Chemistry of Lubricant Additive Components

Lubrication Fundamentals
What's in it for Me?

- After this session you should be able to:
  - Discuss the functions and properties of a lubricant
  - Describe what an additive is and how it works
  - Name the 9 main lubricant additives
  - Explain the basic functions of these 9 additives

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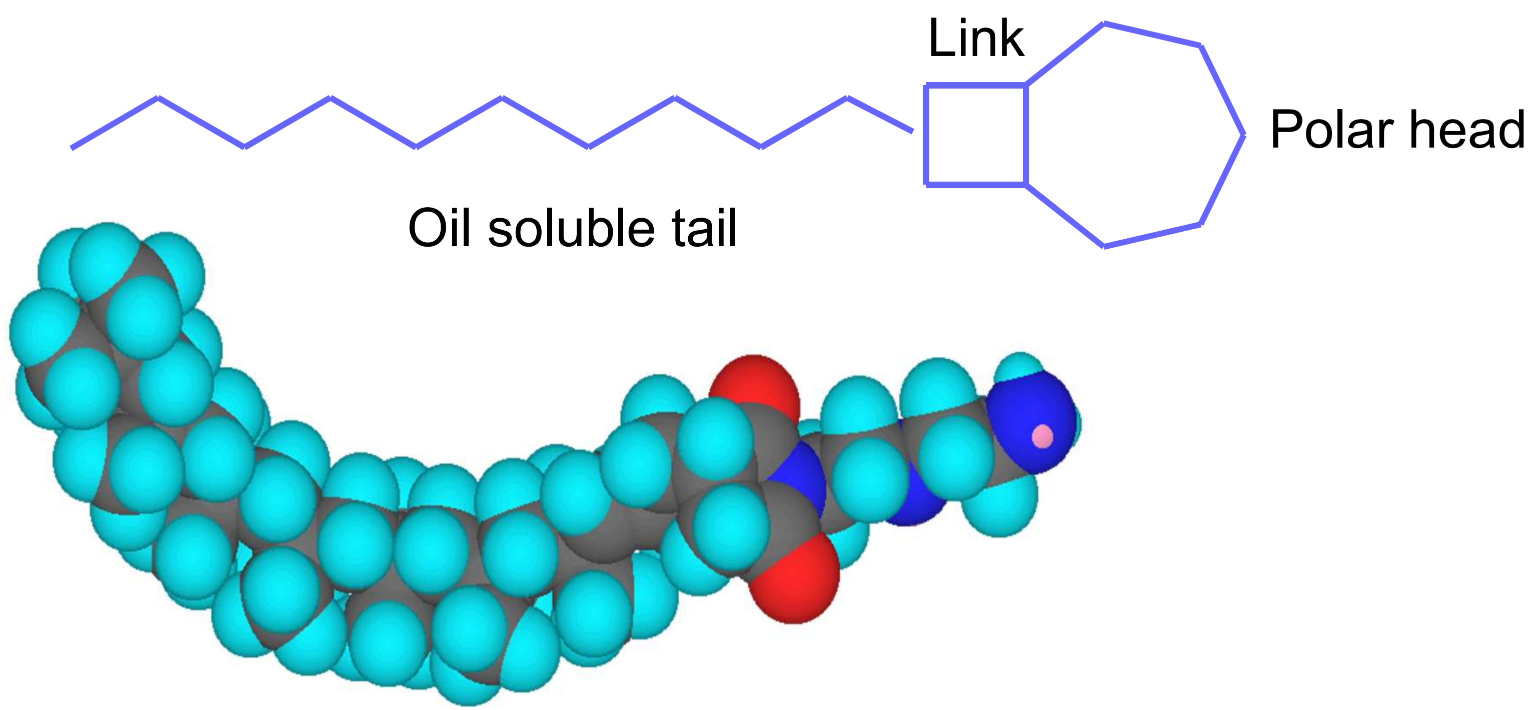
Additive Basics

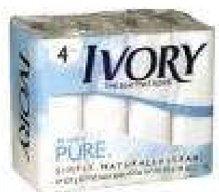
Additive Basics

Definition

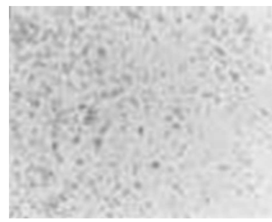
An additive is a material which imparts or reinforces a desirable property of the lubricant – enhances the desirable properties already present or by adding new properties



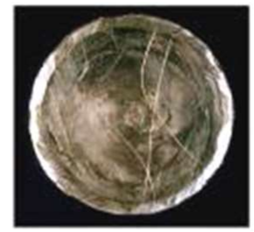
Additive Basics
Package Components



Detergent



Dispersant



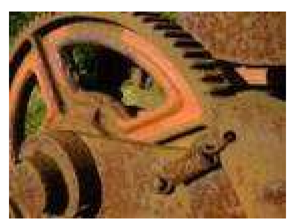
Antiwear

Extreme Pressure Agent

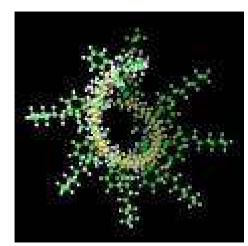
Foam Inhibitor

Friction Modifier

Oxidation Inhibitor

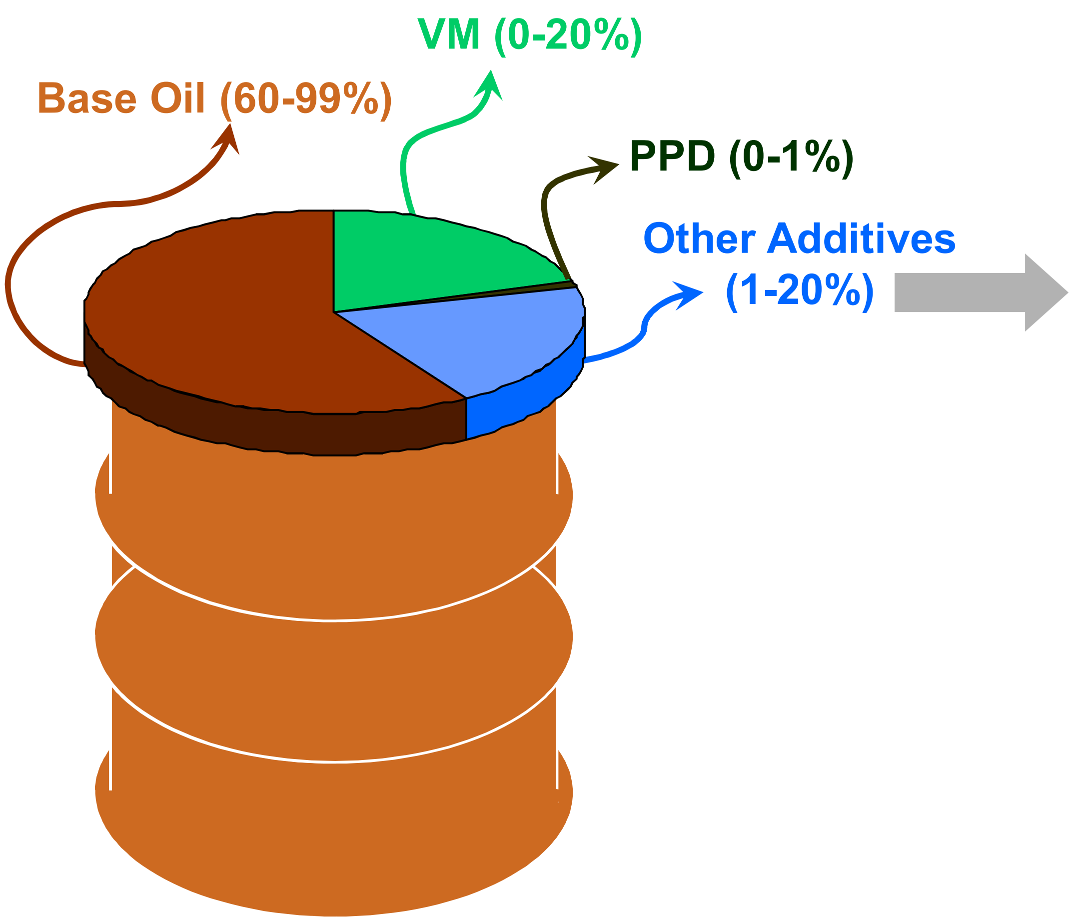


Corrosion Inhibitor



Viscosity Modifier/PPD

Lubrication Fundamentals
Lubricant Formulations



Detergents
Dispersants
Antioxidants
Antiwear Agents
EP Agents
Friction Modifiers
Foam Inhibitors
Corrosion Inhibitors

Additive Chemistry

Detergents

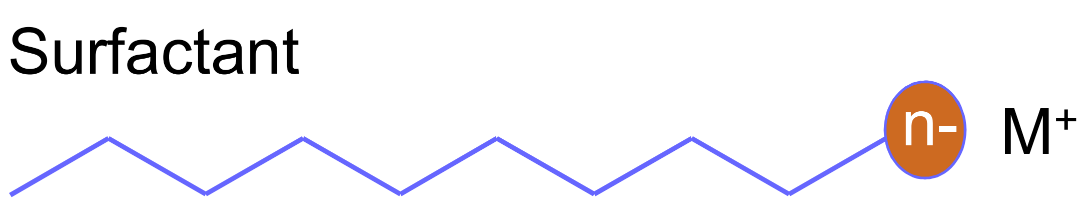
Detergents

Three Main Functions

- Clean internal engine parts
- Neutralize combustion acids
- Inhibit oxidation

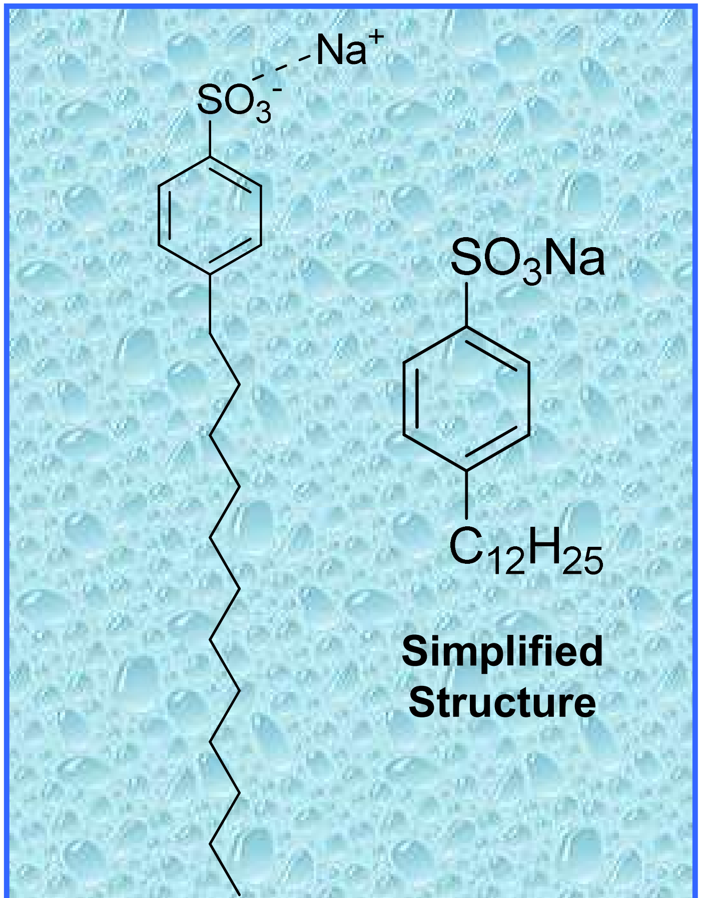
Contain metals which produce ash

- Calcium
- Magnesium
- Barium
- Sodium
- Lithium
- Potassium

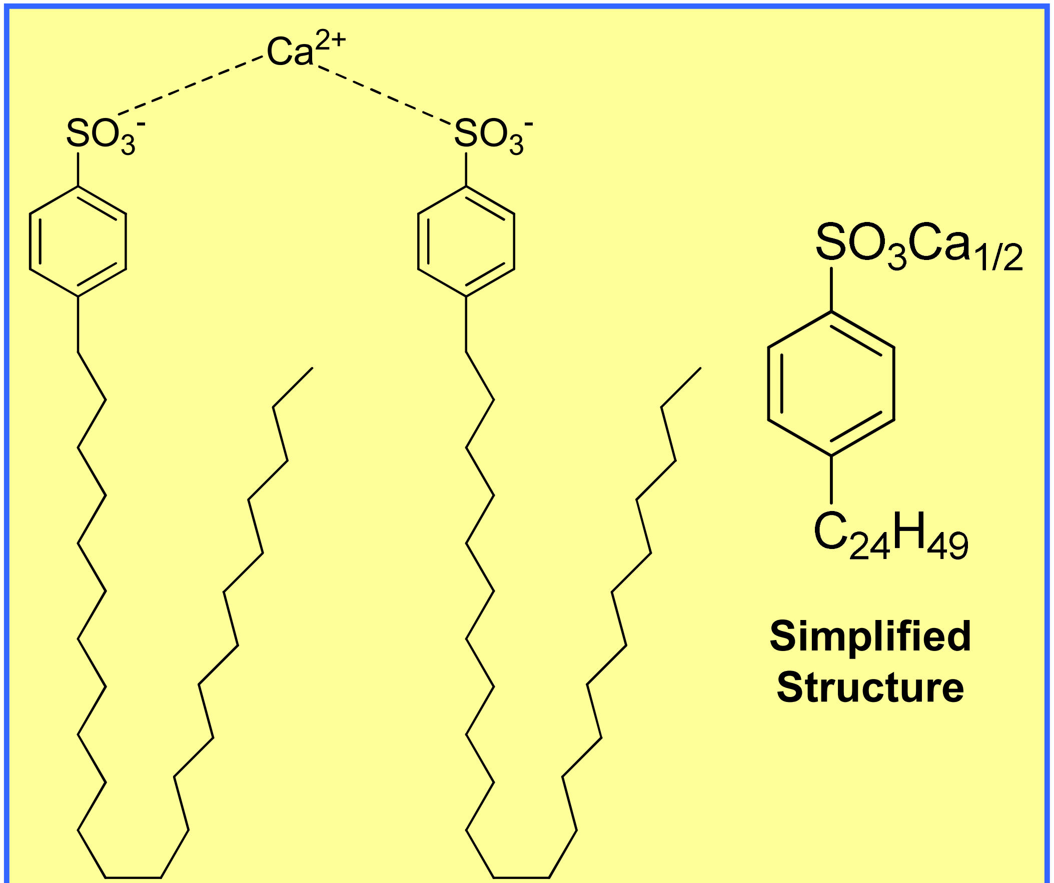


Allow for longer drain intervals

Detergents
Detergent Sulfonates



Aqueous - Household Soap

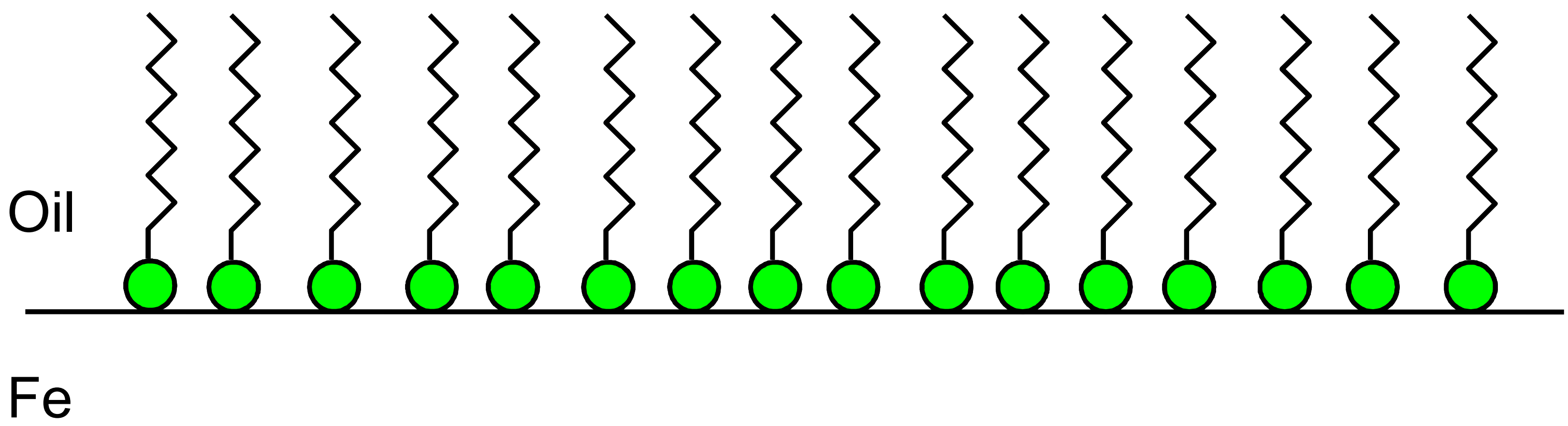


Hydrocarbon - Lube Oil

Detergents

Neutral Detergents

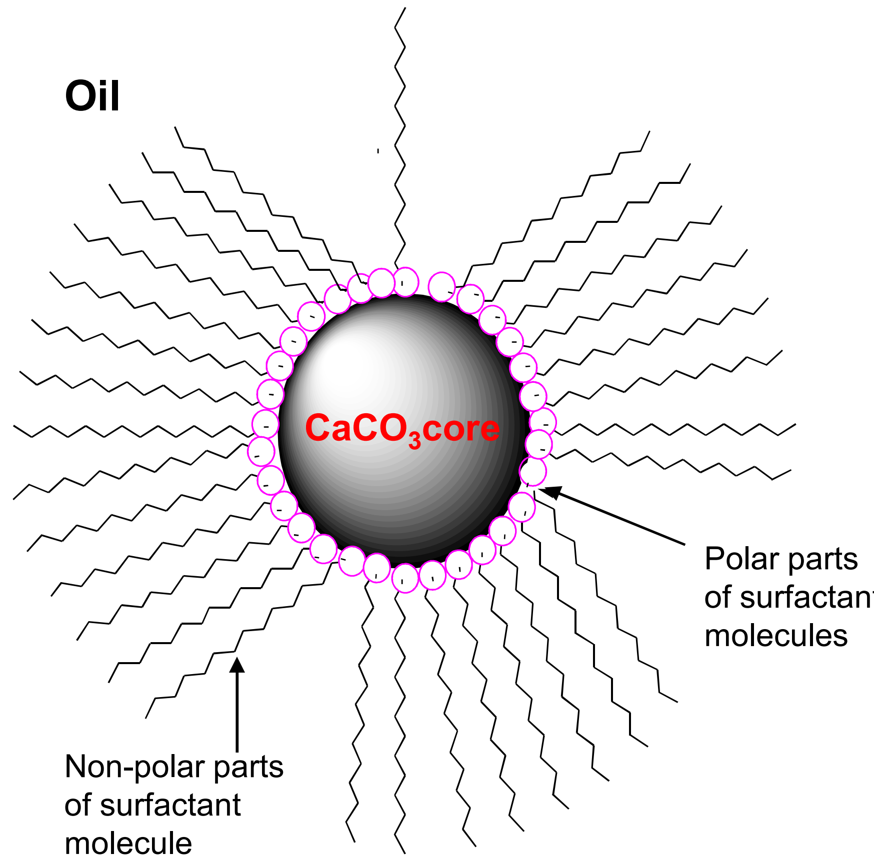
- Remove polar particles from the surface
- Inhibit rust/corrosion
- Friction modifier properties



Detergents

Overbased Detergent

- Can get up to 50% metal carbonate solutions in oil - completely clear!
- Usually spherical "core"
- Surfactants form oil soluble "shell"



5 - 16.55% Ca

Detergents

Overbased Detergents - Preparation

$$\mathbf{M}^{n\oplus}(\mathbf{OH})^{\ominus}_{n} + \mathbf{ROH} \xrightarrow{\text{Heat}} (\mathbf{RO})^{\ominus}_{n}\mathbf{M}^{n\oplus} + \mathbf{H_2O}$$

Metal Base (Excess) — Organic acid — Oil soluble metal salt — Water

M= Ca or Mg

Oil soluble metal salt → (Heat, CO_2; Polar solvents) → Colloidal metal carbonate + H_2O

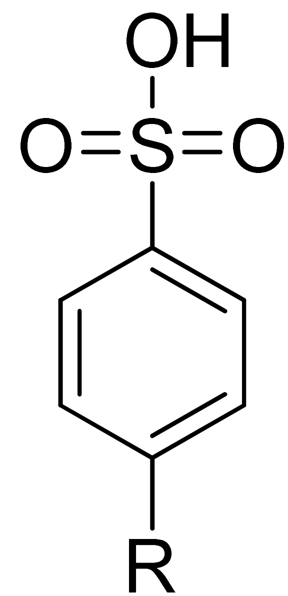
- Excess base is reacted with carbon dioxide to form metal carbonates in an oil soluble form
- Termed **overbased** because far more base is used than is simply required to neutralize the acidic surfactants

Detergents
Total Base Number (TBN)

- The theoretical amount of potassium hydroxide (KOH) present in the lubricant
- A higher TBN indicates greater acid neutralizing capacity
- TBN = (mg KOH)/(g Lubricant)

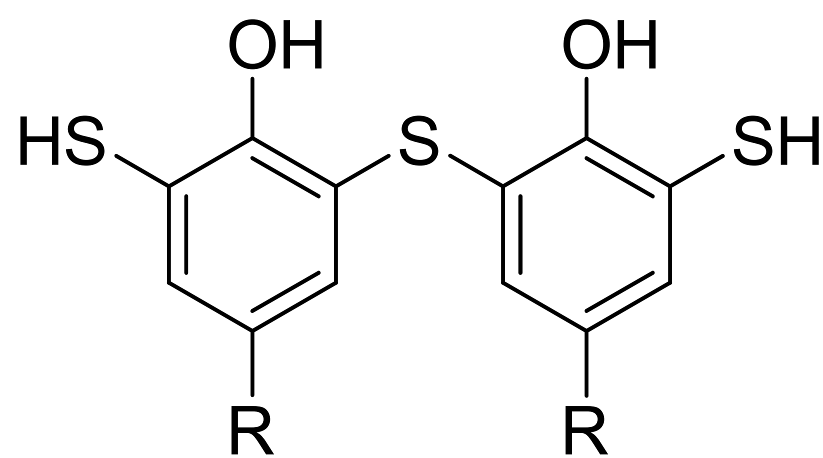
Detergents
Advantages and Disadvantages – Sulfonates

- Advantages
  - Excellent detergency
  - Can be overbased to give very high base contents (e.g. up to 50% $CaCO_3$)
  - Cost effective
- Disadvantages
  - No antioxidancy



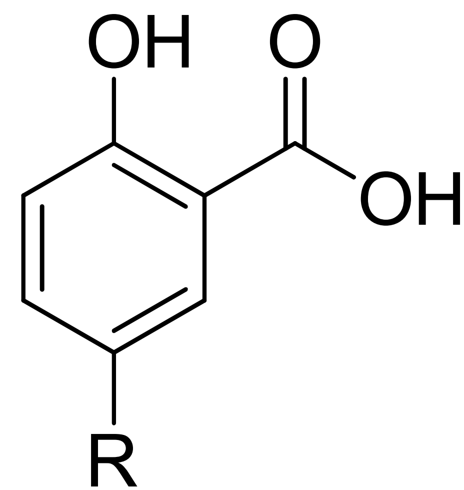
Detergents
Advantages and Disadvantages – Phenates

- Advantages
  - Antioxidant
  - Good detergency
- Disadvantages
  - Cannot get high base levels as sulfonates
  - Can use a carboxylic acid co-surfactants
  - Relatively expensive



Detergents
Advantages and Disadvantages – Salicylates

- Advantages
  - Excellent antioxidants
  - Good detergency
  - Sulphur free
- Disadvantages
  - Cannot get such high base levels as sulfonates
  - Less cost effective



Detergents
Too Much Detergent

- Excessive deposit formation at high temperature
- Interference with anti-wear and dispersant additives
- Long term stability issues
- Certain types of detergents can react with water or acidic contaminants to cause the oil to thicken and ultimately gel

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Additive Chemistry

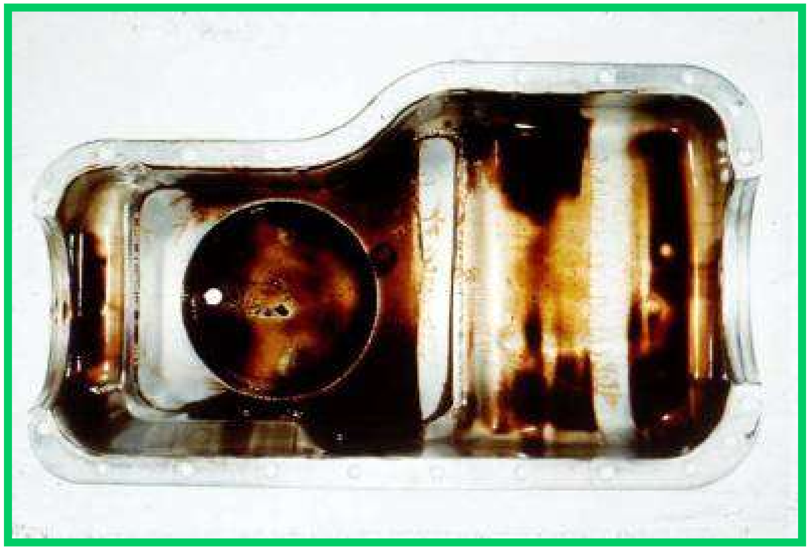
Dispersants

Dispersants
Function of Dispersants

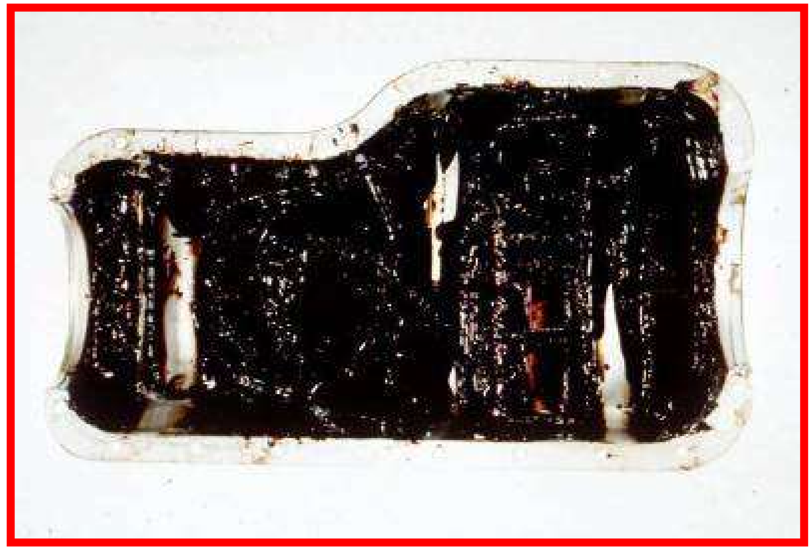
- Dispersants function by stabilizing colloidal dispersions and preventing them from agglomerating and coming out of oil as dirt
- Help keep parts clean at lower temperatures
- Protect against contaminant particle growth
- Can help to minimize oil thickening due to contamination
- Are ashless or metal free
- Molecular weight is typically higher than that of detergents in the range of an order of magnitude

Dispersants

Dispersants Keep Engine Parts Clean



Acceptable



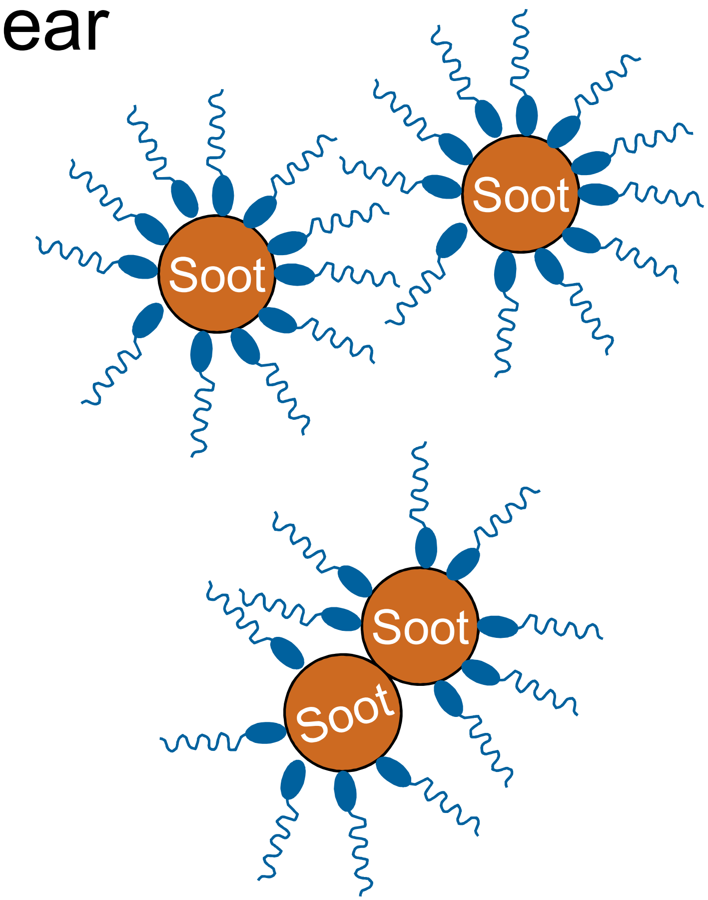
Unacceptable

- Soot results from inefficient combustion of fuel and burning of the lubricant that goes past the piston rings into the oil chamber
- Soot particles have the tendency to aggregate on surfaces as soft and flaky deposits and in oil leading to its thickening

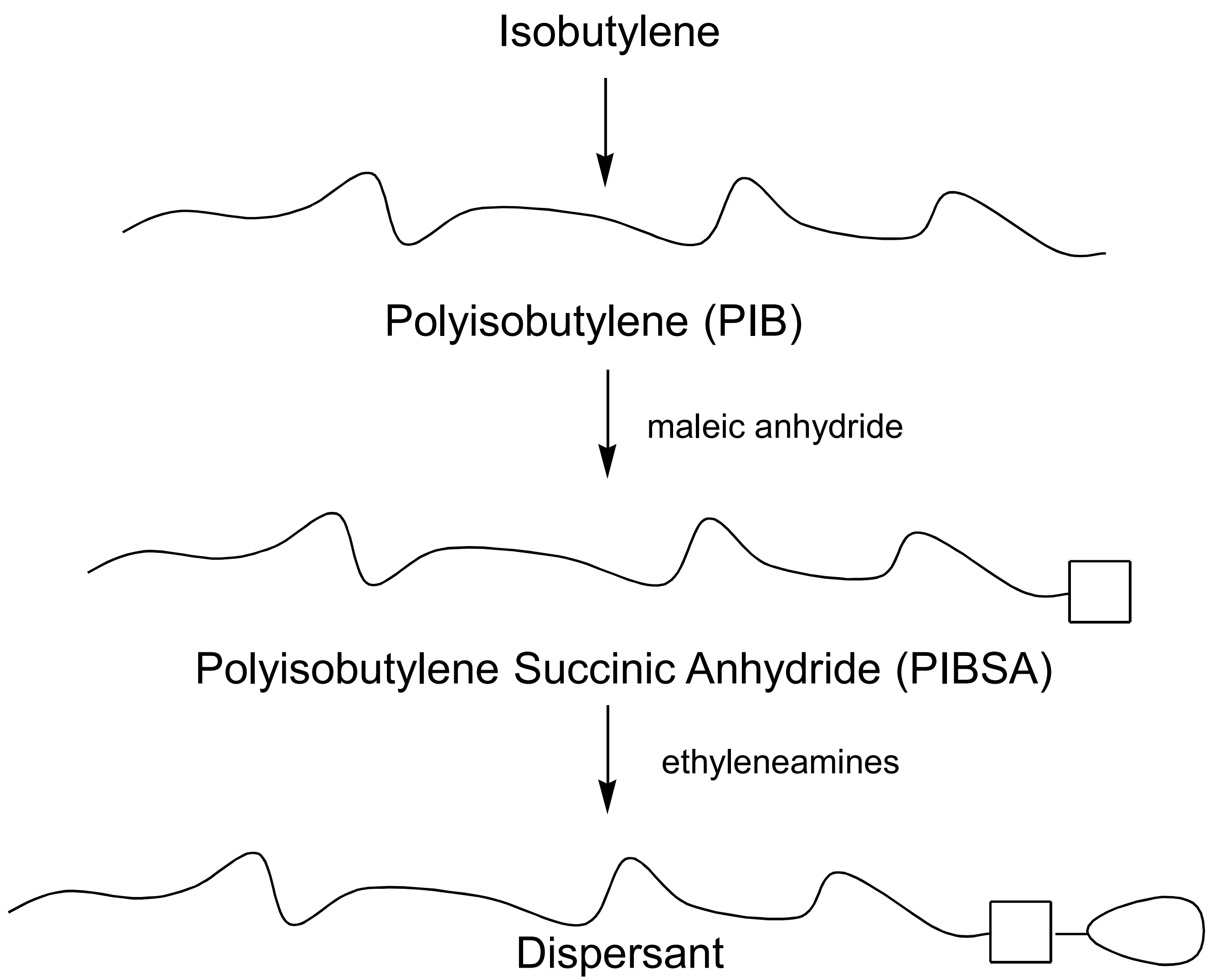
Dispersants

Mechanism of Dispersant Function
Soot Agglomeration and Wear

- Good dispersant coverage, particles do not agglomerate
- "Patchy" dispersant coverage, particles agglomerate - "bare spots" touch
- Requires many collisions or sedimentation
- Requires a long time, so
  - Short term stability
  - Long term instability
- Soot is a particulate contaminate that that results in abrasive wear



General Dispersant Synthesis



Dispersant
Too Much Dispersant

- Dispersants can interact with other additives to negatively impact their performance
- A precise additive balance is needed to optimize different formulations
- Dispersants can affect the viscometrics of the oil making it difficult to meet certain low temperature properties

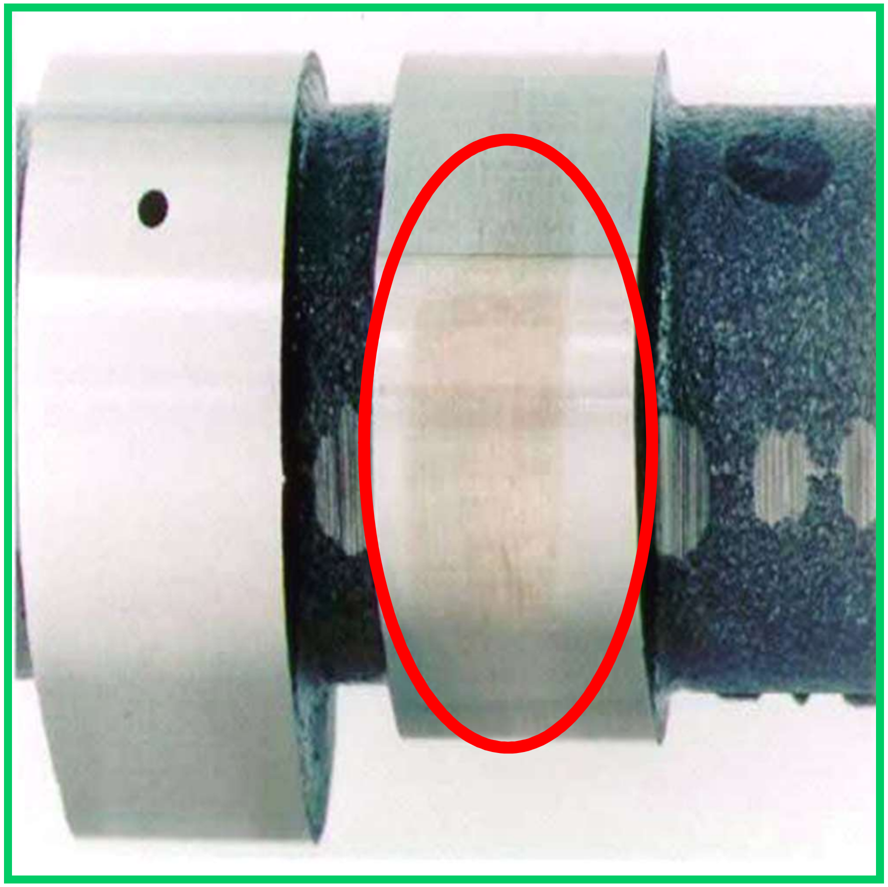
Additive Chemistry

Antiwear and Extreme Pressure Agents

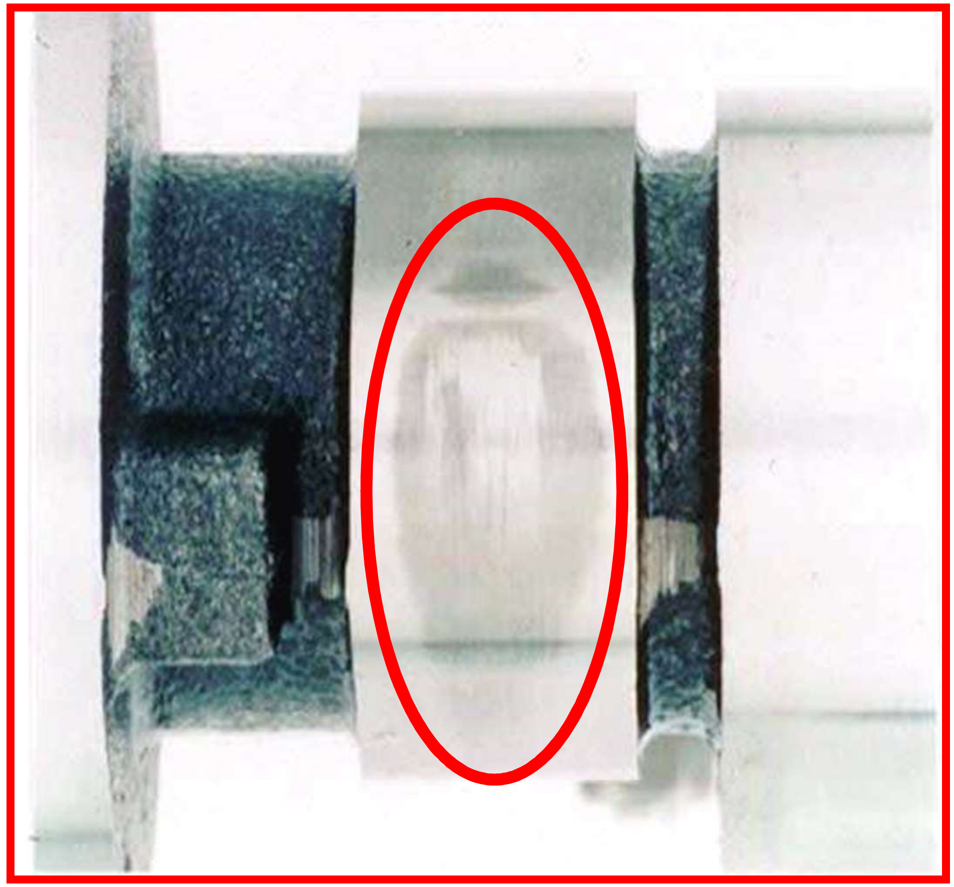
Antiwear and Extreme Pressure Agents
Wear

- Wear is defined as damage to a surface by the action of a harder material or chemical reaction
- Four Wear Modes:
  - Abrasive is caused by hard particles or uneven surfaces in contact
  - Corrosive or chemical wear from the attack of foreign substances
  - Fatigue from temp changes due to frictional heating or periodic impact
  - Sliding wear from surface to surface contact that results in adhesion, welding, or scoring

Antiwear Agents Prevent Camshaft Wear



Good

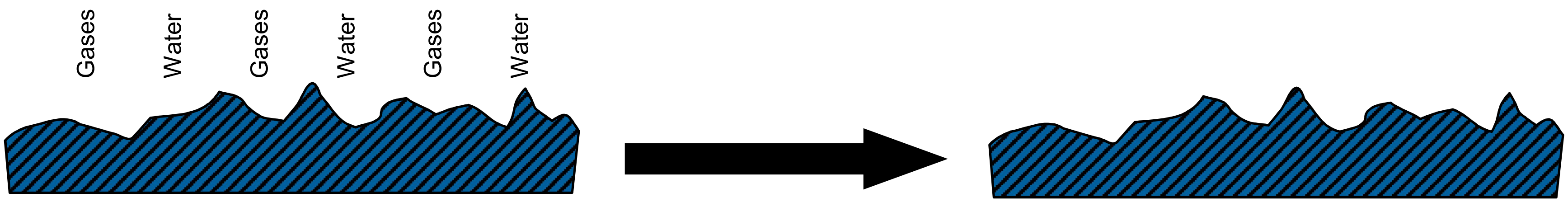


Poor

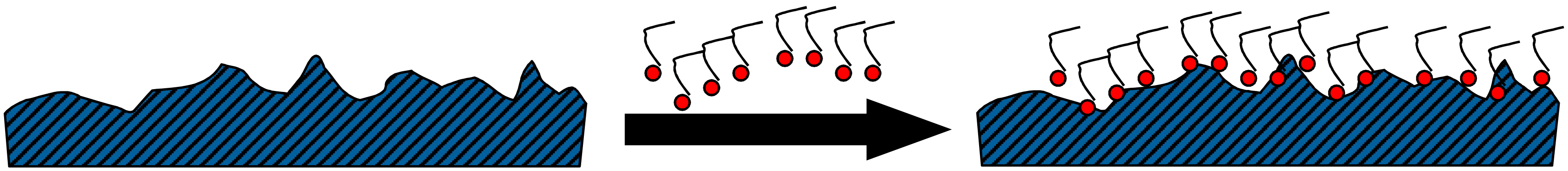
Antiwear and Extreme Pressure Agents

Antiwear/EP Mechanism

Break in Period- Remove Gas and Water



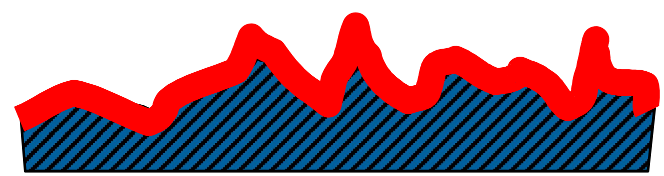
Physical or chemical absorption

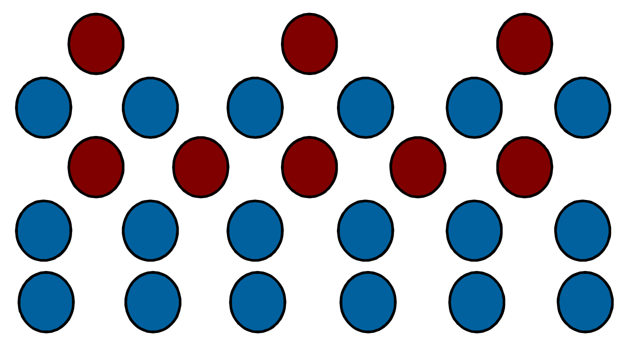


Surface reaction and protective layer growth

Antiwear and Extreme Pressure Agents
Extreme Pressure Additives

- They modify the surface of components:
  - They form chemical layers on the surface of metal components
  - They require even higher temps and / or loads to become activated than AW agents



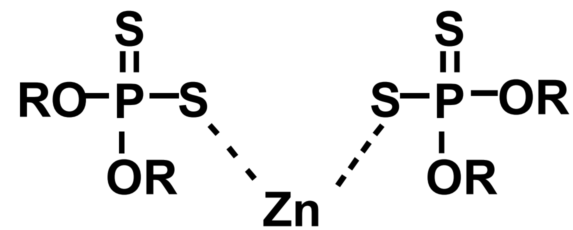


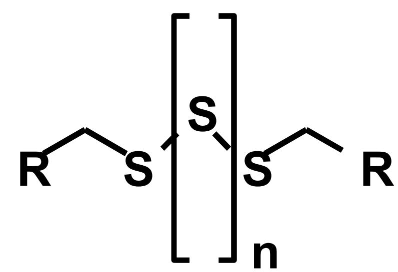
Chemical Reaction

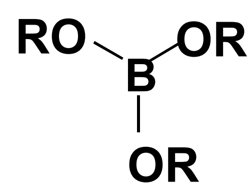
Antiwear and Extreme Pressure Agents

Typical Antiwear and EP Agents

- Zinc dithiophosphates (ZDDP)
- Organic phosphates and acid phosphates
- Organic phosphites
- Organic sulfur and chlorine compounds
- Sulfurized fats
- Sulfides and disulfides
- Borates (intolerant of water)







Antiwear and Extreme Pressure Agents
Too Much AW and EP

- Since they typically contain phosphorous, sulfur, chlorine and/or boron they can cause corrosion to soft metals such as copper or lead in the equipment
- The phosphorous in ZDDP can cause catalyst poisoning in engine oil applications

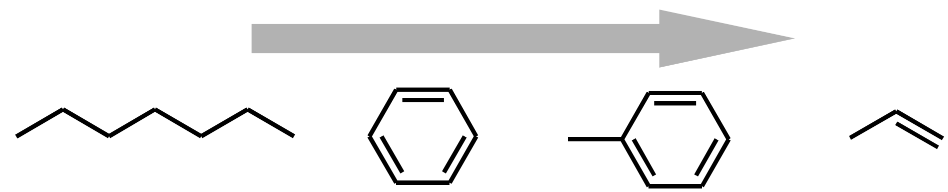
Additive Chemistry

Antioxidants

Antioxidants

- An engine is a harsh environment for lubricants and additives
  - High temperatures and Oxygen
  - Catalytic Cu, Fe and Pb

Decreasing Stability

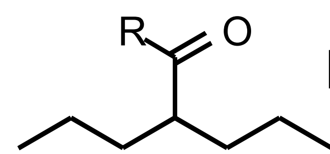


Hydrocarbon

↓ Radicals

Oxidation Products

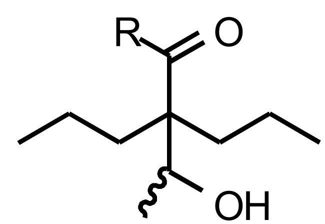
↓ Condensation



R = OH, H, alkyl

High molecular weight species

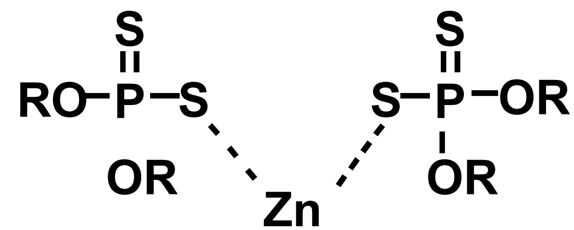
↓ Polycondensation



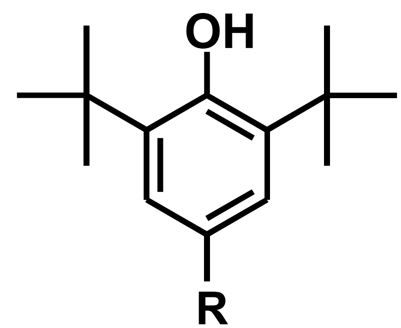
Varnish, Sludge, Acids

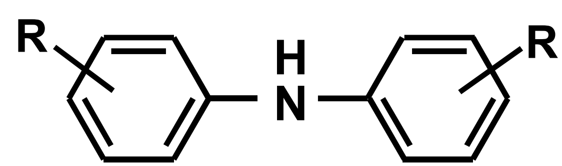
Oxidation Inhibitors

- Peroxide Decomposer
  - Zinc Dithiophosphate (ZDDP)
  - Sulfurized Olefins
- Radical Scavengers
  - Zinc Dithiophosphate (ZDDP)
  - Hindered Phenol
  - Aromatic Amines

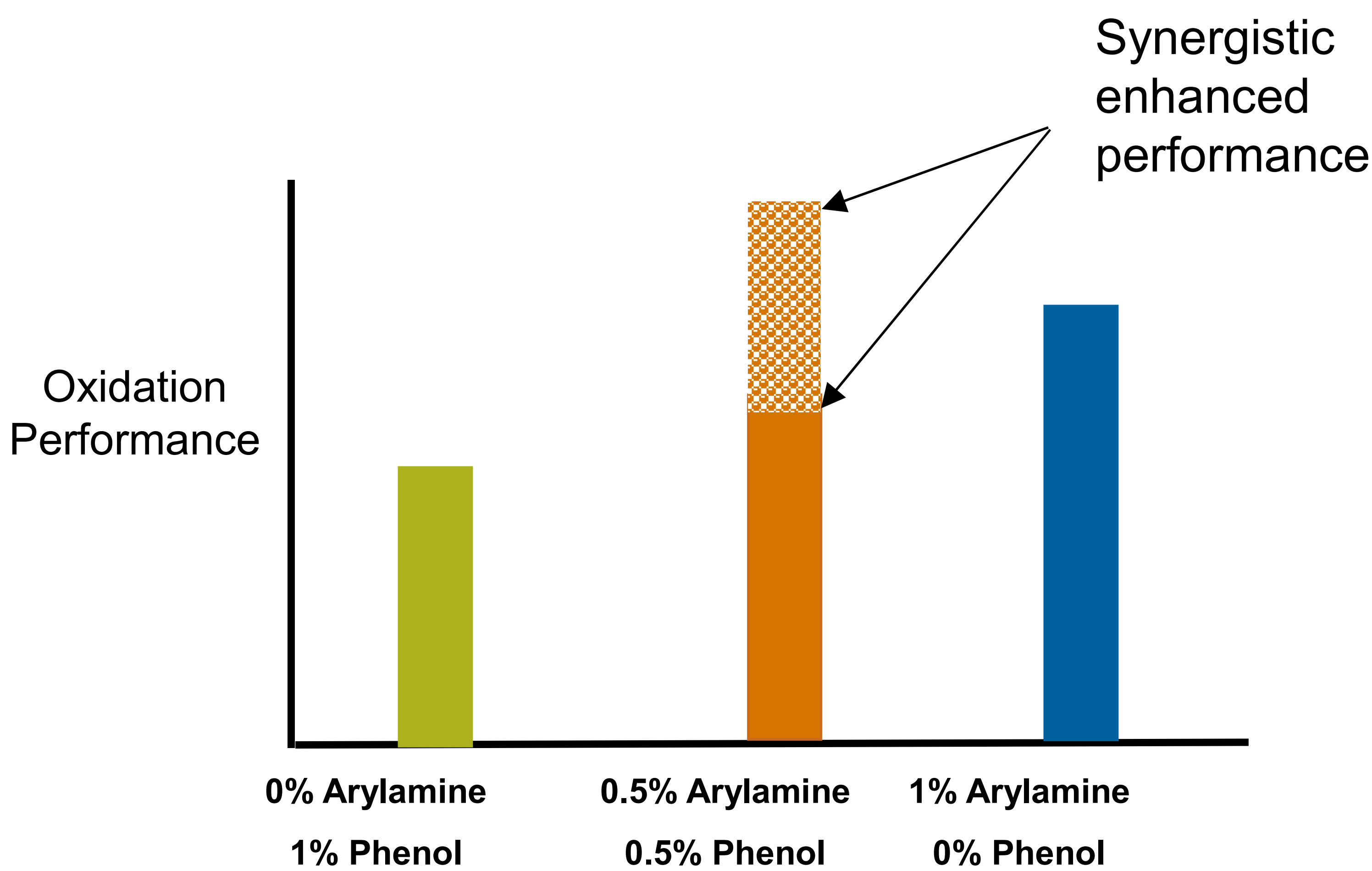


$RS(S)_nSR$





Antioxidants
Inhibition Synergism



Antioxidants
Oxidation Inhibitors

- Dithiophosphates
  - Effective at high temperatures (>93°C); offer little inhibition at low temperatures
  - React with surfaces to form protective coatings
  - Decompose peroxides and scavenge radicals
- Alkylated (hindered) phenols or aromatic amines
  - Function well at low temperatures (<93°C); less effective at high temperatures because of volatility
  - React with initiators forming inactive compounds

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Additive Chemistry

Rust/Corrosion Inhibitors

Rust and Corrosion Inhibitors

- Corrosion is the deterioration of a substance (usually metal) or its properties because of a reaction with its environment
  - Metal is changed from its metallic state into an oxidized form
    - Metal ions that result from corrosion can act as oxidation promoters
  - Corrosion can accompany or accelerate physical deterioration
  - Can alter the structural integrity of the equipment

Rust and Corrosion Inhibitors
Examples of Corrosion

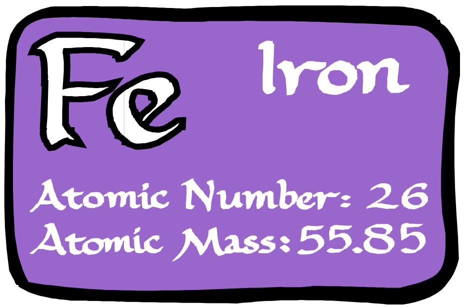
Iron/steel + oxygen + water	→	Iron oxide (rust)
Copper + sulfur	→	Copper sulfide (black, flaky surface)
Lead + carboxylic acids	→	Lead carboxylates (leaches into environment)
Aluminum+ oxygen + water	→	Aluminum oxide (protective layer?)

Rust and Corrosion Inhibitors
Corrosion Types

- Electrochemical corrosion (corrosion in electrolytes)
  - Results from the attack of moisture, water, acid, alkali, or salts on metal
  - Affected by pH, temperature and nature of metal oxide film
- Chemical corrosion
  - Action of an aggressive organic substance on metal. Example: Attack of sulfur-containing organic compounds on metal.
  - Does not need electrolytes

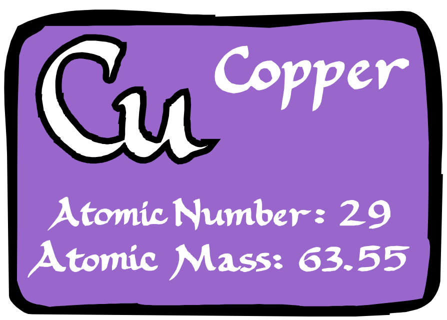
- Atmospheric corrosion
  - Corrosion of metals in the atmosphere and moist gases
- Gaseous corrosion
  - Corrosion of metal surface without moisture. Usually occurs at elevated temperatures

Rust and Corrosion Inhibitors
Metals to Protect

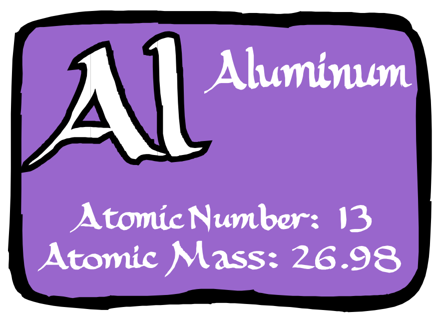


Forge engine and auxiliary equipment

Bearings and seals

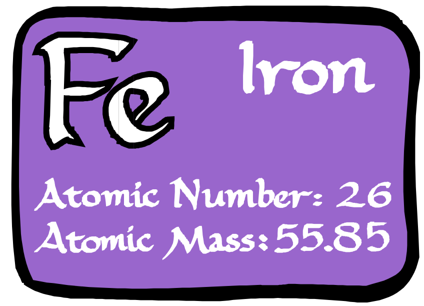


Bearings



New vehicles

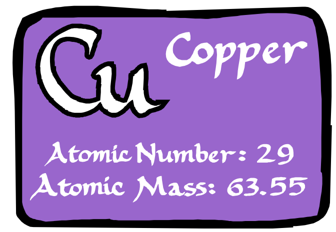
Rust and Corrosion Inhibitors
Ferrous Corrosion



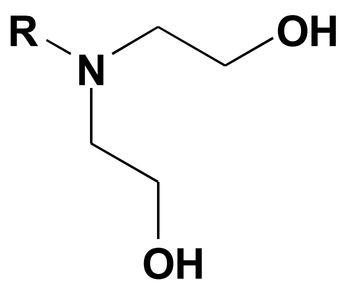
- Corrosion of iron and its alloys
- Primarily electrochemical in nature
- Commonly called rust
- Can involve both liquid and vapor phase
- Needs water, electrolyte, and oxygen
  - Water results from fuel combustion
  - Oxygen comes from the air
  - Electrolytes are the metal salts that form by the reaction of metals and certain additives with combustion and oxidation acids
- Mainly occurs in engines that are run in short cycles (stop-and-go driving)

Rust and Corrosion Inhibitors

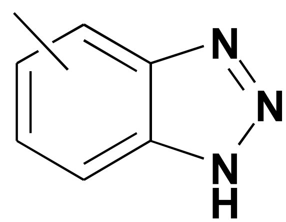
Yellow Metal Corrosion



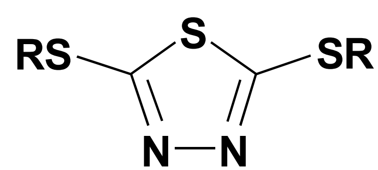
- Corrosion of copper and bronze
- These metals are part of seals and bearings
- Usually occurs because of the attack of aggressive species on metals
  - Oxidation products
  - Sulfur-containing additives



Alkanol amines



N-containing Heterocycles

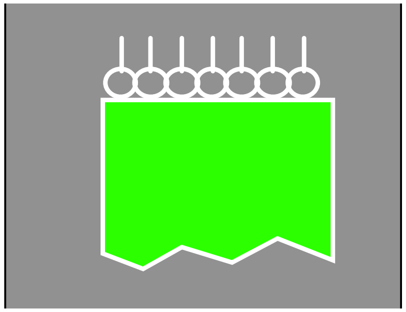


DMTD

Rust and Corrosion Inhibitors
Yellow Metal Corrosion

Rust and Corrosion Inhibitors
Protection Mechanism

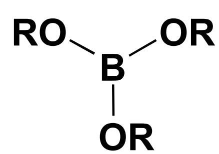
- Acid-neutralizers = "Offensive Protection"
  - These additives neutralize aggressive acidic product and make them innocuous
- Film-formers = "Defensive Protection"
  - These additives physically or chemically adsorb on the metal surfaces via their polar ends and associate with lubricant via their non-polar end to form a protective film
  - Changes a chemically active surface of a metal to a less reactive state
  - Forms a thin, compact film on metal surface
  - Reduces the oxidation of the metal surface
  - Reduces the dissolution of metal ions into the surrounding environment



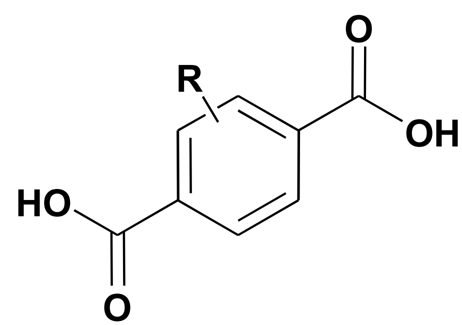
Rust and Corrosion Inhibitors

Lead Corrosion

- Preferential removal of lead from copper-lead bearings (lead-leaching), primarily in diesel engines
- Partly, it may result from the attack of aggressive species on metals
- The process perceived to be chemical and not electrochemical



Borate Esters



Terephthalic acid

Additive Chemistry

Foam Inhibitors

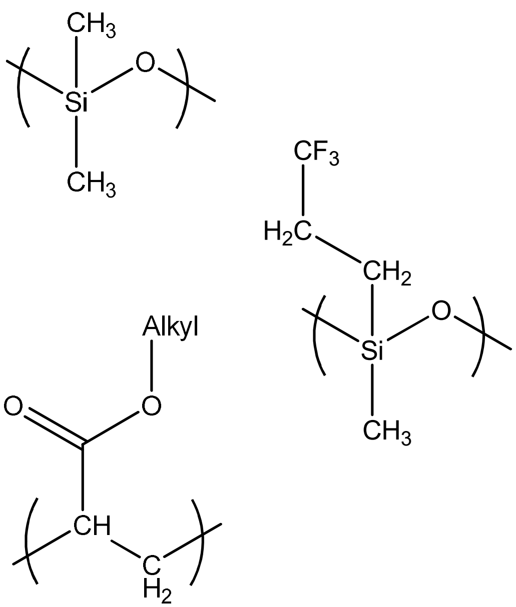
Foam Inhibitors
Foam Formation

- Foam forms when a large amount of low solubility gas gets entrained into a liquid by agitation
- In lubricants, foam can result in power loss and reduced performance

Foam formation in a gear box

Foam Inhibitors
Foam Inhibitor Description

Foam inhibitors are compounds of poor oil solubility. They break foam bubbles by adsorbing on the surface of the bubbles and changing its surface tension.



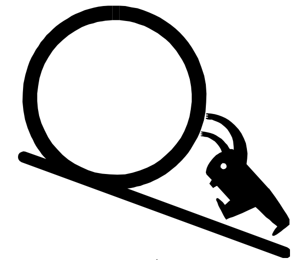
- Partly insoluble chemicals
- Silicon compounds
- Polyacrylates
- Very low concentrations-ppm range

Additive Chemistry

Friction Modifiers

Lubrication Fundamentals

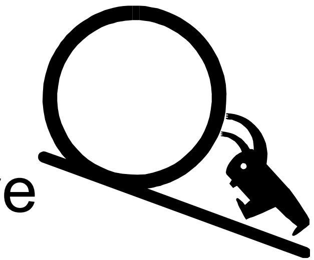
Frictional Heat and Lubrication



- Friction always produces heat and uses power
- The most important function of a lubricant is to prevent metal-to-metal contact or to minimize friction between metal surfaces in motion with respect to each other
- Lower cohesive forces of a fluid are substituted for higher sliding or rolling friction forces
- Friction can never be totally eliminated

Lubrication Fundamentals

Relationship Between Friction and Wear



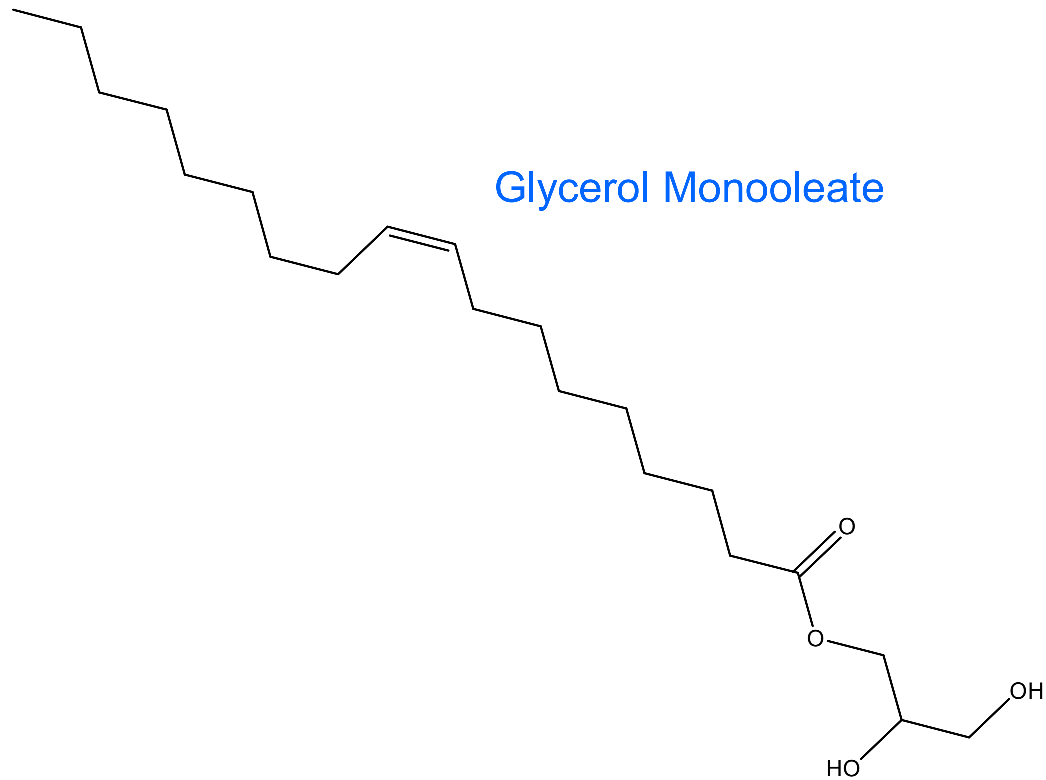
Friction is the force that hinders or resists the relative motion of two bodies in contact

Friction Regime	Coefficient of Friction (μ)	Wear
Dry friction (sliding)	0.300	High
Dry friction (rolling)	0.005	Very low
Mixed friction (rolling)	0.005-0.300	Noticeable
Fluid friction	0.005-0.100	Practically zero

Friction Modifiers

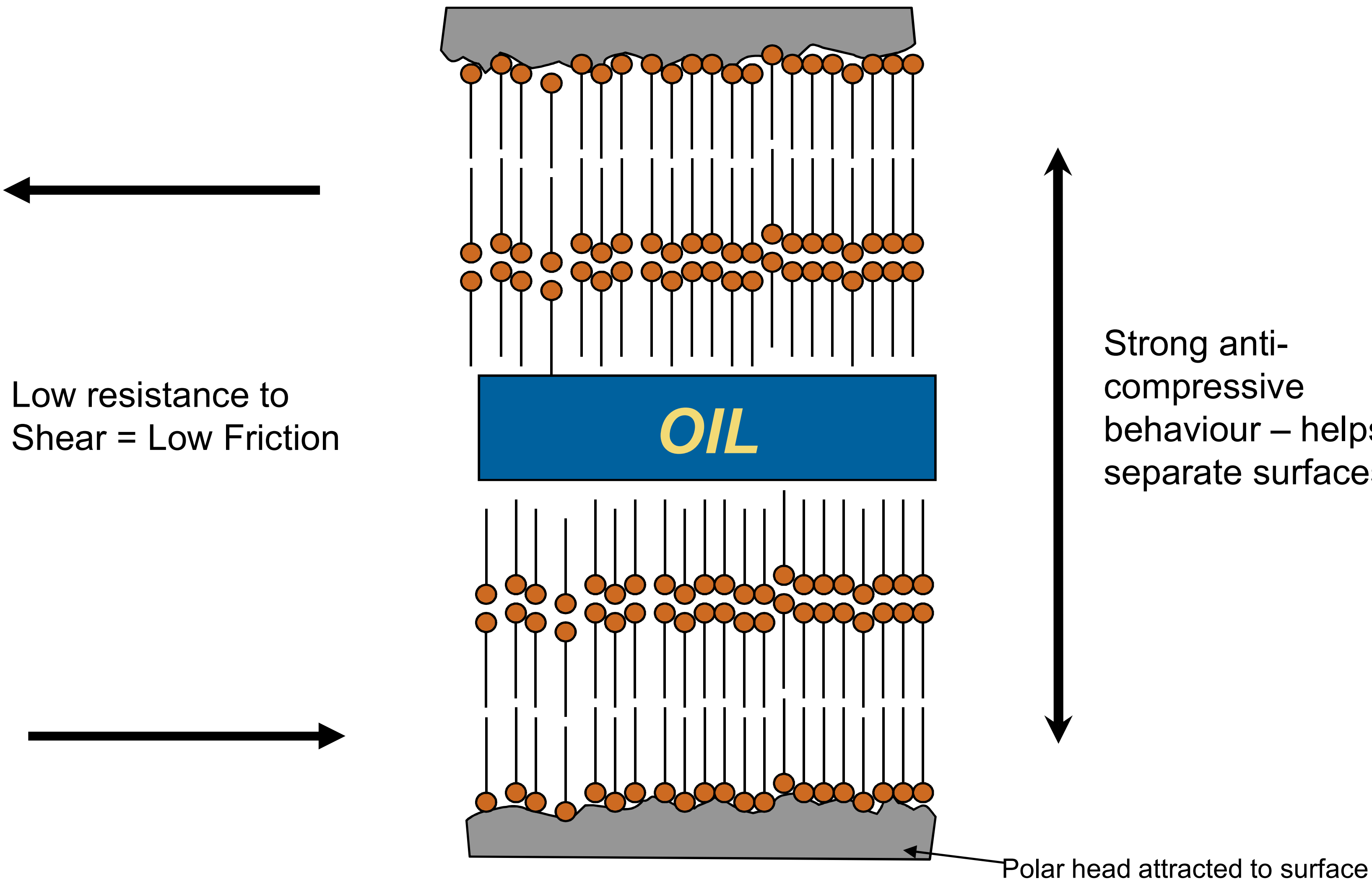
- Used to reduce friction and wear when mild sliding conditions occur
- Consist of a hydrocarbon chain and small polar functional head group
- Adsorb on the metal surface rather than chemically reacting with the surface as EP agents do
- Align in regular pattern and act to reinforce fluid film

Glycerol Monooleate



Friction Modifiers

Low resistance to Shear = Low Friction



Strong anti-compressive behaviour – helps to separate surfaces

Friction Modifiers

Goal of Use

- Synergistic with Antiwear agents forming a physical adsorption film
- Fuel economy improvement-less friction means less energy consumed
- Remove heat from metal-metal contact region
- Non-reactive
- Friction modifier chemical composition varies by application

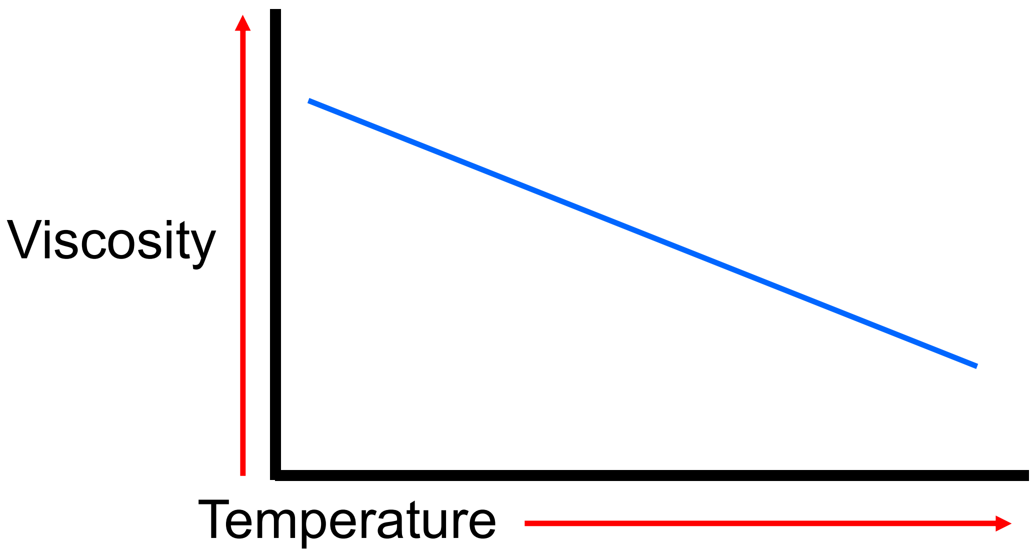
Friction Modifier Types

- Fatty amines
- Fatty acids
- Fatty amides
- Fatty esters
- Paraffin waxes
- Oxidized waxes
- Fatty phosphates
- Sulfurized fats
- Others

Viscosity Fundamentals

Lubrication Fundamentals
Viscosity

- Resistance to flow
- Varies inversely with temperature
- Varies directly with pressure

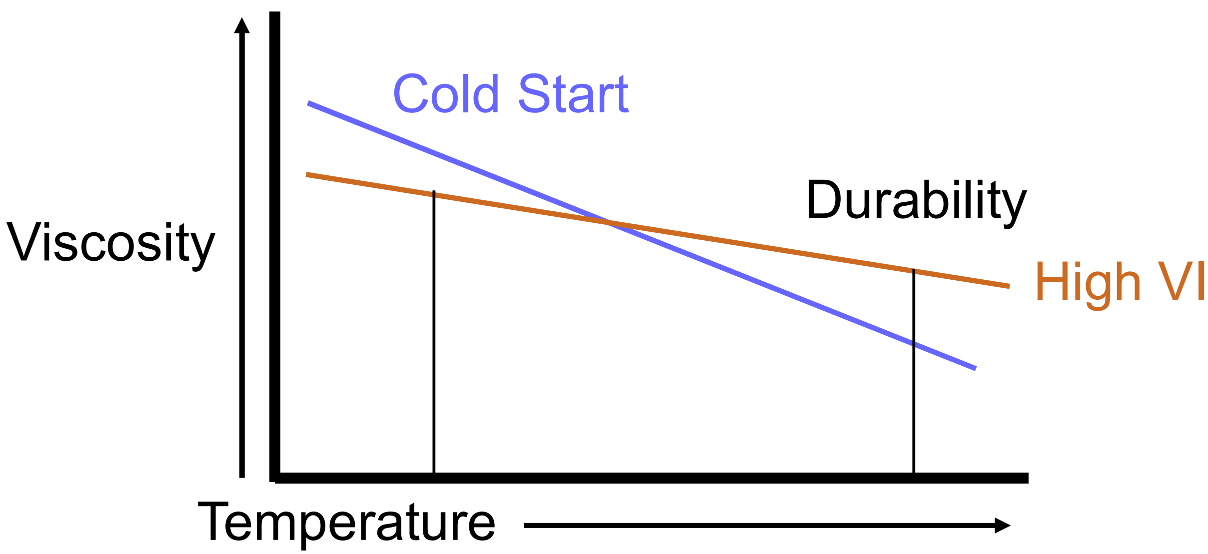


	Low Viscosity	High Viscosity
High fluid friction		X
Good cooling	X	
Good load carrying		X
Easier starting	X	

Fundamentals of Viscosity

Viscosity Index - VI

- Empirical number
- Rate of viscosity change with temperature
- Adopted in early 1930's
- High VI fluids may improve fuel economy
- Lubricating oil thins when heated
- VI developed to compare with practical examples of good and bad oils
- VI depends on chemical composition
- Can be boosted by adding polymers to oil



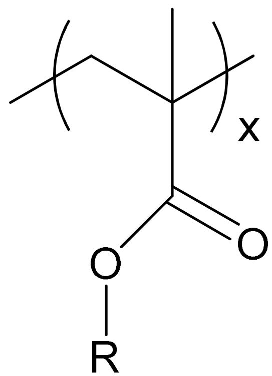
Additive Chemistry

Viscosity Modifiers

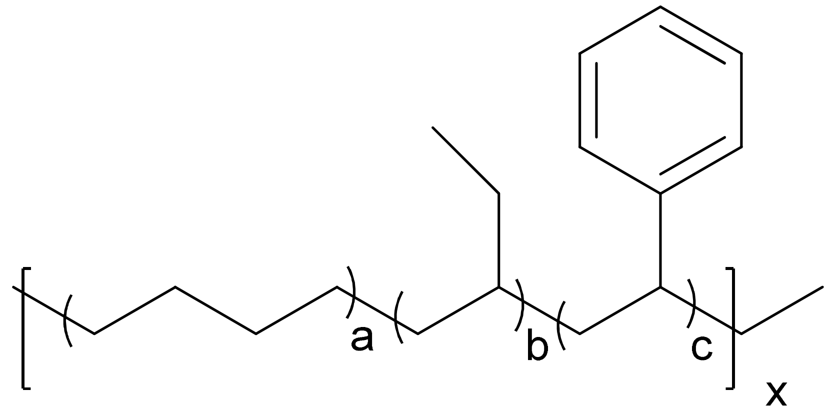
Multigrade Properties
VMs Improve Viscosity Temperature Relationship

- Viscosity modifiers provide
  - Thickening at high temperatures
  - Minimum thickening at low temperatures
- This allows the formulation of multigrade oils
  - Adequate viscosity at high temperatures for engine protection
  - Low viscosity at low temperatures for start-ability

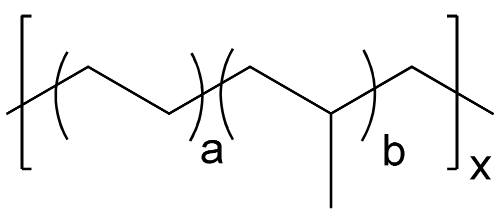
Viscosity Modifiers
Examples



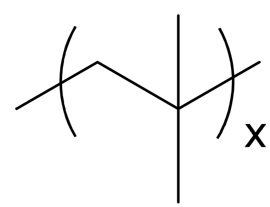
Polymethacrylates (PMA)



Styrene Butadiene Copolymers (SBR)



Olefin Copolymers (OCP)



Polyisobutenes (PIB)

Pour Point Depressants

What is Pour Point?

- Pour point is the lowest temperature at which a fuel or oil will pour when cooled under defined conditions
- Reflects the amount of wax, or straight chain paraffins, in an oil

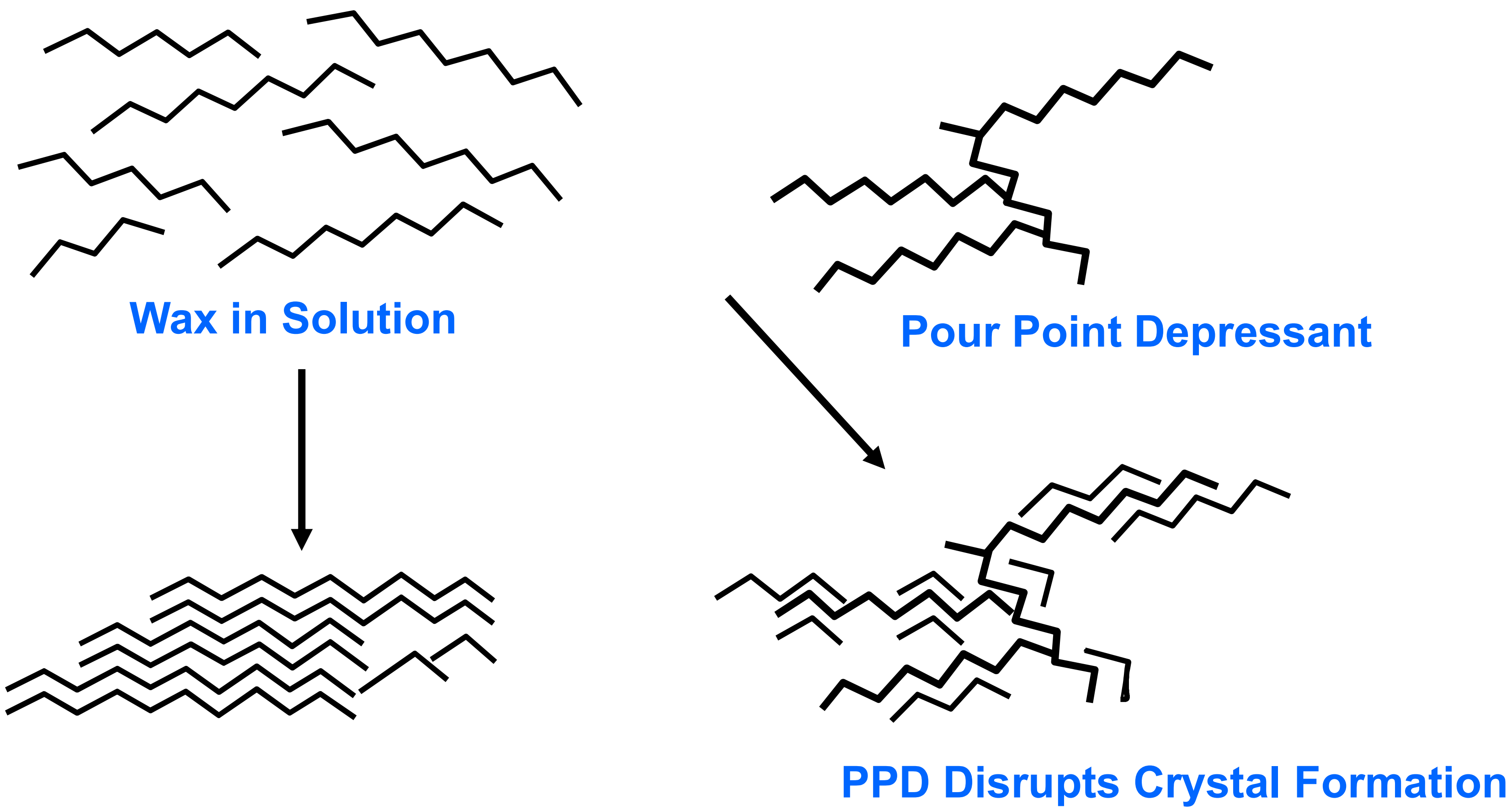
Why Use Pour Point Depressants?

- Waxes in mineral oils precipitate at lower temperatures, forming interlocking crystal networks
- Light oils form large, soft crystals; heavy oils (bright stocks) form harder microcrystalline waxes

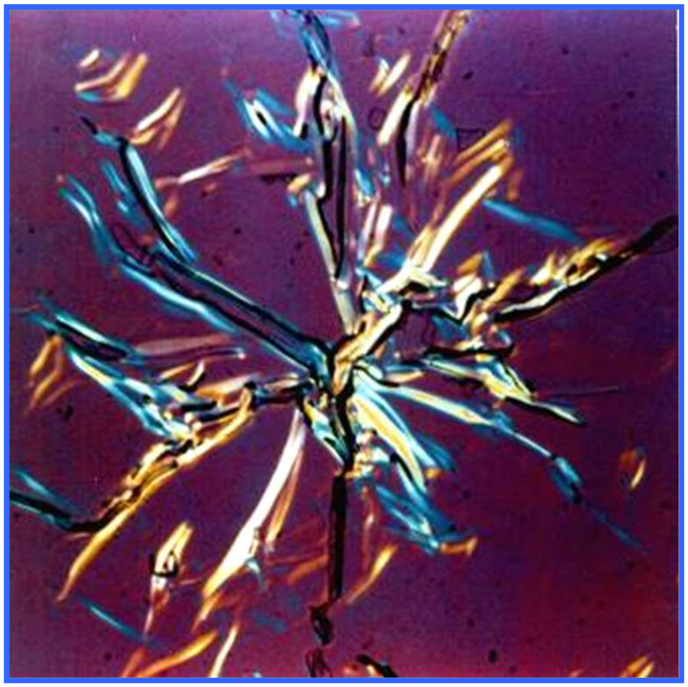
- Polyalkylmethacrylate
- Styrene ester
- Poly(vinyl acetate - alkylfumarate)
- Alkylene-coupled naphthalene
- Coupled alkylphenols
- Poly(ethylene/vinyl acetate)

Pour Point Depressants

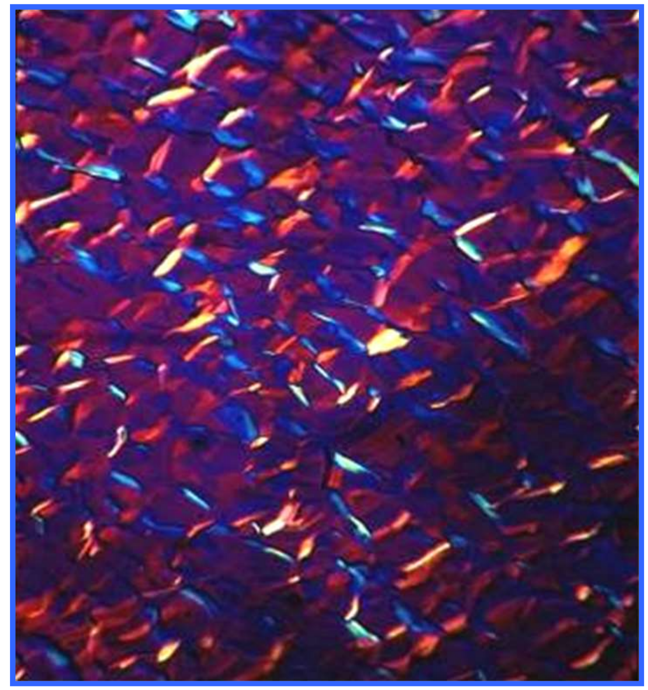
Mechanisms by which Pour Point Depressants Act



Pour Point Depressants
Wax Crystal Morphology



Wax Crystals Without PPD

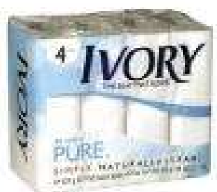


Wax Crystals With PPD

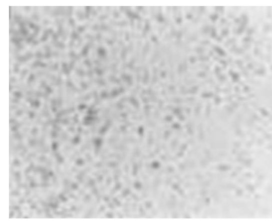
Additive Chemistry

Review

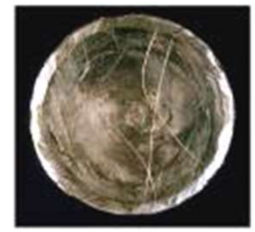
Additive Chemistry
What Are They, Why Are They Important?



Detergent



Dispersant



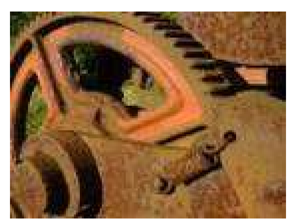
Antiwear

Extreme Pressure Agent

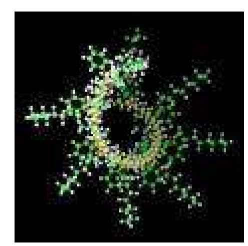
Foam Inhibitor

Friction Modifier

Oxidation Inhibitor



Corrosion Inhibitor



Viscosity Modifier/PPD

Society of Tribologists & Lubrication Engineers

EXTRA OVERHEADS

Lubrication Fundamentals
Lubricant Properties

- Suitable viscosity
  - High temperature
  - Low temperature
- High film strength
- Low pour point
- Suitable frictional properties
- Low corrosivity
- Good cleansing and dispersing ability
- Non-toxicity
- Low flammability

Lubrication Fundamentals

Functions of a Lubricant

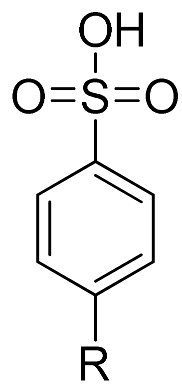
Lubrication	Protection
Reduces Friction	Barrier
Cooling	**Cleaning**
Removes Heat	Removes debris…

Additive Basics

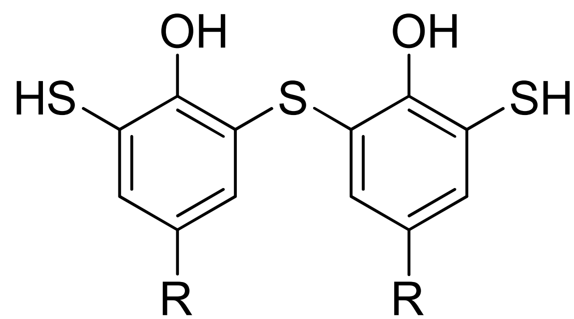
Chemically Active	Chemically Inert
Detergents	Foam Inhibitors
Dispersants	Viscosity Modifiers
Antiwear Agents	Pour Point Depressants
Extreme Pressure Agents	Emulsifiers
Antioxidants	Demulsifiers
Corrosion Inhibitors	
Friction Modifiers	

Detergents

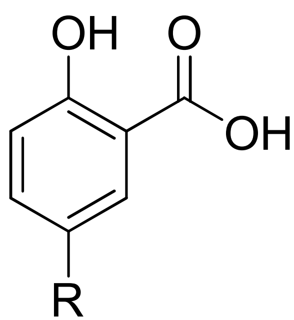
Types of Detergent Substrates



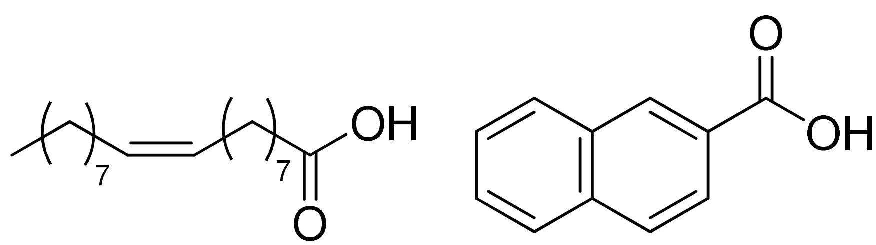
Alkyl benzene sulfonic acids



Sulfurized alkyl phenols



Alkyl salicylic acids



Carboxylic acids

Detergents
Detergent Types

- Neutral
  - Prepared by reacting an acid with a stoichiometric amount of base
    - Low TBN
- Overbased
  - Prepared by reacting an acid with an excess amount of base in the absence or in the presence of carbon dioxide
    - High TBN

Detergents
Sulfated Ash

- A measure of the metal content of a lubricant (mainly Zn, Ca, Mg)
- Calculated from the residue following combustion of a lubricant in the presence of sulfuric acid
- Different metals provide varying contributions to the sulfated ash content

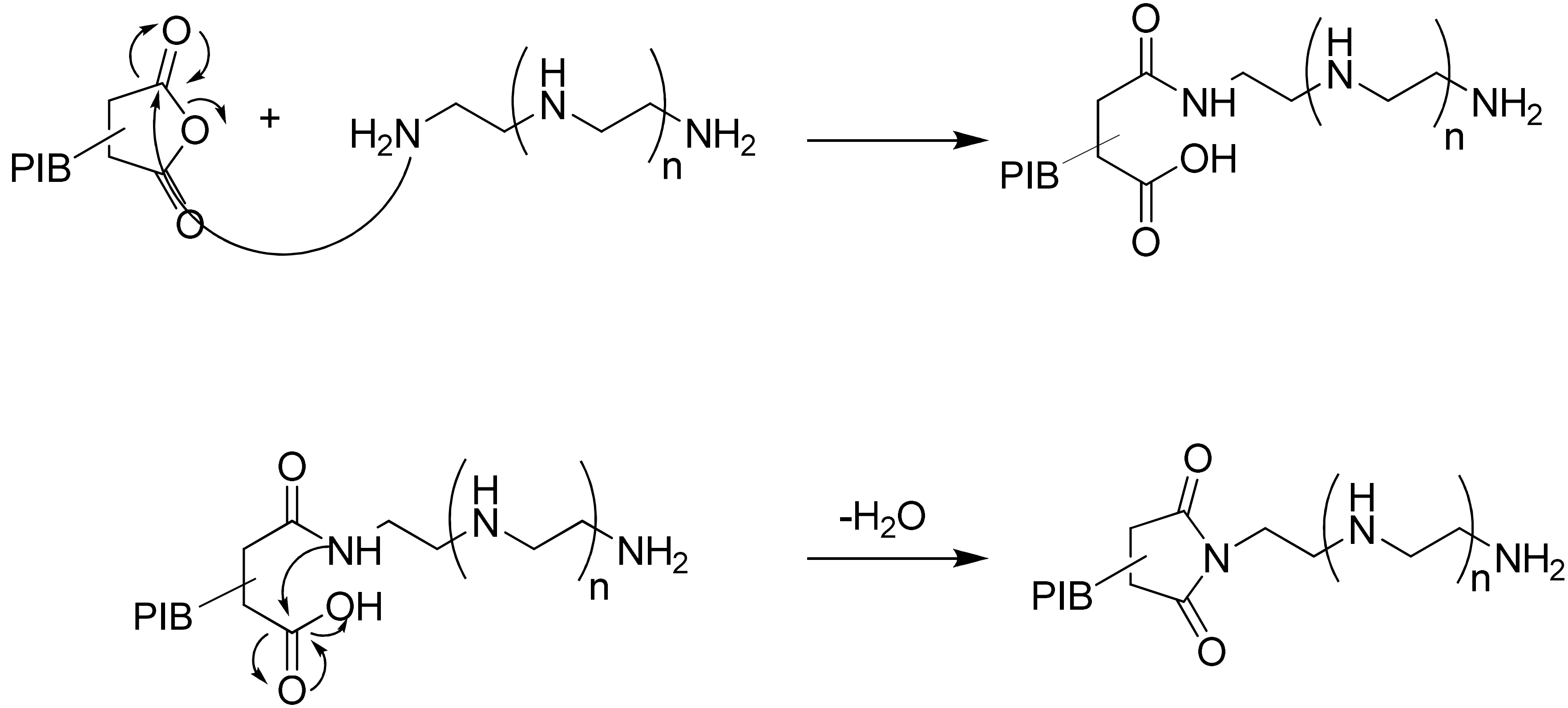
Dispersants

Dispersants Aid in Preventing Sludge

Acceptable

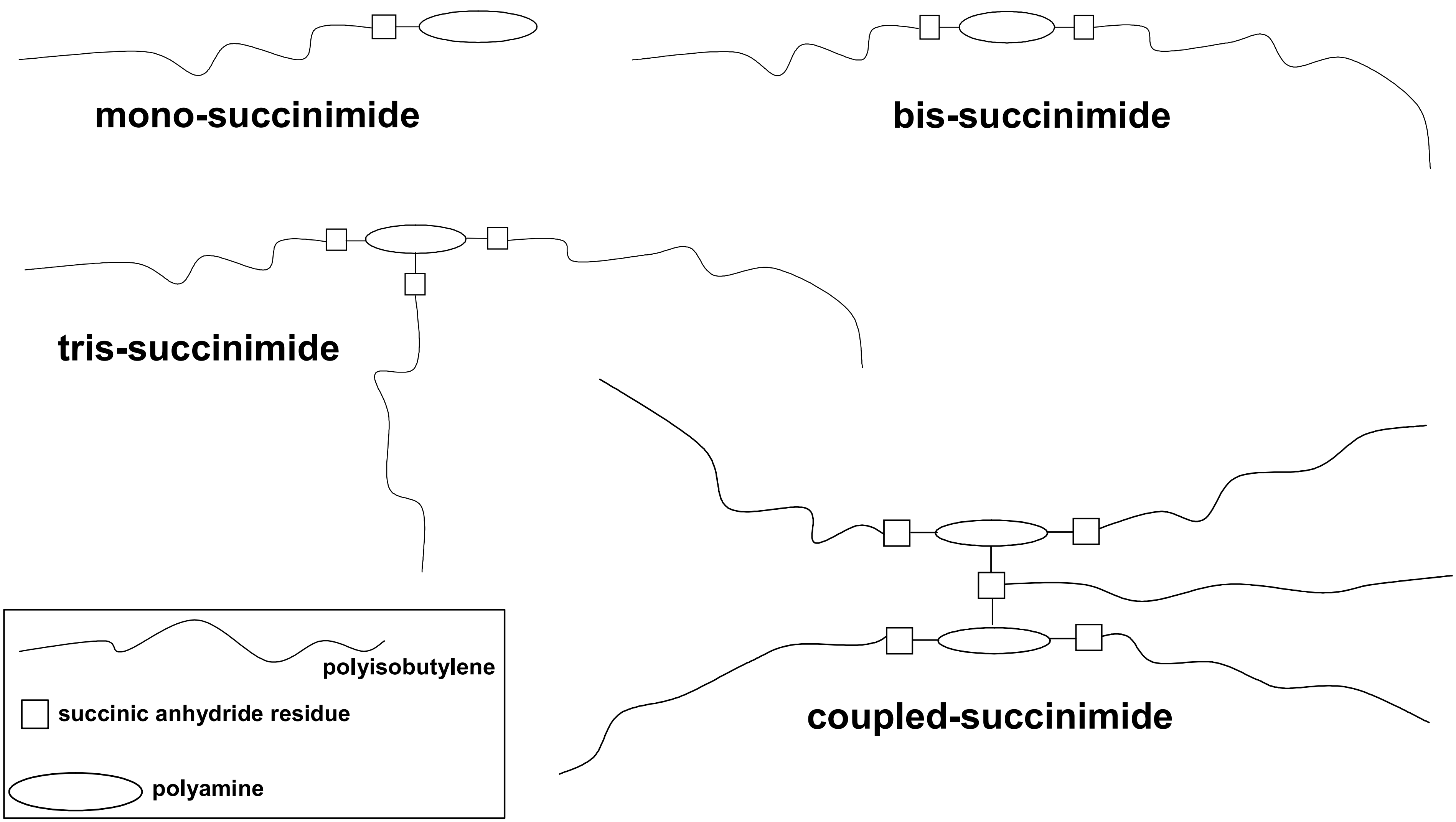
Unacceptable

Dispersant Formation



Succinimide

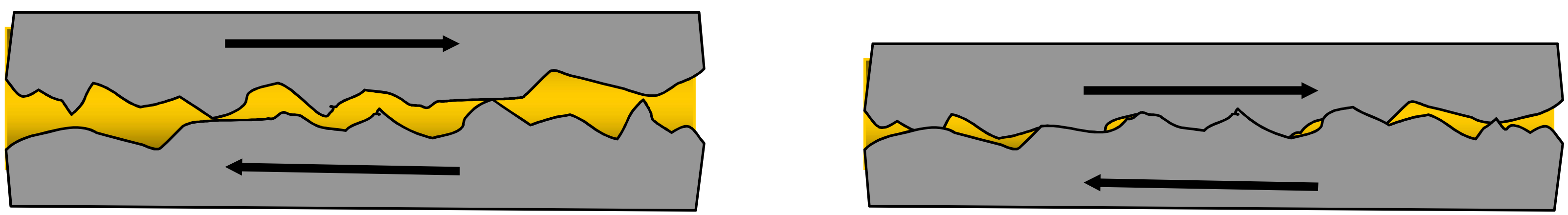
Another Look at Simple Structural Models



Antiwear and Extreme Pressure Agents

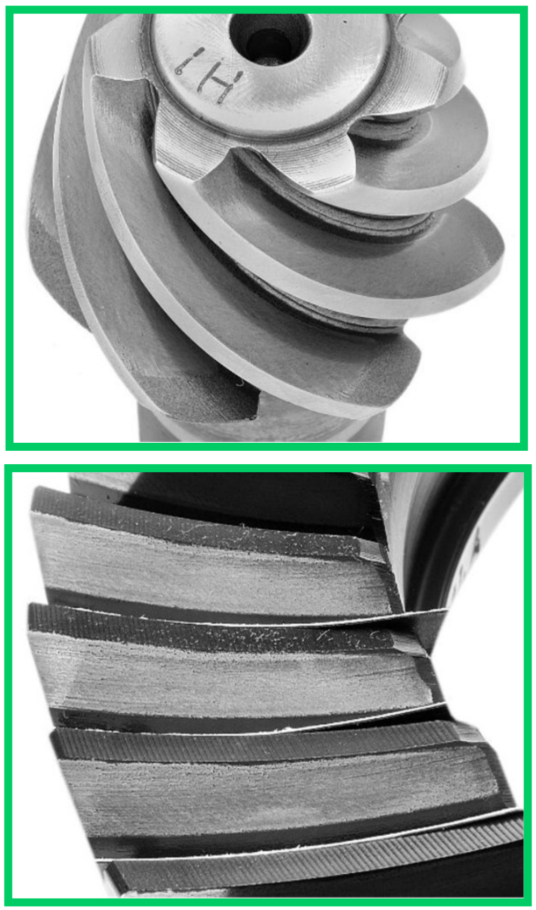
Types of Lubrication

- Boundary lubrication
  - Maximum speed and load
    - Lubrication changes from mixed film to boundary condition
    - Surface to surface contact
  - Antiwear and EP additives are effective under mixed film and boundary lubrication conditions



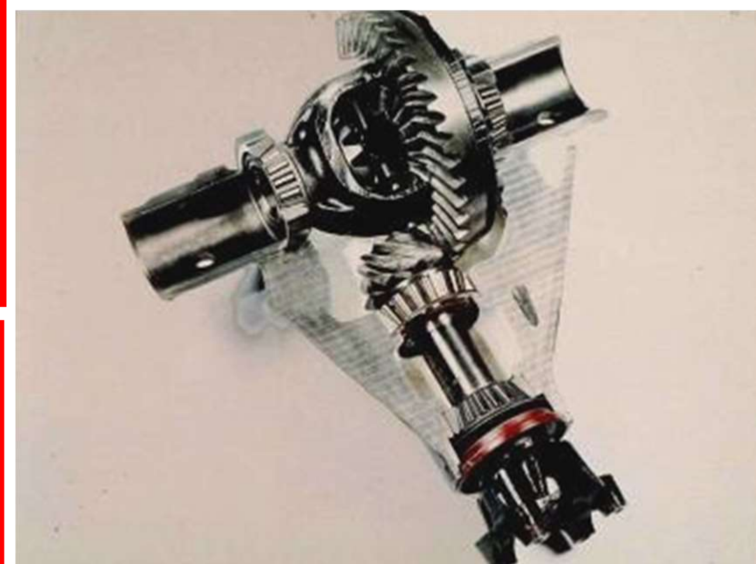
Antiwear and Extreme Pressure Agents

Prevent Gear Wear

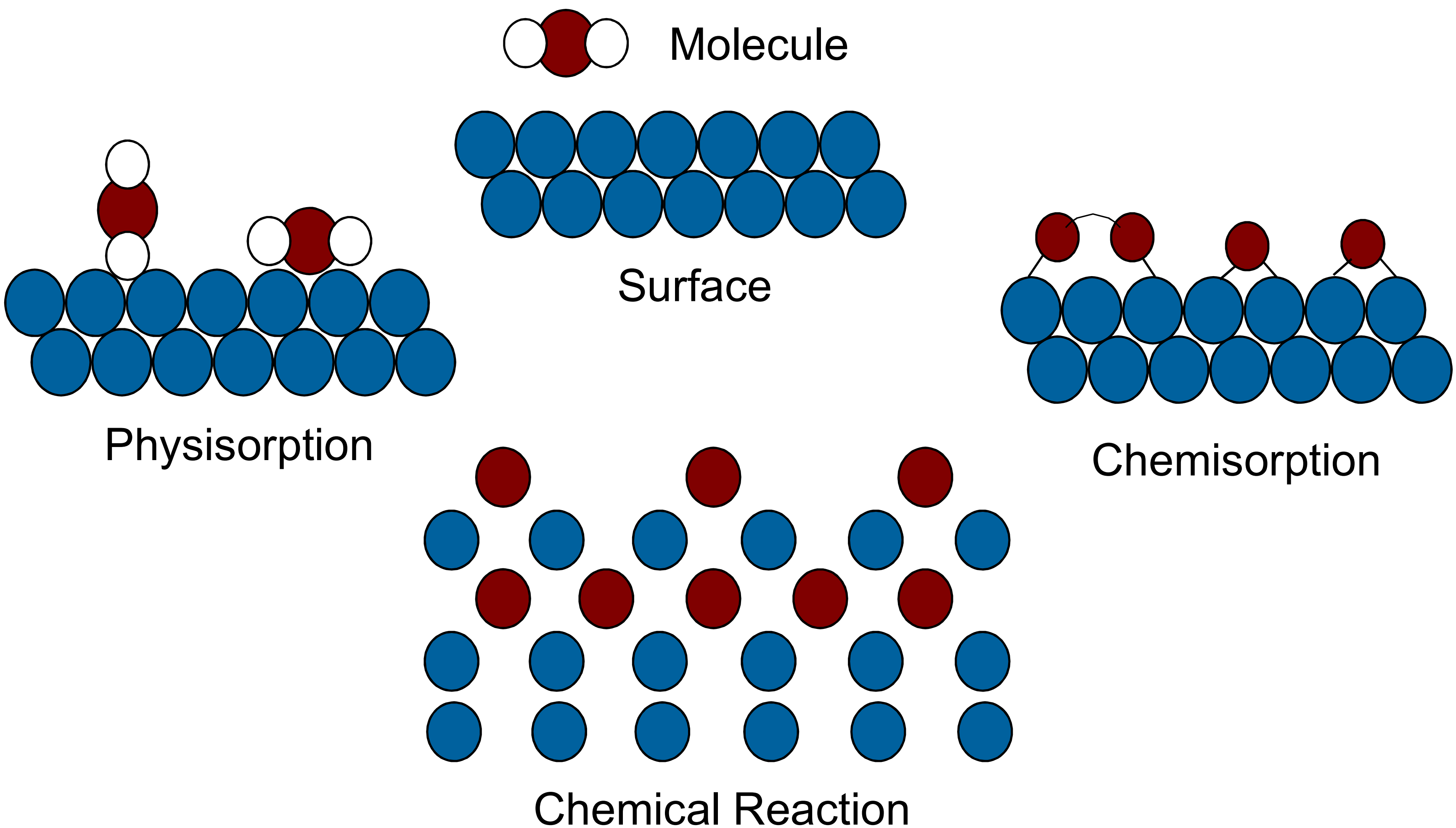


Good

Poor

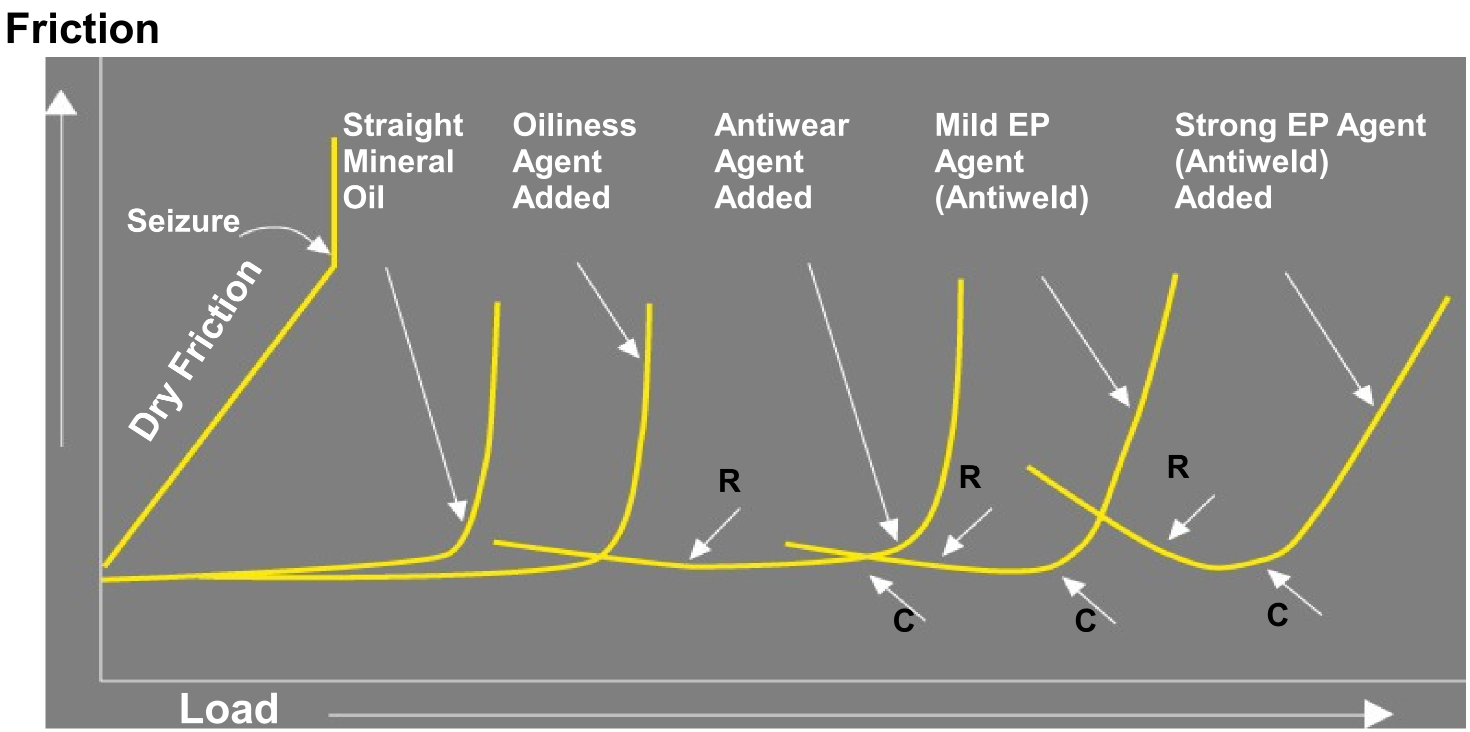


Antiwear and Extreme Pressure Agents
How Molecules Interact With Surfaces



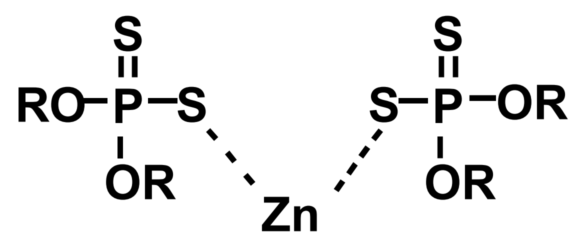
Antiwear and Extreme Pressure Agents

EP Protection Requirements as a Function of Load



R:The Point at Which the EP Film-Forming Action of the Additive Starts
C:The Point at Which the Reaction Ceases and the Lubricant's Load-Carrying Ability Diminishes

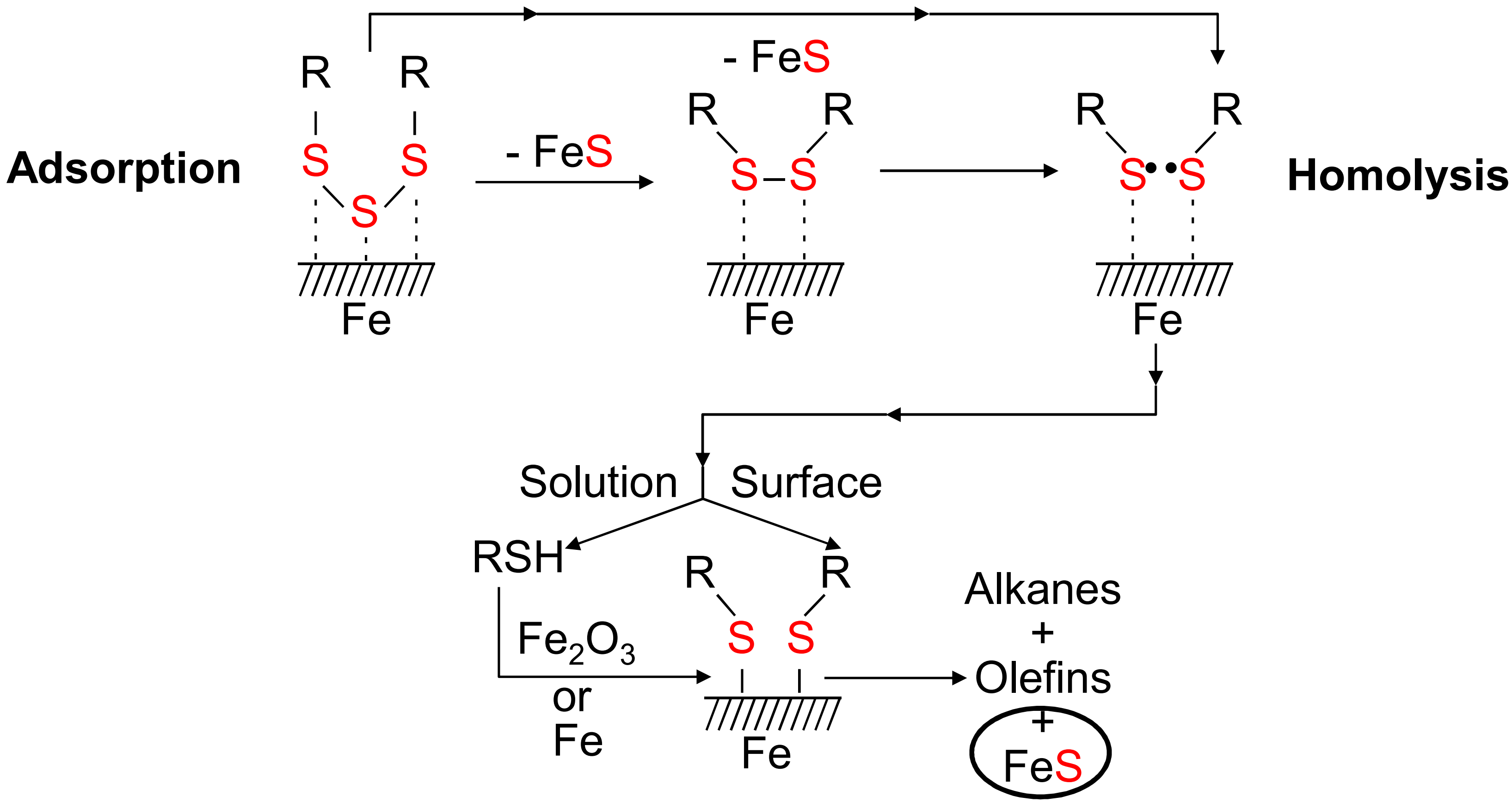
Antiwear and Extreme Pressure Agents
Properties ZDDP



Parameter	Aryl	Primary	Secondary
Thermal Stability	Best	Middle	Worst
Antiwear performance	Worst	Middle	Best
Antioxidancy	Worst	Middle	Best

Antiwear and Extreme Pressure Agents

EP Protection: Sulfurized Olefins



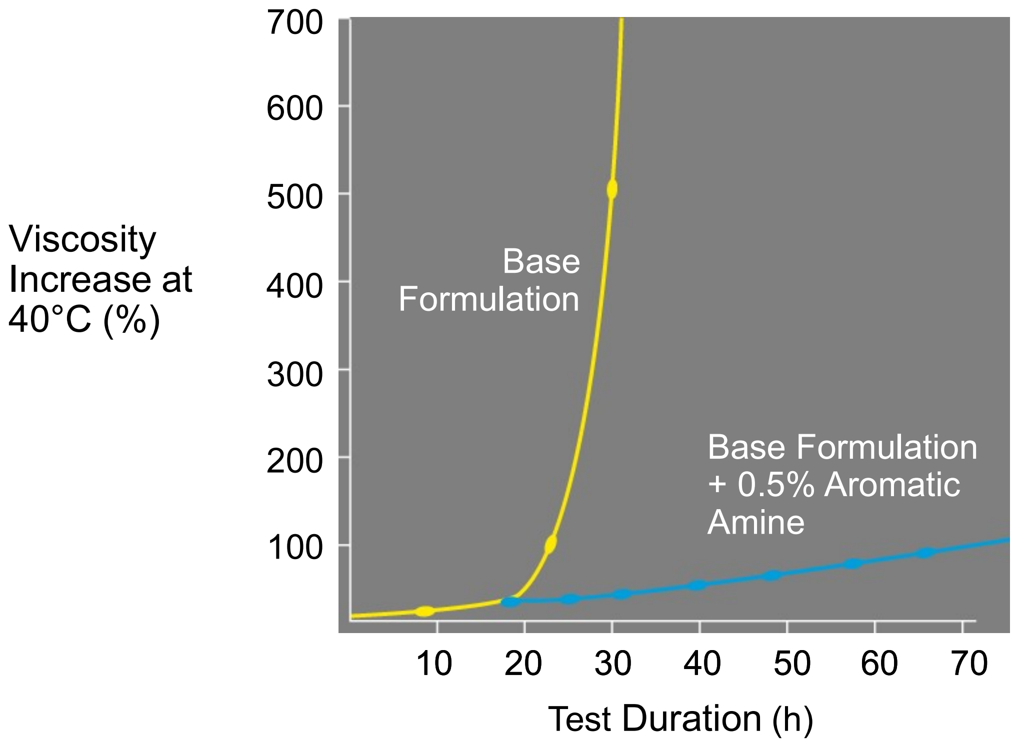
Graphitic sheets of FeS protect the surface

Antiwear and Extreme Pressure Agents
EP/Antiwear Additive Synergy

- Most formulations that use EP additives are also supplemented with AW additives
- Insures that formulations will be effective over broad temperature and load ranges

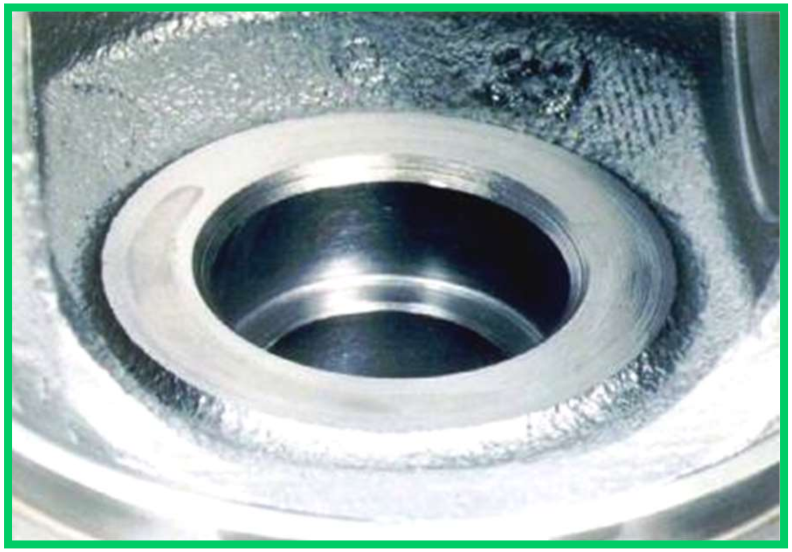
Antioxidants

Oxidative Viscosity Control by an Arylamine in a Sequence III Test



Rust and Corrosion Inhibitors
Corrosion Inhibitor

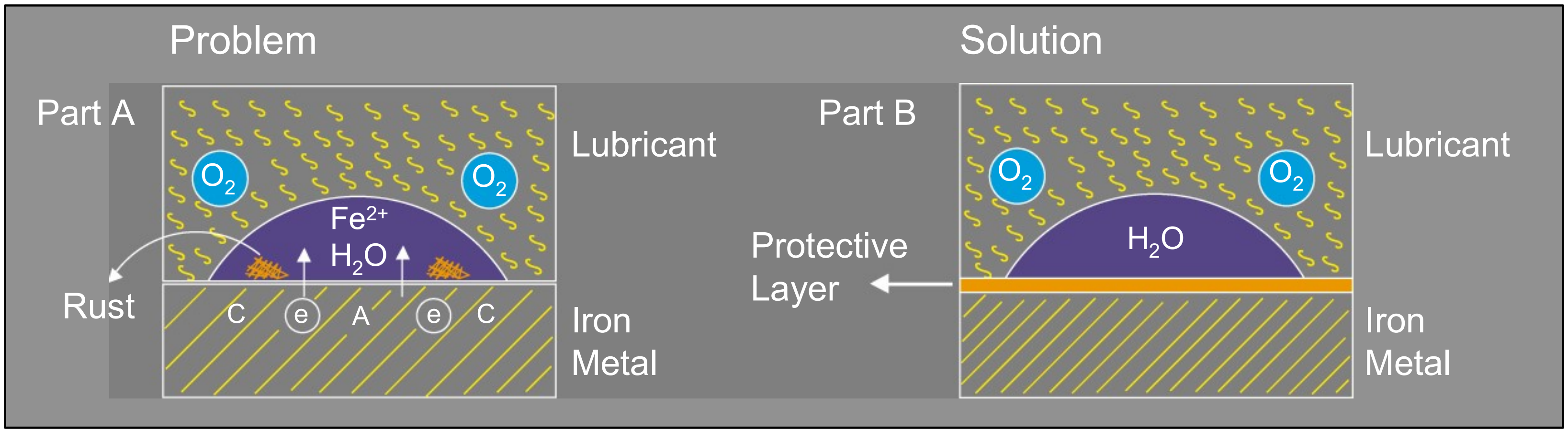
A chemical substance or combination of substances that, when present in the environment, prevents or reduces corrosion



Good

Poor

Rust and Corrosion Inhibitors
Mechanism of Rust Inhibition



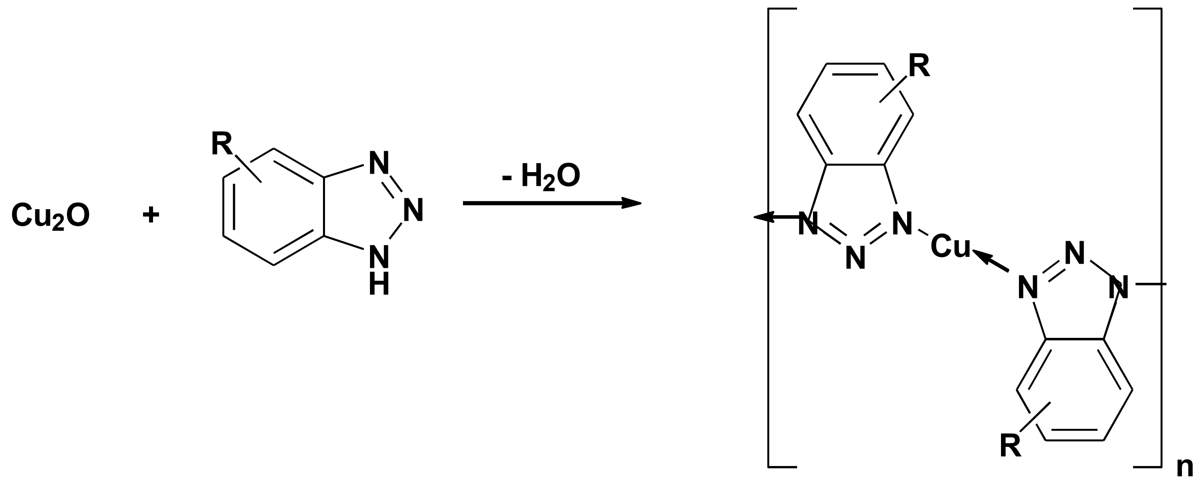
Cathodic Reaction (C)

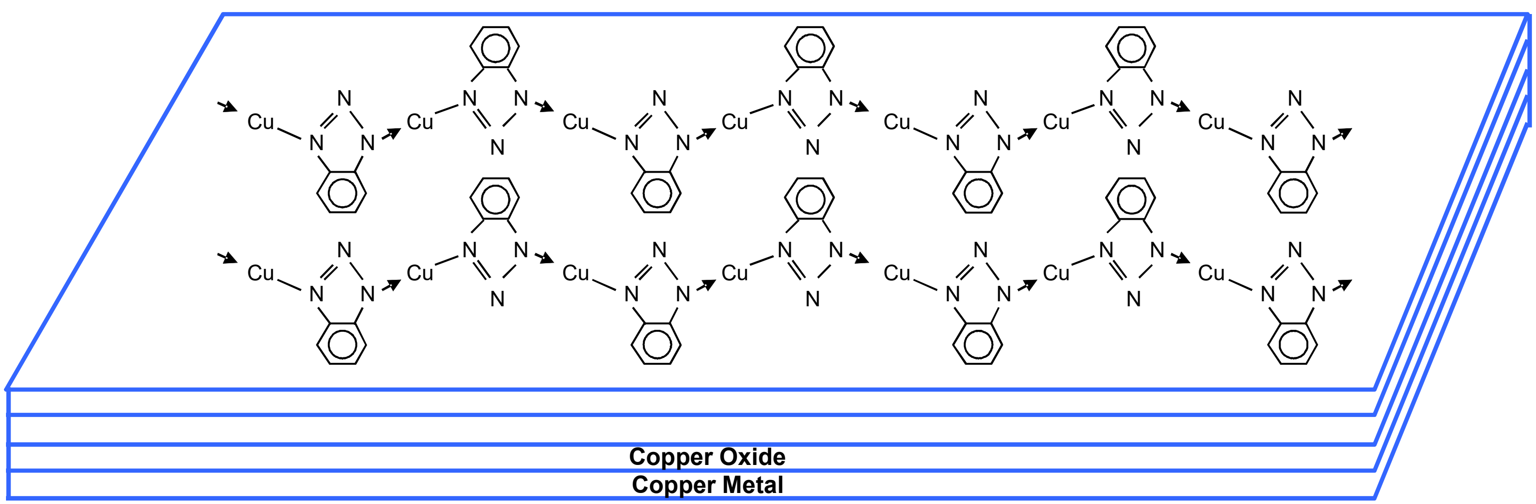
$O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Anodic Reaction (A)

$Fe \rightarrow Fe^{2+} + 2e$

Corrosion Inhibitors
Yellow Metal Inhibitors





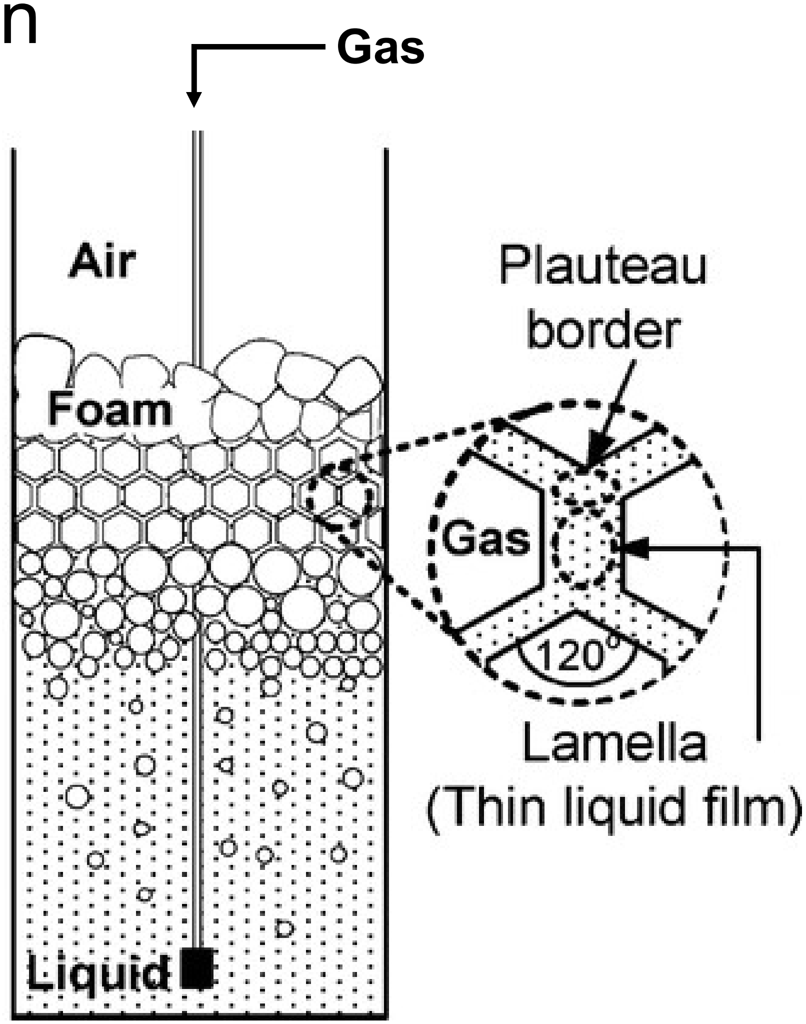
Foam Inhibitors
Foam Formation

Foam Inhibitors
Foam Formation

- Foams are dispersions of gas in liquid
- Foams typically are more persistent in high viscosity liquids than low viscosity liquids
- Dissolved surfactant molecules diffuse to the liquid-gas interface with the bulk liquid sandwiched in between
- Usually air is entrained by mechanical means, but can also be from a chemical reaction

Foam Inhibitors

Foam Formation



B. Thitakamol, A. Veawab, Ind. Eng. Chem. Res., 47, 2008, 216.

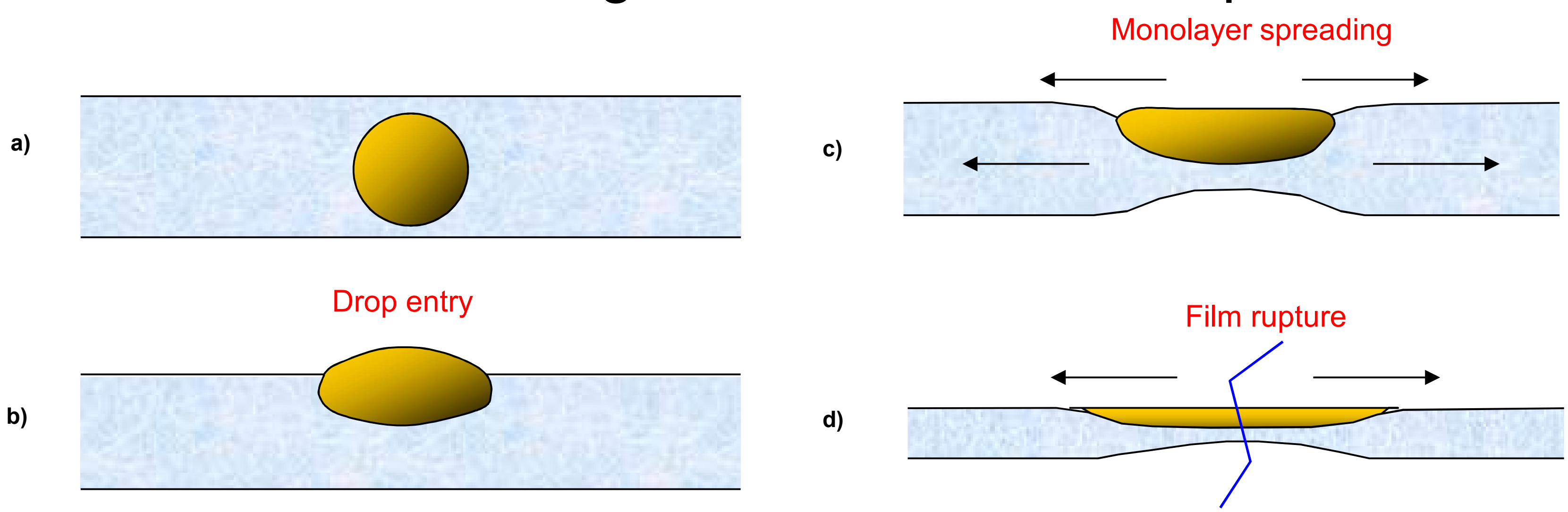
Foam Inhibitors
Foam Rupture

- Foam lamellae are under constant stress due to surface tension
- Rupture may be due to statistical fluctuations in film thickness
- Reducing the thickness below a critical value will lead to rupture
- Solids and insoluble liquids are particularly disruptive

Foam Inhibitors

Foam Rupture

Schematic representation of the spreading of an anti-foam globule to cause film rupture

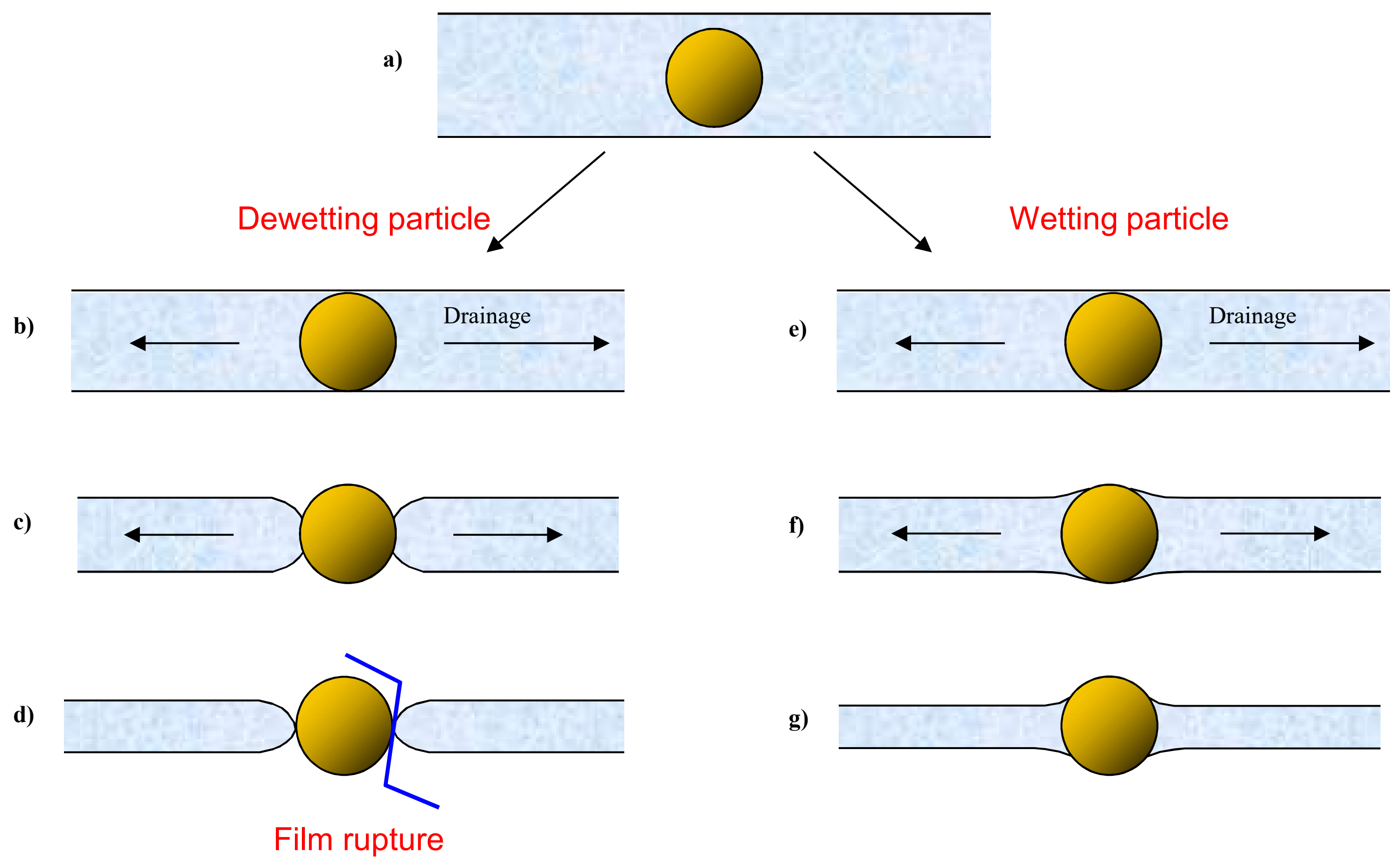


The globule enters the film layer

The flow of oil away from the spreading globule leads to local film thinning and eventually its rupture

Foam Inhibitors
Foam Rupture

Schematic representation of the bridging-dewetting mechanism



Fundamentals of Viscosity
Viscosity of Familiar Materials

Fluid	Centipoise	Centistokes
Water	1.0	1.002
SAE 10 oil	70	80
Olive oil	100	111
SAE 30 oil	300	341
Glycerine	500	396
SAE 50 oil	800	909
Honey	2,000	1,428

Fundamentals of Viscosity
Viscosity Modifier Applications

- Driveline Fluids (GO, ATF, CVT, MTF)
  - Provide optimum shear stability, while contributing to lower operating temperatures
- Hydraulic Fluids (Farm Tractor)
  - Provide good low temperature fluidity as well as increased viscosity and film strength at peak operating temperatures
- Crankcase (EO, PC/HD)
  - Provide long-term lubrication while contributing to engine cleanliness and used oil pumpability