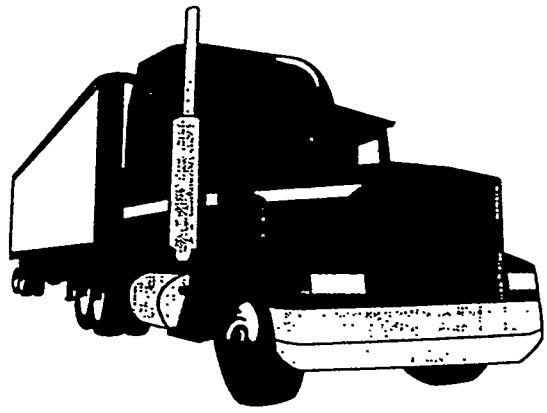
Lubricant Additives

Strategies for Low Emission Diesel Oils

Dr. Stephen Hsu
National Institute of Standards & Technology
Tel: 301-975-6120
Fax: 301-975-5334
stephen.hsu@nist.gov

Heavy Duty Truck Technology

- Fuel economy
- Durability
  - MM miles
  - Engine built for life
- Emissions
  - Hydrocarbons
  - Nanoparticles



Lubricants

- Base oils
  - Paraffins & cycloparaffins
  - Polynuclear aromatics
  - Polar speices (0.5 - 3%) (sulfur & oxygen)
- Additives
  - dispersants
  - detergents
  - inhibitors (antiwear, antioxidants, corrosion, rust)
  - Viscosity Index Improver
- Base oil - Additives interactions ➤ Lubricant performance

Lubricant Performance

- Largely controlled by design, operating parameters, fuel/combustion, duty cycles
- Lubricant defines the limits of operability for a given set of conditions

- So far, base oil is a given, different formulations are developed for a base oil and a performance level
- Lubricant performance is defined by additive combination, individual additive concentration, & materials

Material-Lubricant Relationship

- Most additives are metal-specific (steel assumed)
- Antiwear additives demand can be substantially reduced if steel surfaces are not used
- Engineered surfaces can also substantially reduce the antiwear demand
- Changing the materials can substantially change the additive chemistry requirement

Surface Texture Engineering

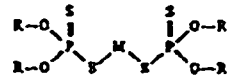
- Surface texture to control friction
- Surface texture to provide fine particle trapping
- Perpetual surface texturing by surface layering composite material
- Control flow path of vapor and soot

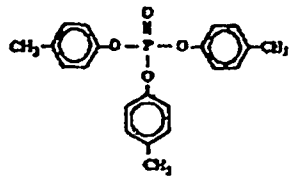
Additive Chemistry

- Dispersant: succinimides, Mannich reaction prods
- Detergents: sulfonates, phenates, salicylates
- Antiwear: Zinc dithiophosphates
- Friction modifiers
- Anticorrosion
- Antirust
- Pour depressant
- antifoam
- Viscosity Index Improvers

Antiwear Additives

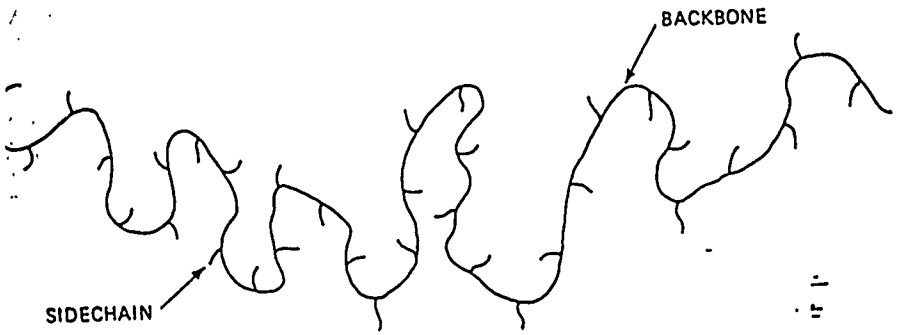
- Zinc dithiophosphates
  - alkyl vs aryl
  - primary vs secondary
  - decomposition temps
- Tricresyl phosphate
  - acid phosphate
  - phosphites
- Phosphate esters





VI IMPROVER GENERAL

STRUCTURAL REPRESENTATION



OIL SOLUBLE, HIGH MOLECULAR WEIGHT
(20,000-1,000,000) LINEAR POLYMER

Lubricant oxidation is a free radical chain reaction involves chain initiation, propagation, branching, and termination.

Initiation $RH \xrightarrow{O_2} R\cdot$

Propagation $R\cdot + O_2 \longrightarrow R_2O\cdot$

$R_2O\cdot + RH \xrightarrow{K_p} ROOH + R\cdot$

Branching $ROOH \longrightarrow RO\cdot + \cdot OH$

Termination $R\cdot + R\cdot \longrightarrow$ Products

$RO_2\cdot + R\cdot \longrightarrow$ Products

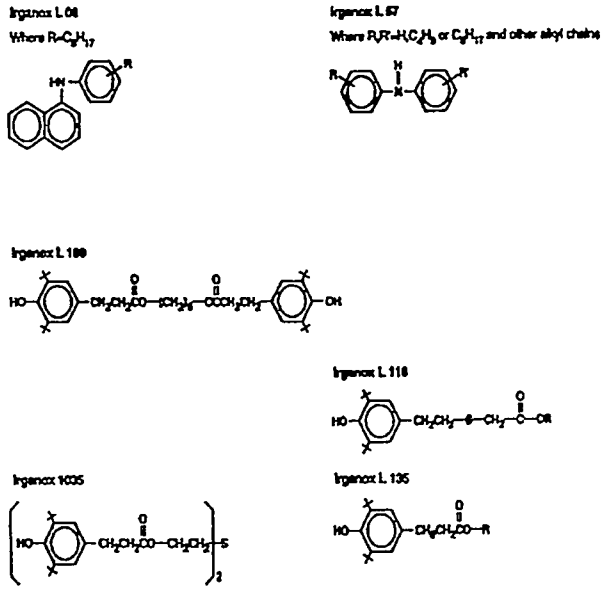
$RO_2\cdot + RO_2\cdot \xrightarrow{kt} R{=}O^* + ROH + O_2$

$R{=}O^* \longrightarrow R{=}O + h\nu \uparrow$

Chemiluminescence detected by a photon counter

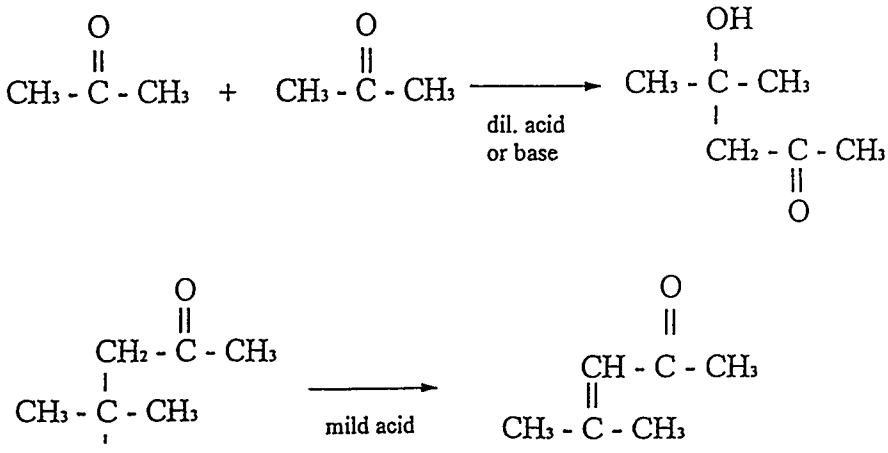
Antioxidants

- Hindered phenol
  - simple titration
  - radical termination
- Amines
  - complex reactions
  - different radicals
  - longer inhibition



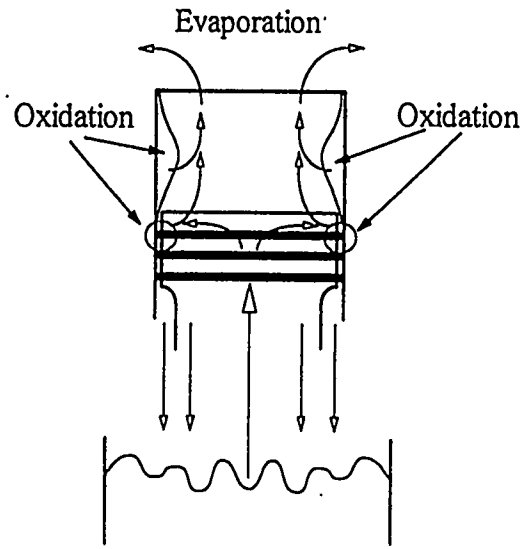
Polymerization Mechanism

- Condensation
- Example (Aldol Condensation)



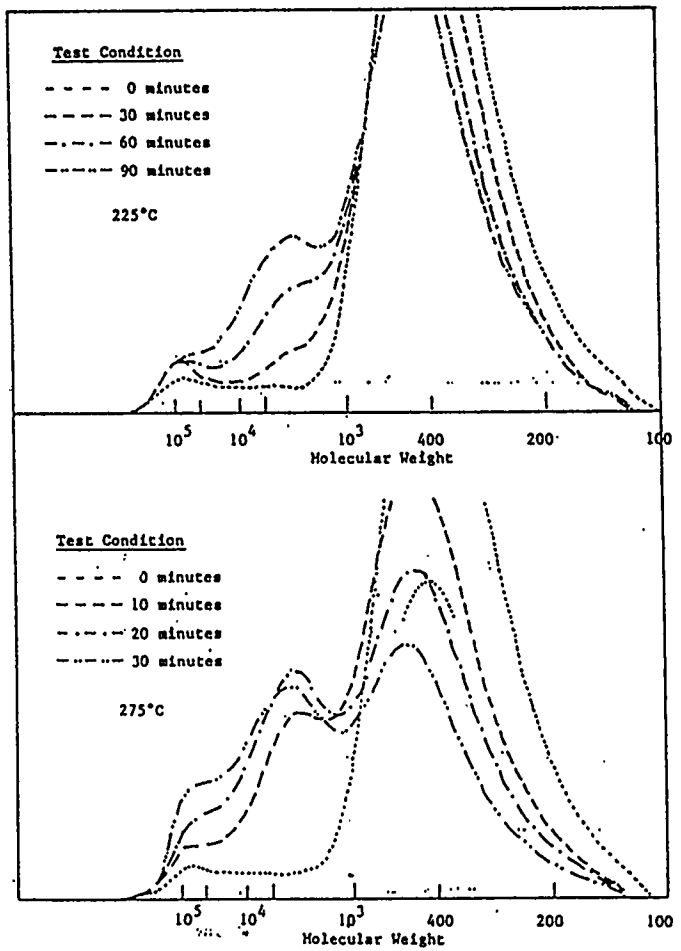
Modelling Oil Degradation:

- To characterize the lubricant in terms of reaction, the following factors must be determined:
  - Evaporation
  - Thermal degradation
  - Oxidation
  - Oxidative volatility
  - Polymerization
  - Deposit formation



Polymer Formation

- Molecular weight increase with oxidation time

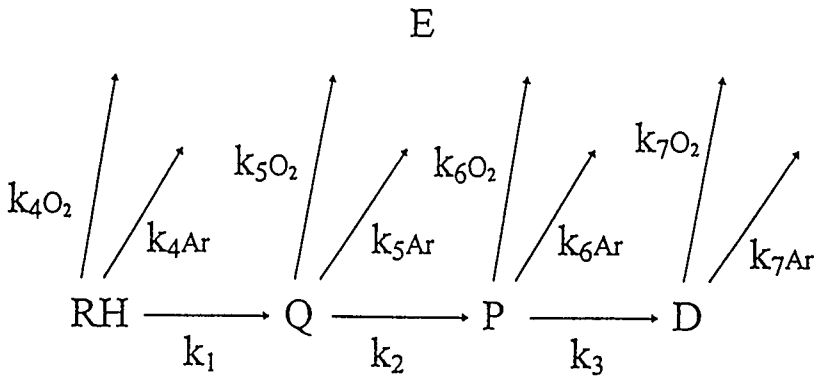


GPC Differential Refractometer Chromatograms of PRL4247 Oxidized in the Micro-Oxidation Reactor at 225°C and 275°C.

Final simulation results:

Lubricant	CT5113	CT5126	CT5213	CT5214	CT5215
Test Time, hr	252	125	252	252	252
Engine Test					
WDK	526	577	214	242	328
TGF	50%	100%	10%	50%	24%
Oil Consumption (g/kW h)	0.48	3.84			
Simulation					
TGF	42%	85%	8%	60%	25%
Oil Consumption (g/kW h)	0.42	3.69	0.31	0.5	0.5

Reaction Model



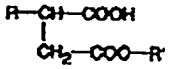
where:

- RH : the original lubricant
- Q : primary oxidation products
- P : polymer (high MW products)
- D : deposit
- E : evaporation
- k_n : rate constants
- k_{Ar} : evaporation rate const.
- k_{O_2} : oxidative evap. rate const.

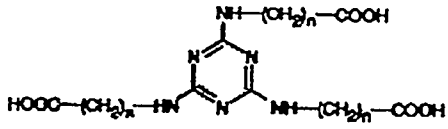
Corrosion Inhibitors

Reocor 12

Succinic acid half ester



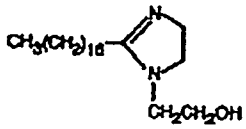
Reocor 190



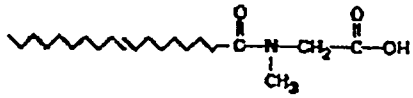
Reocor DSSG

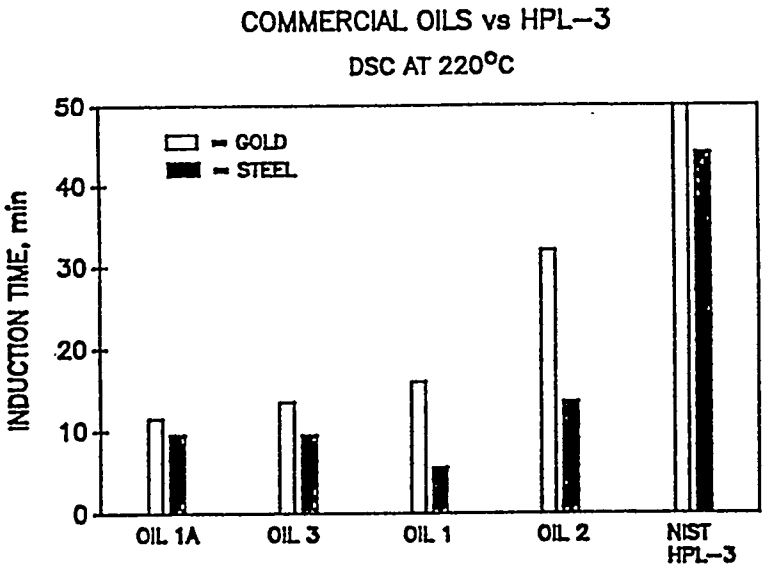
$NaOOC(CH_2)_nCOONa$

Amine O



Sarkosyl O





Current Lubricant Technology

- Polarity stacking (preferential attachment to rubbing surfaces)
- Chemical kinetic rate selectivity (antiwear always react the fastest to the rubbing surfaces)
- Optimum reactivity of additives towards the surfaces in terms of concentrations, aggregation tendencies, aggregation sizes, free molecules available in base oils

Dispersancy vs Solvency

- Base oils containing aromatics or esters can disperse insoluble particles or aggregations
- Dispersants are used to help to keep these particles in solution to prevent deposition onto surfaces

- to keep the amount of insolubles low by altering the reaction pathways (stop polymerization)
- to allow the base oil structures to carry more dispersancy or solvency

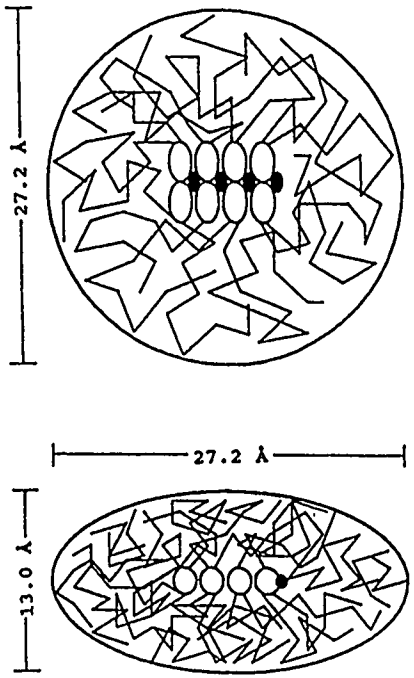


Figure 6.11 The size and shape of a ZDDP micelle

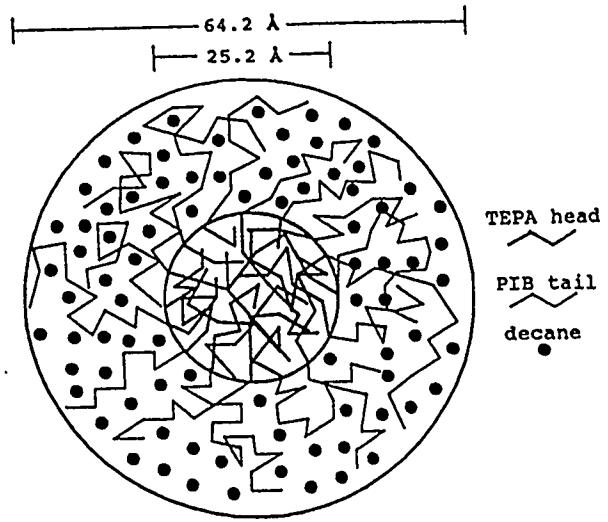
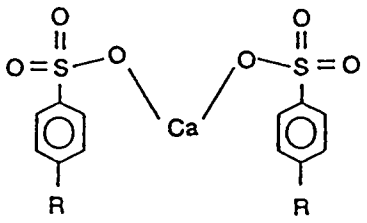
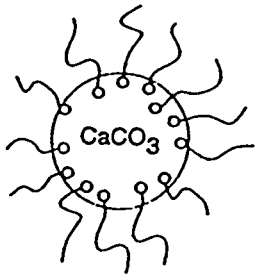


Figure 6.13 The size and composition of a PIB-TEPA micelle



NORMAL CALCIUM SULFONATE
(NCS)



OVERBASED CALCIUM SULFONATE MICE
(WHERE ~o = NCS)

re 3—Normal and Overbased Sulfonates

Nanoparticles Emission

- Measurement issues: accuracy, precision
- Dust particle contamination
- Lack of calibration standards

Definitive measurement techniques

- Transmission microscope
- AFM tapping mode in clean room

Lubricant to reduce Nanoparticles

- Sulfur free lubricant
  * ZDDP major issue--wear
  * Sulfonate free -- detergent
  * Synthetic base oil
- Metal free lubricant
  * Ca major issue -- detergent
  * Carbon soot accumulation

CLEAR TOPPER

Strategies for low emission lubricants

- Super-stable lubricant
  - Base oils
  - Additives
  - LHRE engine experience
- Decomposable lube.
  - Polylactone structure
  - tailored MW
  - largely inhibitors
  - almost once through
- Multifunctional baseoil structures
- Additive that blocks the polymerization reactions
- additive that promotes decompositions
- Do we really need VII in diesel oils?

Strategy for LEO

- Revolutionary rethinking lubricant composition
- Simpler additive package
- Cleaner additive chemistry
- Combination of base oil structure and additive structure as a designed package rather than take one and tailor to it.