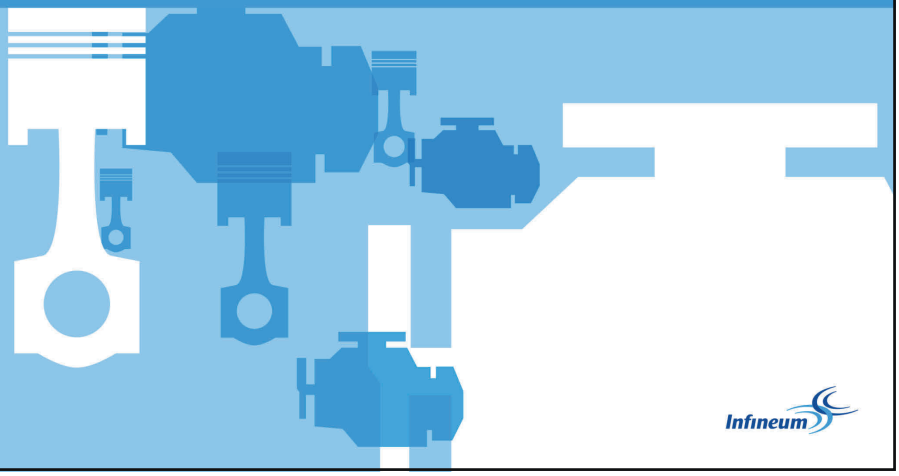
= **RH**

RH is really R:H

R:H ➔ **R•** + H•

Unpaired electron = **Radical**

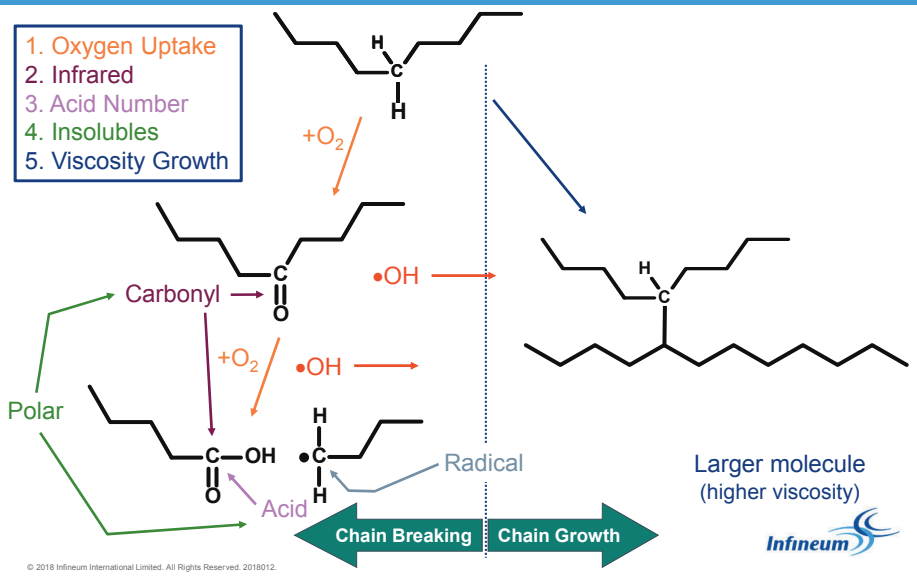
Oxidation



Chemically, what is oxidation?

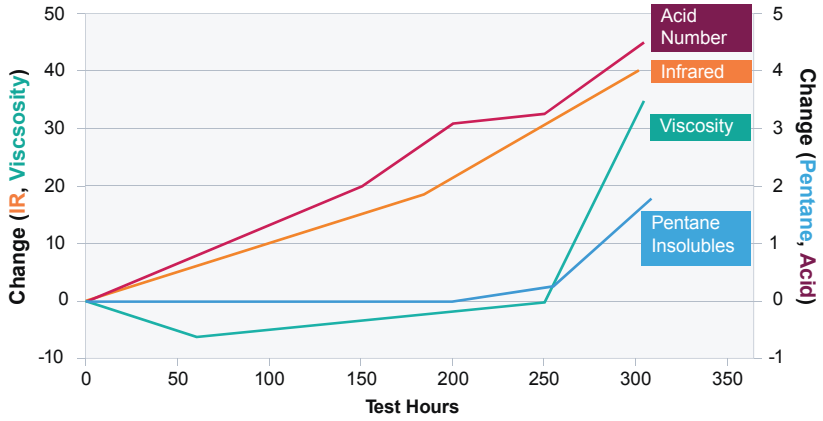
- Destruction of molecules by exposure to oxygen at elevated temperatures
  - Technically, oxidation can occur without oxygen, but we don't need to consider those cases
- Initiated by **Radicals**
  - Molecular fragments with an unpaired electron
  - Very unstable and reactive
- Radicals attack and "pull apart" the base stock molecules
  - To pair their lone electron
- The process can be **catalyzed** by metals
  - Catalyzed = Accelerated

How to measure oxidation

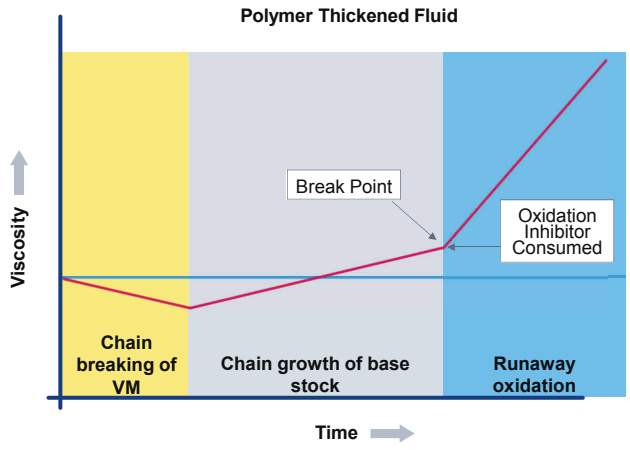


Indicators of oxidation

Aluminum Beaker Oxidation Test (ABOT)



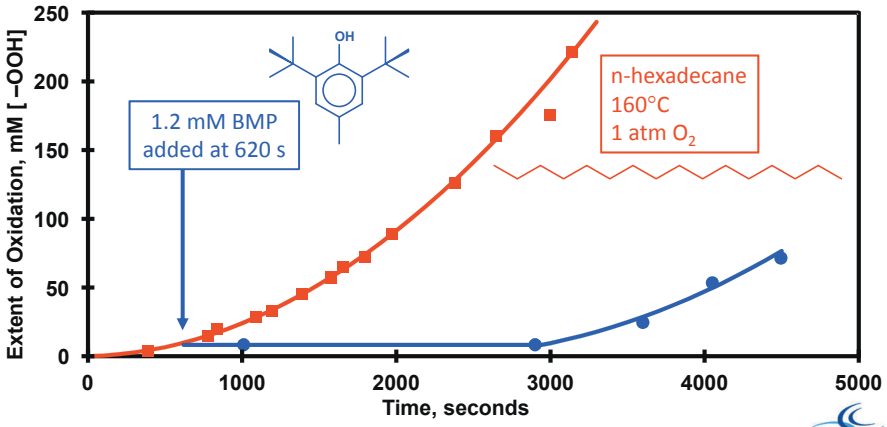
Viscosity changes due to oxidation



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

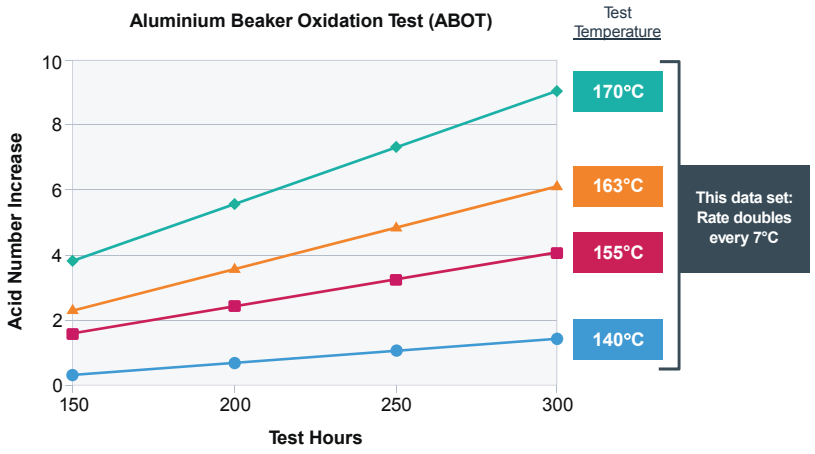
Anti-oxidant example

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



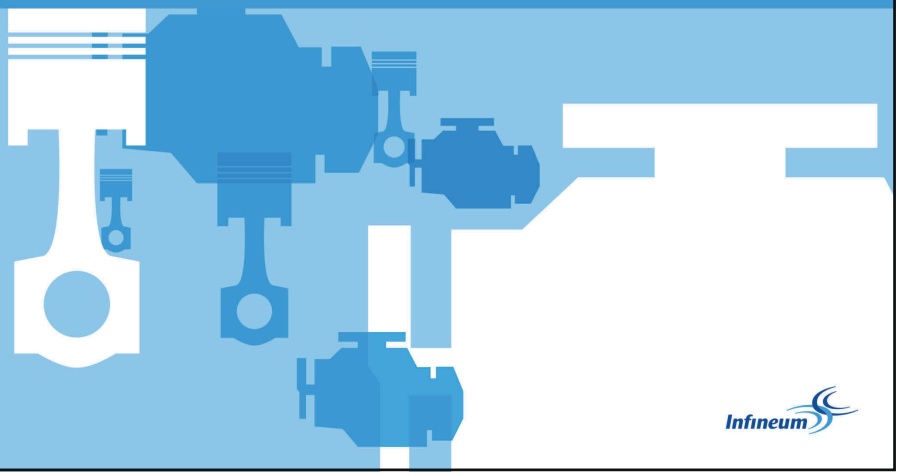
Source: Igarashi, *et. al.*, J. Am. Chem. Soc. 1992, 114, 7727-7736

Effect of temperature



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

Oxidation inhibitors (or anti-oxidants)



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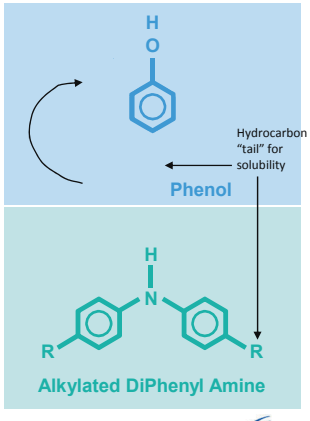
Anti-oxidant

- 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)



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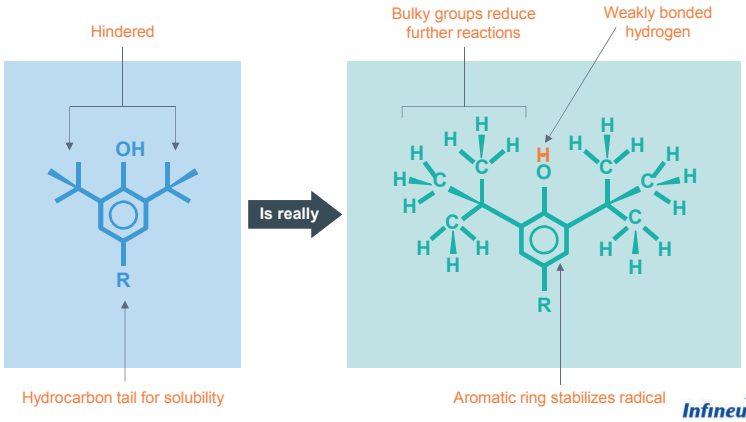
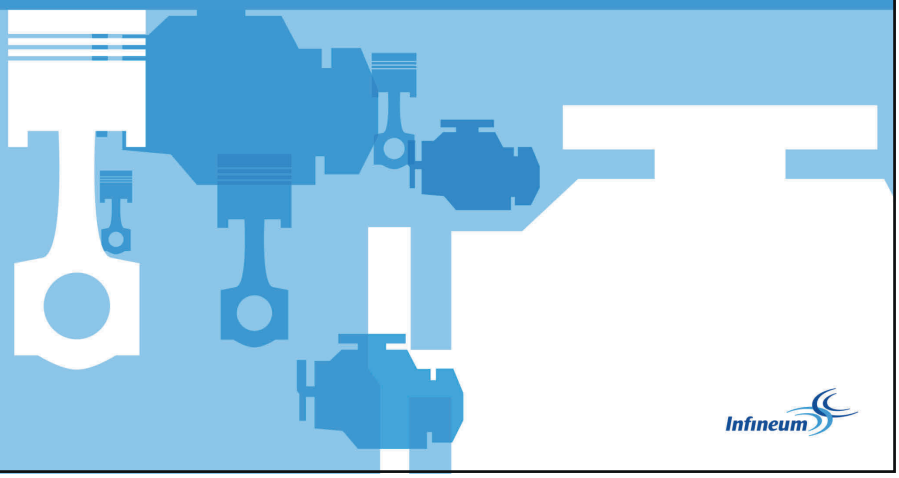
How do hindered phenols work?

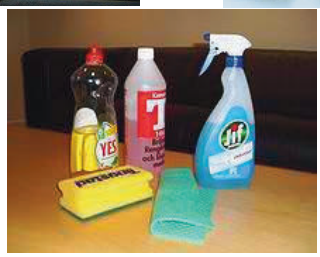
- Easily lose a hydrogen to form a stable radical
  - Stabilized by aromatic ring
- Further reaction inhibited by molecular structure



Detergents

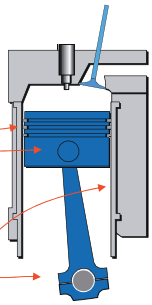


Detergents



Detergents

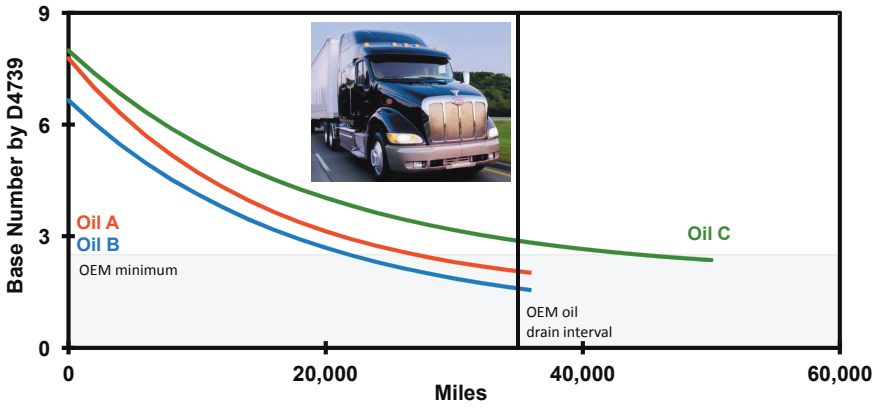
- Functions
  - Neutralize acids
    - Combustion products: Sulfur and Nitrogen (strong) acids
    - Oxidation products: organic (weak) acids
  - Reduce high-temperature deposits
    - Prevent piston ring sticking
    - Lacquer, varnish, and carbon
    - Prevent bore polish (abrasive or corrosive liner wear)
- Mechanisms
  - Basic (alkaline) to neutralize acids
  - Surface-active to reduce deposits
- Composition
  - Basic metal with organic “tail”
    - Sulfonate
    - Phenate
    - Salicylate



Deposit prevention

Function of detergent

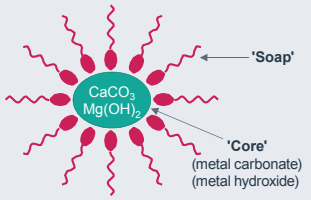
- Acid neutralization



Function of detergent

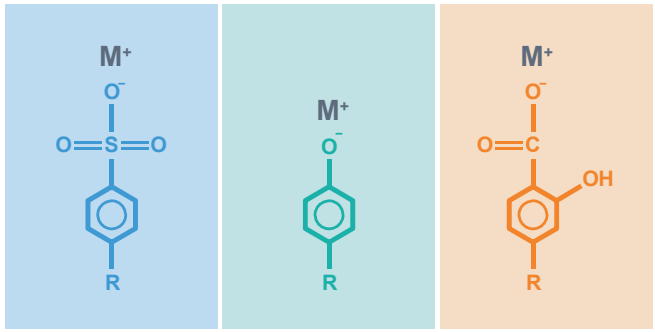
- Piston cleanliness

Detergents

H– O – M – O –H	Strong Inorganic Base
O – M – O	Neutral
O – M – O –H	Basic
	Overbased

"M" is a metal, such as calcium, magnesium, sodium, *etc*.

Typical lubricant detergents



Sulfonate	Phenate	Salicylate

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

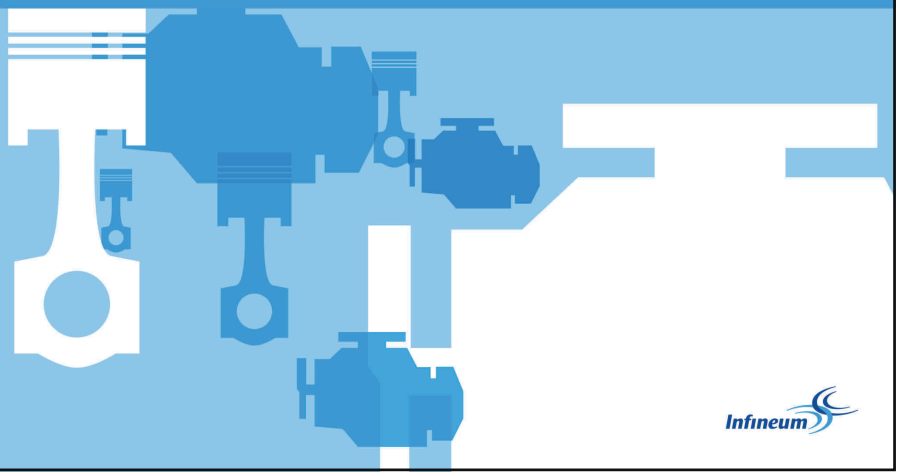
SASH and ash

- 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
  - 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



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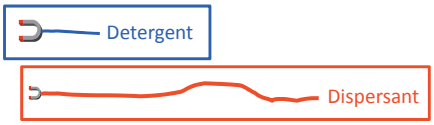
Performance you can rely on.

Dispersants

- Definition
  - Also called “Ashless Dispersants”
  - “Ash” really means “SASH” means “contains a metal”
    - Sodium, calcium, magnesium, zinc, *etc*.
  - Dispersants don’t contain metals
    - Only carbon, hydrogen, nitrogen, oxygen, boron, *etc*.
- 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”
- Composition
  - Long chain hydrocarbon for solubility
  - Small (non-metal) polar “head group” to stick to soot and deposits

Fuel additives call these “detergents”



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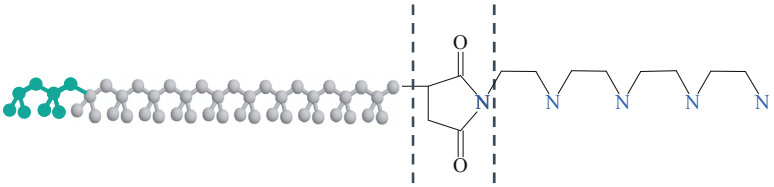
Dispersants – composition



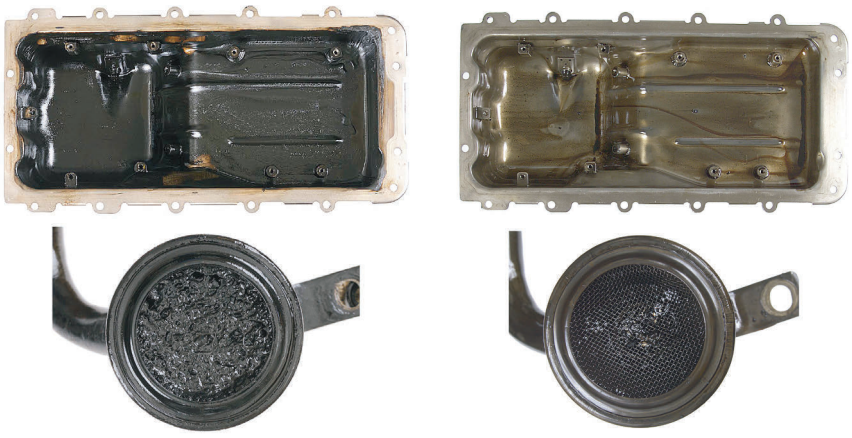
Non-Polar tail | Bridging Group | Polar head

Example:

Poly IsoButylene | Succinic Anhydride | PolyAMine

= PIBSA/PAM

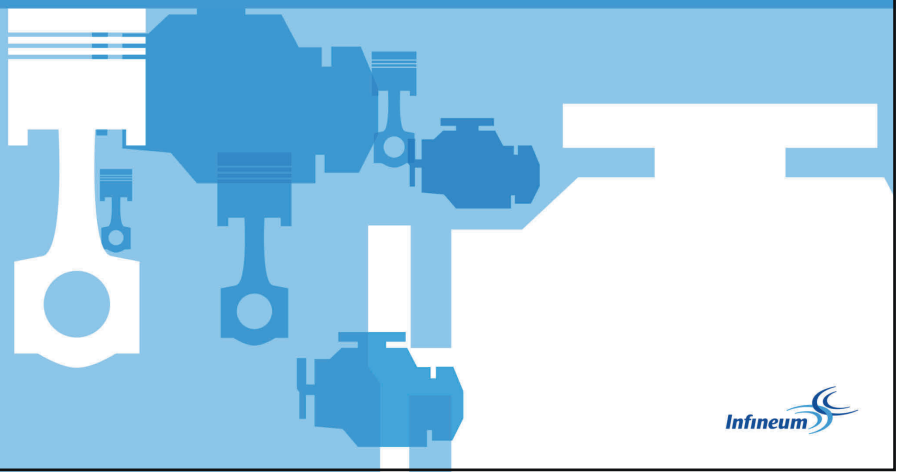
Dispersant example



Bad Results

Good Results

Friction and wear



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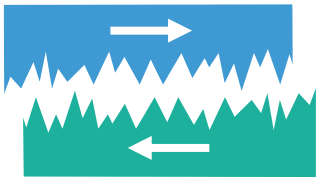
Performance you can rely on.

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



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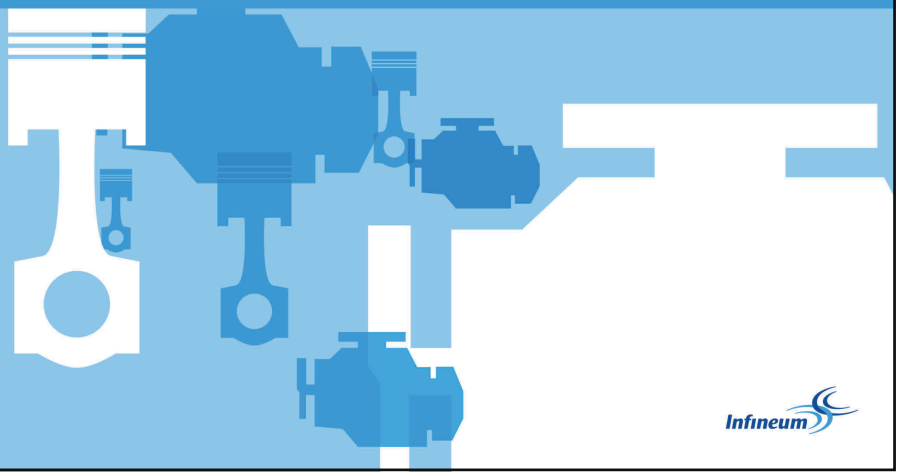
Antiwear agents



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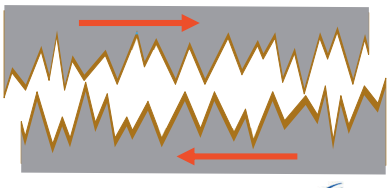
Performance you can rely on.

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:



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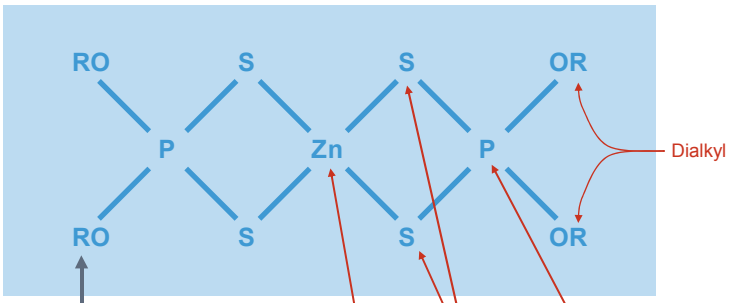
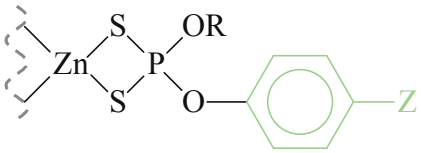
Zinc Dialkyl DithioPhosphate (ZDDP)



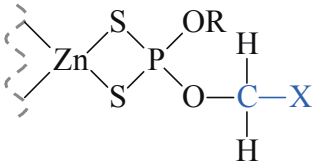
Note: Not exact chemical structure; for illustration only

ZDDP "alkyl" structures

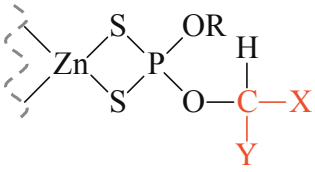
Alkyl type, length, and branching affect ZDDP properties



Aryl ZDDP – aromatic group



Primary ZDDP – one 'alkyl' group

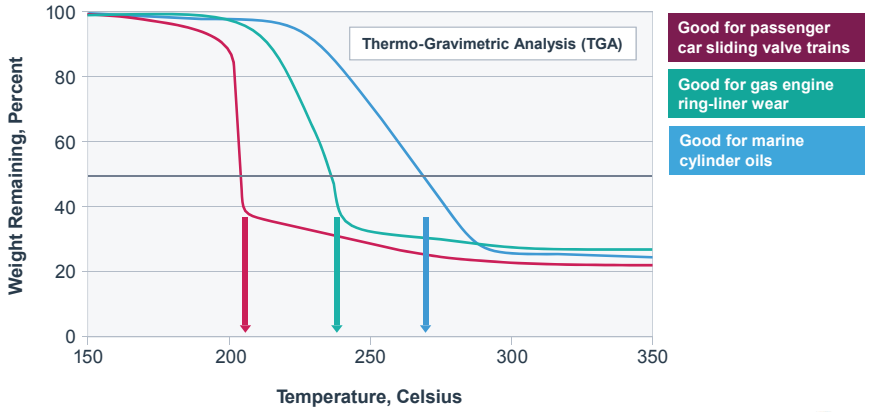


Secondary ZDDP – two 'alkyl' groups

Decreasing Decomposition Temperature

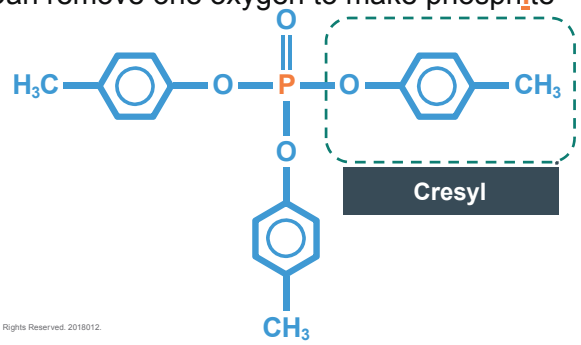
ZDDP decomposition

ZDDP decomposition temperatures highly dependent on method and conditions



Ashless phosphorus type

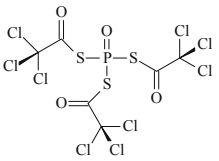
- Tri-cresyl phosphate (TCP)
  - And variations
    - Can substitute other chains for CH_3
    - Can substitute sulfurs for oxygens
      - Thiophosphate
    - Can remove one oxygen to make phosphite



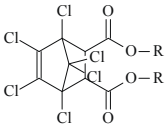
Extreme pressure (EP) additives

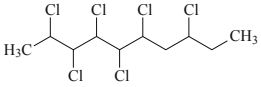
- 'Extreme' is a relative term
  - ZDDP sometimes called 'EP'
- EP more commonly refers to
  - Additives for high loads in gear oils
    - Chlorine-containing molecules
    - Highly reactive sulfur or sulfur-phosphorus compounds
- Work similar to ZDDP, but
  - More active
  - More corrosive
- Balance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

Trichloromethyl ester of thiophosphoric acid

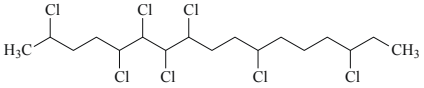


Ester of chlorendic acid



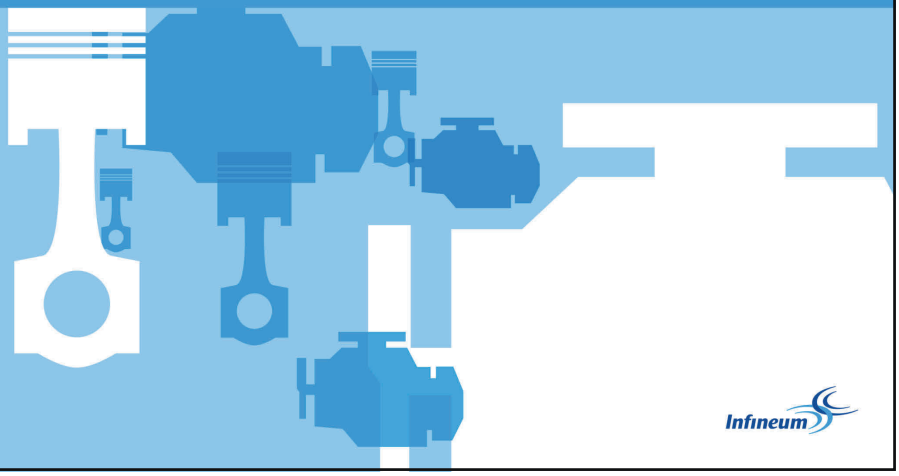


Short-chain chlorinated paraffin



Medium-chain chlorinated paraffin

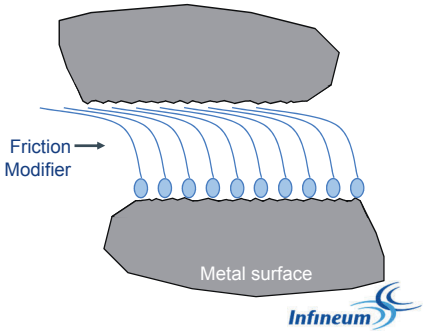
Friction modifiers



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:



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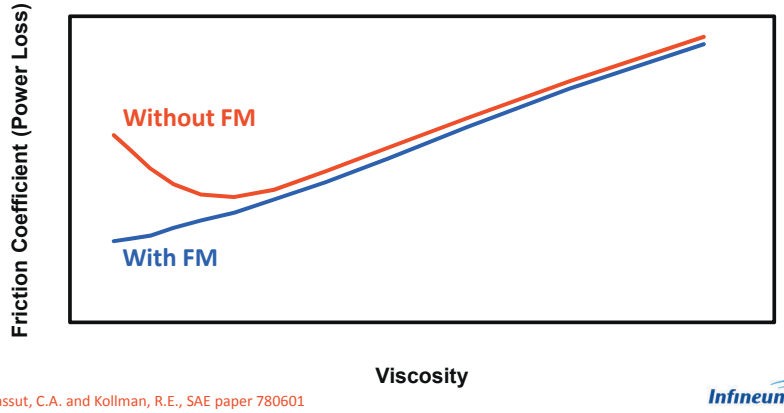
Friction modifier example

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



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

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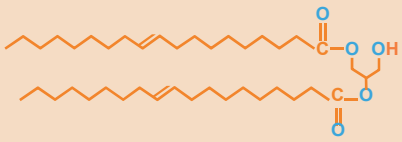
Typical friction modifiers

Oleic acid	
Dioleyl phosphite	
Glycerol dioleate	

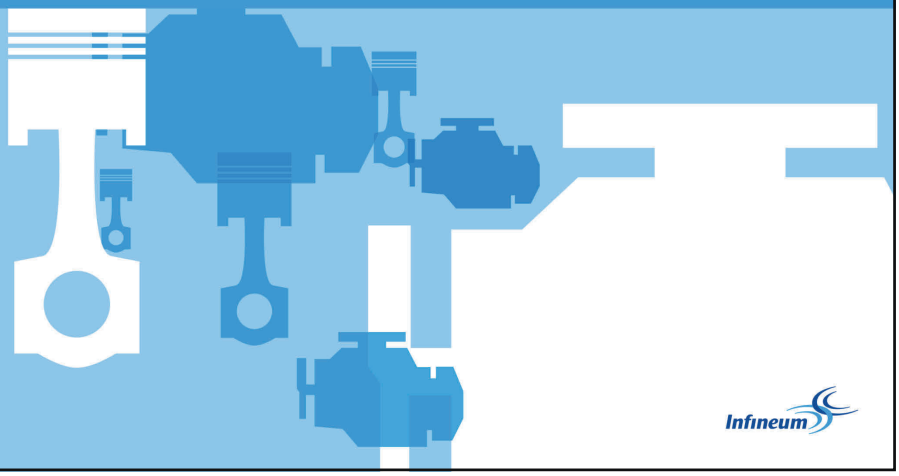
Solid friction modifiers

- '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

Performance you can rely on.

Comparison of additives



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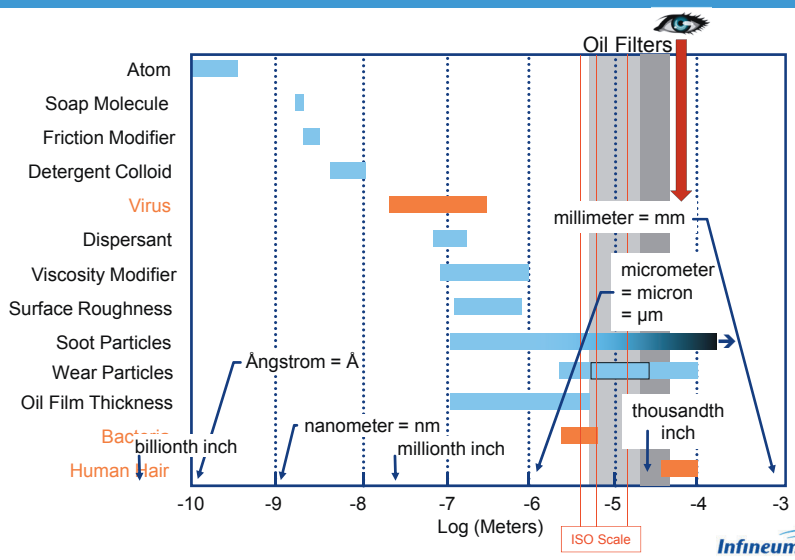
Performance you can rely on.

Relative sizes of things



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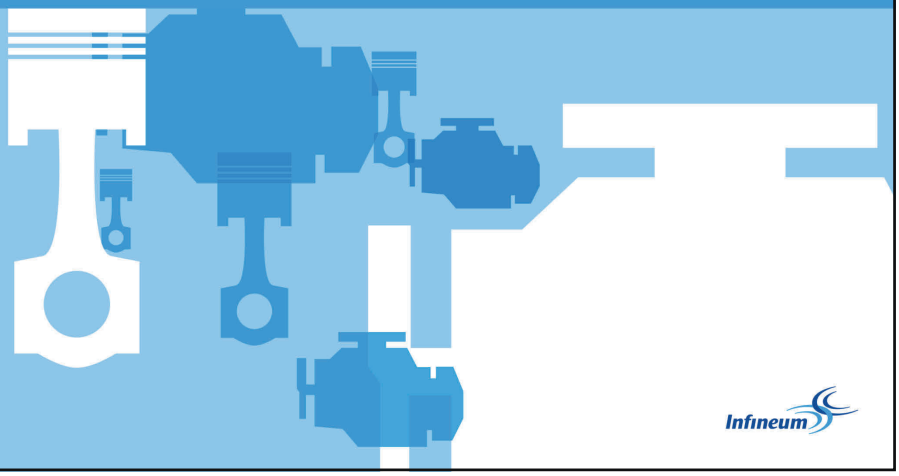
Formulation
(Putting it all together)



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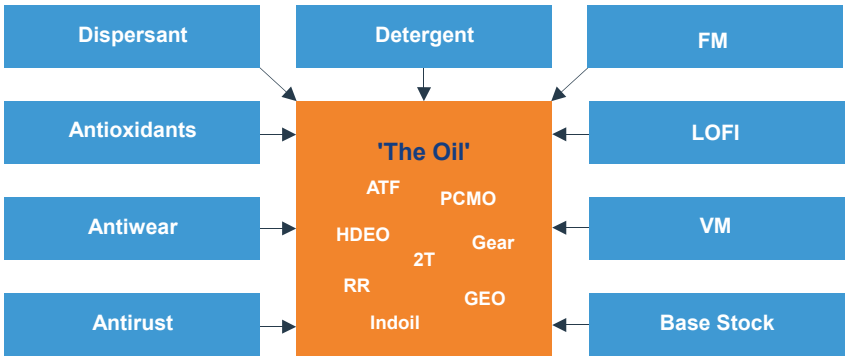
Formulation science

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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