Lubricant Additives

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Overview

General additive comments

Additives that protect the base oil Additives that improve the base oil performance Additives that protect the lubricated surface

Questions



Functions of Lubricants

- Reduce friction and wear
- Remove heat
- Seal
- Reduce corrosion
- Remove and contain wear debris and contaminants
- Prevent deposits
- Neutralize combustion products
- Transmit power



Lubricant additives

Improve the good properties

Minimize the bad properties



FUCHS LUBRITECH (UK) LTD

TYPICAL STRIBECK CURVE

Showing typical conditions from start-up to normal running.





Lubrication Regimes





Additive Response

The effectiveness of an additive depends on the system where it is used.

- An oxidation inhibitor may work well in one oil and not in another oil
- Polar additives compete with each other for the same metal surfaces

The final response of the system may not be the sum of all the components. It will be greater or lower depending on the interaction of the components.



Additive Dosage

The ideal treat rate may be different for different systems.

The additive may be effective at low dosages and the effectiveness can decrease as the dosage increases.

The additive may need to reach a specific dosage before it becomes active.

The performance may continue to increase as the additive concentration increases.

There may be an ideal treat rate.

The ideal treat rate is influenced by the system in which it is used.



Three general categories





Additive Systems

• Additives may be combined to produce well balanced/optimized additive packages to meet certain performance criteria.

e.g. Dispersant Inhibitor (DI) Packages for Engine Oils



• Some additives may have multifunctionality.

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Dispersants

- Non-metallic or ashless cleaning agents
- Solubilize and disperse contaminants
 - Soot
 - Sludge
 - Deposit precursors

Structure



Hydrocarbon Tail (Solubilizer) Polar Head (N and O atoms)



Dispersants

Action Mechanism



Types

- Succinimides
- Succinate Esters
- Mannich types
- Phosphorus types
- Polymeric Dispersants
- Combinations



Typical Dispersant Structures

N Substituted Long Chain Alkenyl Succinimides



Succinate Ester

Phosphorus Dispersant



$$\begin{array}{c} S & CH_3 \\ \parallel \\ PIB - P - (OCH_2 - CH - OH)_2 \end{array}$$



Typical Dispersant Structures

Mannich Base



Polymeric Dispersant Additives



Where O = Oleophilic group P = Polar groupR = Hydrogen or Alkyl group



Detergents

- Metal-containing cleaning agents
- Prevent build-up of deposits on surfaces
- Neutralize acidic products



Hydrocarbon Tail (Solubilizer)

Polar Head (Metal attachment point)

Types

- Sulfonates
- Phenates
- Salicylates
- Phosphonates

Ca & Mg ; most common metal ions



Typical Detergent Structures

Phenate



<u>Salicylate</u>



Phosphonate

$$\mathbf{R} - \mathbf{P} - \mathbf{O}$$

$$\mathbf{O} - \mathbf{M}$$

$$\mathbf{M} = \text{metal ion}$$



Typical Detergent Structures

Sulfonates





Boundary Lubrication Additives

- Friction Modifiers
- Antiwear Additives
- EP Additives



- Reduce friction and wear at the interface of rubbing surfaces
- Form surface films
 - Adsorbed layers (physical or chemical adsorption)
 - Formed by tribochemical reactions
- Prevent/reduce adhesion and interlocking of surface asperities



Antiwear and EP Additives

Form surface films by tribochemical reactions

Typical AW additives:

Sulfur and/or phosphorus-containing compounds e.g. ZDDP, TCP, amine phosphates

Effective at moderate loads and temperatures

Typical EP additives:

Sulfur, phosphorous , and chlorine compounds are elements found in most EP additives

Used under highly loaded conditions to prevent welding



EP Additives

Activation Temperature



Highly reactive EP additives/high concentrations may cause corrosive wear



Some additives are multifunctional

Zinc dithiophosphates

•Protect the metal surfaces from wear by forming sulfides and phosphates

- •Protect Cu, Pb, and Al surfaces from corrosion
- Protect the baseoil from decomposition by reducing oxidation
- •But; can poison the catalyst in the catalytic converter



Antioxidants

Reduce oxidation rate of base oil

Oxidation rate determines the useful life of the lubricant

Oxidation leads to:

Viscosity increase (oil thickening)

Sludge/varnish and deposit formation

Corrosion



Oxidation Mechanism

• Free-radical mechanism



Oxidation Mechanism

Typical oxidation products:

- Peroxides, alcohols, acids, esters, aldehydes, and ketones; all oil soluble
- Further reactions resulting in high molecular weight products that are not oil soluble

Oxidation rate increases by:

- Oxygen in the oil
- Temperature (rate ~ doubles/10 °C or 18 F)
- Light
- Metal catalysts
- Acids



Antioxidant Types

- Radical Scavengers
- Peroxide Decomposers
- Metal Passivators
- Radical Scavengers (primary antioxidants)
 - Prevent chain propagation by reacting with free radicals
 - Phenolic Antioxidants





Antioxidant Types

• Radical Scavengers (continued)

Aromatic Amines

Sulfur and Phosphorus Compounds

e.g. zinc dithiophosphates and dithiocarbamates

$$\begin{array}{ccc} S & S \\ \parallel \\ (RO)_2 P - S - Zn - S - P(OR)_2 \end{array}$$



Antioxidant Types (continued)

Peroxide Decomposers (secondary antioxidants)

- Convert hydroperoxides into non-radical products
- Organosulfur compounds
- (e.g. dialkyl sulfides, dithiocarbamates)
- Organophosphorus compounds
- (e.g. triaryl- and trialkylphosphites)

Metal Passivators

- Reduce catalytic effect of metal ions on oxidation
 - Surface film-forming compounds
 - Stable complex-forming chelating agents
 - e.g. benzotriazole, N-salicylidene ethylamine

Synergistic mixtures of different types of antioxidants are generally used in lubricant formulations.



Friction Modifiers

Function by forming thin monomolecular layers on metal

long chain (C_{12} - C_{18}) carboxylic acids, fatty acid esters, alcohols, ...

e.g. CH_3 -(CH_2)₇ $CH = CH(CH_2)_7 COOH$

sulfurized fatty acids, esters, olefins, ...

organometallic compounds: molybdenum dithiophosphates, molybdenum dithiocarbamate,

solid compounds: molybdenum-sulfur compounds, graphite, PTFE



Viscosity Index (VI) Improvers

- Viscosity
 - Determines lubricant film thickness and flow properties
 - Changes with:
 - Temperature
 - Pressure
 - Shear rate (for non-Newtonian fluids)
- Viscosity Index (VI)
 - Empirical number measuring the temperature response of viscosity (ASTM D 341, Walter relationship)
 - Defined by the gradient between
 40 ℃ and 100 ℃





VI Improver Structure

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Viscosity Index (VI) Improvers

- Improve viscosity-temperatures properties of lubricants
- Oil soluble polymers
 - Typical molecular weights: 10,000 250,000
- Effect of polymer on viscosity



Viscosity Index (VI) Improvers

• Types of VI Improvers:

- Olefin copolymers
- Polyisobutylene
- Hydrogenated styrene-isoprene copolymers
- Hydrogenated styrene-butadiene copolymers
- Polyalkyl methacrylates
- Dispersant VI improvers (multifunctional)
- Performance influenced by:
 - Shear stability
 - Temporary viscosity loss (moderate shear stress)
 - Permanent viscosity loss (high shear stress)



Pour Point Depressants (PPD)

- Modify crystal morphology of wax structures
- Improve flow properties at low temperatures
- Mainly polymeric compounds





Corrosion Inhibitors

- Protect metal surfaces against chemical attack
- Form surface films by adsorption



- Compete with other polar additives (FM, AW, EP) for surface
- Two types of corrosion inhibitors
 - Rust inhibitors ferrous metals
 - Metal passivators nonferrous metals



Corrosion Inhibitors

• Typical Rust Inhibitors

- Sulfonates
- Carboxylic acid derivatives
- Phosphoric acid derivatives
- Fatty acid amides
- Typical Metal Passivators
 - Surface film-forming types (benzotriazole)
 - Oil-phase, complex forming chelating agents (N-Salicylidenepropylenediamine)
 - Sulfur scavengers (mercapto-thiadiazole derivatives)
 - Zinc dithiophosphates and dithiocarbamates (multifunctional)



Antifoam Agents

- Destabilize Foam
- Reduce
 - Air entrainment, cavitation damage, oxidation
 - Lubricant starvation
- Two types:
 - Silicone Polymers



- Silicone-free Defoamers (cutting fluids, hydraulic fluids)
 - Polyethers
 - Organic copolymers



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Questions?

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