Alternative Fuels & Advance in IC Engines

Fundamentals and Case Study of Automotive Lubricating Oil Tribology for Biodiesel vis-a-vis Diesel Fuelled Engines

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Machine Maintenance is a $250 Billion Industry

1. DOW Chemicals: $1 Bn
2. Union Pacific Railroad: $1 Bn
3. Mobil Oil: $800 Mn

“Six to seven percent of the National Gross Product is required just to repair the damage caused by mechanical wear”-Massachusetts Institute of Technology
### Function of Lubricating Oils

- **Friction Control**: Separates Moving Parts
- **Wear Control**: Reduces Abrasive Wear
- **Corrosion Control**: Protects Surfaces From Corrosive Substances
- **Temperature Control**: Absorbs & Control Heat
- **Contamination Control**: Transports Particles and Other Contaminants to Filter/ Separators
- **Power Transmission**: In Hydraulics, Transmits force and motion

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### Diesel Engines Require Oils To Perform Many Functions

- **Lubrication**
  - Hydrodynamic Lubrication
  - Wear Reduction in boundary and elastohydrodynamic lubrication
- **Cooling**
- **Sealing**
- **Hydraulic Fluid**
- **Corrosion Protection**
- **Contaminant Sink / Cleaning Action**
Diesel Engine Oils (DEO) Perform Many Functions

- Hydrodynamic Lubrication
  - This property is provided by the lubricating oil viscosity (SAE grade i.e. 30, 40)
  - Hydrocarbon oils are characterized by their large pressure viscosity coefficients which provide thick oil films under pressure
  - Surface active materials provide wear protection in boundary lubrication and increased oil films
  - In general most Diesel Engine Oils are multigrade oils and are non-newtonian
  - Low temperature fluidity properties are required for easy starting and adequate lubrication at low temperatures (SAE W grade)

- Cooling
  - In general hydrocarbon based oils have a low Cp but they are still critical in reducing internal engine temperatures. Piston cooling jets are standard in most heavy duty engines
  - Deposits on critical surfaces can reduce heat transfer

- Sealing
  - Piston rings use oil viscosity to seal gas pressure
  - Deposits in ring grooves can reduce sealing and increase oil consumption
Diesel Engine Oils (DEO) Perform Many Functions

- Hydraulic Fluid
  - Modern hydraulically operated injectors require consistent oil viscosity with low thickening or shear loss
- Corrosion Protection
  - Oil films provide surface protection for Fe and non-ferrous metals
  - Combustion contaminants destroy the oils ability to protect surfaces

Diesel Engines are Dirty!

*Especially if you’re a motor oil*

- Contaminant Control
  - Oils become loaded with
    - Soot (Wear and Viscosity)
    - Combustion acids (Corrosion & Oxidation)
    - unburned fuel (Viscosity Loss)
    - Wear metals (Ash)
    - Dirt (Abrasives)
    - Oxidized oil products (Thickening)
  - Oils are required to clean surfaces and suspend solids
**Temperature Effects**

MacCoul-Walther-Wright Equation

\[ \log \log (\eta) = a - c \log (T \, ^{\circ}K) \]

**Effect Of Pressure**

Barus equation: \[ \eta_0 = \eta_p \exp \alpha \times p \]

\( \alpha \): Pressure/Viscosity coefficient
**Effect Of Shear Rate**

- Shear Rate (1/s)
- Viscosity (cP)

**Lubrication Regimes**

- Friction Coeff.
- Film Thickness (nm)
- Valve Train & Gears
- Pistons, Transmissions, & Gears
- Bearings
Structure of Lubricating Oil

<table>
<thead>
<tr>
<th>Base Stock</th>
<th>Additives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mineral or Synthetic</td>
<td>Organic and Inorganic</td>
</tr>
</tbody>
</table>

- Provides Viscosity for control of friction and wear
- Provides corrosion and Oxidation Resistances
- Provides heat transfer

- Enhances existing base stock properties
- Suppresses undesirable base stock properties
- Imparts new properties

Diesel Engine Oils Perform These Tasks Using Unique Balanced Formulations

- Base oils or stocks are 75 - 88% of the lubricant
  - These may be mineral oil based or synthetic
  - Base oils alone cannot provide all the required functions
- Additives are Required
  - Viscosity Modifiers 5 - 10 %
  - Additive Packages 10 - 20 %
Mineral Base Stocks

- Derived from petroleum crude oils through a series of solvent and distillation subtraction processes. Approximately 95% of all lubricants are mineral based.

Properties of Base Stock Mineral Oils

<table>
<thead>
<tr>
<th>Naphthenic Base Stocks</th>
<th>Paraffinic Base Stocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Operating Temp</td>
<td>Higher Operating Temp</td>
</tr>
<tr>
<td>Low VI</td>
<td>Higher VI</td>
</tr>
<tr>
<td>Low Pour Point</td>
<td>Higher Pour Point</td>
</tr>
<tr>
<td>Viscosity Pour Point</td>
<td>Wax pour Point</td>
</tr>
<tr>
<td>Good additive Solvency</td>
<td>Higher Flash point</td>
</tr>
<tr>
<td>More Scarce</td>
<td></td>
</tr>
</tbody>
</table>
Synthetic Base Stocks

- Man Made Material (Similar to Plastic) derived from petroleum
  - Chemically identical molecules designed by scientists
  - Molecular Structure is precisely planned and controlled
  - Naturally occurring low molecular weight compounds are enlarged (Polymerized) by chemical reactions forming higher molecular weight structures of desired viscosity
  - Predictable properties

Synthetic Lubricants

Approx. 3% of Lubricating Oils employ synthetic base stocks

Possible Advantages
- High Flash Point lower pour point
- Wider thermal operating range
- Fire resistance
- Improved Lubricity
- Oxidation Stability
- Higher VI
- Improved shear resistance
- Lower Friction
- Natural Detergency
- Extended Oil Drains

Possible Disadvantages
- High Cost
- Hazardous Disposal
- Toxicity
- Seal Compatibility
- Contaminant Sensitivity

Examples
- Polyalphaolefins
- Alkylated aromatics
- Cycloalephatics
- Dibasic Acid esters
- Polyol Esters
Water Based Fluids

- **Possible Advantages**
  - Low cost
  - Fire-Resistant
  - Non-Hazardous disposal

- **Possible Disadvantages**
  - Viscosity and Lubricity stability
  - Corrosion
  - Additive Stability
  - Limited Temperature Range

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**Lubricant Additive Formulations**

**Diesel Engine Oil Additives**

- **DISPERSANTS**
- **DETERGENTS**
- **ANTISNARE AGENTS**
- **FRICTION MODIFIERS**
- **ANTIOXIDANTS**
- **RUST INHIBITOR**
- **POUR DEPRESSANT**
- **FOAM INHIBITORS**
Types of Additives Typically Found in Diesel Engine Oils

- Dispersants
  - Nitrogen and Hydrocarbon based
- Detergents & Detergent/Inhibitors
  - Sulfonates, Phenates, Salicylates
  - Contain Alkaline Metals
- Anti-wear
  - Zinc dithiophosphate (ZDDP) predominates
- Rust and Corrosion Inhibitors
  - Detergents, ZDDP, Triazoles, Thiodiazoles

Types of Additives Typically Found in DEOs (cont.)

- Anti-oxidants
  - ZDDP, Phenates, Phosphonates, Salicylates
  - Phenolics, amines, carbamates, copper compounds, molybdenum compounds
  - Many A/O's are sulfur and Ash containing
- Anti-foam
  - Silicone oils
- Friction Modifiers
  - Various, many contain sulfur, oxygen or molybdenum
- Viscosity Modifiers & PPD's
  - Hydrocarbon and oxygen based, some are dispersant with Nitrogen
### Lubricant Additive Formulations

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Additives Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel Engines</td>
<td>Anti-oxidant, Corrosion Inhibitors, Detergents/Dispersant, Anti-wear, Anti-Foam, Alkalinity Improver</td>
</tr>
<tr>
<td>Steam turbine Compressors</td>
<td>Anti-Oxidants, Corrosion Inhibitors, Anti-emulsifier</td>
</tr>
<tr>
<td>Gear, Spiral bevel or hypoid</td>
<td>Anti-wear, anti-oxidant, anti-foam, sometimes corrosion inhibitors, extreme pressure</td>
</tr>
<tr>
<td>Gear, Worm</td>
<td>Extreme pressure, anti-oxidant, corrosion inhibitor</td>
</tr>
<tr>
<td>Hydraulic systems</td>
<td>Anti-oxidants, anti-wear, anti-foam, corrosion inhibitor, pour point depressant, viscosity index improver</td>
</tr>
</tbody>
</table>

### Antioxidants

- Three main types: hindered and/or aromatic amines, hindered phenols, and dithiophosphate derivatives
- The proper choice of the type of AO depends on the operating conditions
- Phenols and amines work as radical traps while ZDTPs work as peroxide decomposers and metal deactivators
Additives: Anti-Oxidants and Oxidative Inhibitors

- Purpose: To prevent the oxidation of a lubricants base stock, resulting in undesirable by-products
- The additive oxidizes in preference to the oil. It sacrifices itself.
- Hindered phenol (Chain breaking), zinc di-thio-phosphate (Peroxide destroying), aromatic amine.

Additive: Boundary Lubrication Films

- Oiliness Agents (Friction Modifiers)
  - Modifies Contact Resistance
  - Polar materials form uniform layered film on surfaces. Some react with surface forming metal soap.
  - Fatty Acids
- Antiwear Additives
  - Reduces friction and wear from sliding contacts
  - Surface active materials form low shear strength film between sliding surfaces
  - Zinc-di-alkyl-di-thio-phosphate (ZDDP), Tricresylphosphate (TCP).
**Extreme Pressure (EP) Additives**

- Mitigates the effect of high load boundary lubrication
- Reacts with surface under high heat and pressure to form ductile films
- Surface active compounds of chlorine, phosphorous, sulphur

**How Anti-wear Additives Work**

- Anti-wear Molecules form films by attaching to the surfaces by adsorption
- Under boundary conditions, anti-wear films shear instead of surface material
Antiwear and Extreme Pressure Agents

- Form a protective chemical boundary between oil and engine surface
- Most contain sulfur and/or phosphorus capable of depositing sulfide and phosphorus films on the metal surface
- Also effective as antioxidants and corrosion inhibitors
- ZDDP is the most common

Types of ZDDP

\[
\begin{align*}
\text{R-O-P-S-Zn-S-P-O-R} \\
\text{R-O-P-S-Zn-S-P-O-R}
\end{align*}
\]

<table>
<thead>
<tr>
<th>R</th>
<th>ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary alkyl</td>
<td>(\text{CH}_2)</td>
</tr>
<tr>
<td>Primary alkyl</td>
<td>(\text{CH}_3)</td>
</tr>
<tr>
<td>Aryl</td>
<td>(\text{R} - \circ)</td>
</tr>
</tbody>
</table>
Additives: Viscosity Index (VI) Improver (Modifier)

- Purpose: Reduces viscosity sensitivity to temperature
- Long chain oil soluble polymers thicken oil at high temperature by swelling action.
- e.g. Ethylene, Propylene co-polymers, polymethacrylates

VI Molecules swell as temperature rises
Friction Modifiers

- Friction modifiers (FM) improve fuel economy.
- Many are derivatives of fatty acids.
- FMs include sulfur-containing molybdenum compounds and graphite.
- They are surface active agents - reducing friction coefficient further than AW/EP.
- They function by either forming a multi-layered, adsorbed film or by forming layers of microcrystalline plates.
Corrosion Inhibitors

- **Rust Inhibitor**
  - Purpose: To reduce rust formation on iron surfaces
  - Additive is metalophillic and hydrophobic. Coats metal surface and rejects moisture.
  - E.g. Long chain fatty acids, naphthalene sulphorates, phosphoric acid derivatives.

- **Copper corrosion Inhibitors**
  - Prevents corrosion and tarnishing of copper alloy metals.
  - Forms chemically adsorptive film on surfaces
  - E.g. Chelating compounds of imidazole and benzotriazole.

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Dispersant Additives

- Dispersants are used primarily to protect engines operated at low to moderate temperatures - keeping contaminants like soot and sludge in suspension
- They are generally ashless, containing a polar head (polyamine) and a long, non-polar, hydrophobic tail
- The basic nitrogen atoms may be borated or acylated
- More complex dispersants have been developed to meet more severe requirements
Detergent Additives

- Detergents protect engines operated at high temperatures - removing and preventing carbon-like deposits in the ring-belt area
- They also act as dispersants - keeping insolubles in suspension
- They neutralize acids from combustion (fuel Sulfur) and provide rust protection
- They usually contain a polar head and a long hydrophobic tail
- They can be neutral salts with a counter ion of Na, Ba, Ca, or Mg or highly overbased
Common Detergents used in Lubricants

\[
\begin{align*}
&\left[ (\text{a-C}_{12}\text{H}_{25})_2 \text{SO}_3 \right]_{\text{Ca}^{++}}^2 \\
&\left[ \text{C}_{12}\text{H}_{25-S} \text{O}^- \right]_{\text{Ca}^{++}}^2 \\
\end{align*}
\]

- Calcium didodecylbenzene sulfonate
- Calcium dodecylphenolate

Phenates

- Calcium hexadecylsalicylate

Salicylates

Structure of an Overbased Detergent

- Base = Ca(OH)\(_2\) or CaCO\(_3\)
- Moles of base per mole of sulfonate = overbasing ratio
Dispersants and Detergents

- Keeps engine surface free of deposits
- Surrounds particles (Soot) with oil solubilizing molecules to keep them suspended and finely divided (Peptized).
- E.g. Various organo-metallic soaps of barium, calcium, and Magnesium.

Increasing amount of contaminants can overload dispersants causing the formation of deposits and sludge (Agglomeration of particles).

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Detergency Test - 1K

<table>
<thead>
<tr>
<th>Good</th>
<th>Poor</th>
</tr>
</thead>
</table>

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21
Pour Point Depressants

- Purpose: To prevent congelation of the oil at low temperatures due to wax crystallization.
- Modifies the interface between the crystallized wax and the oil.
- E.g. Alkylated wax naphthalene, poly, ethacrylates, Alkylated wax phenols

Antifoam

- Purpose: To prevent the formation of the stable foam

Small entrained bubbles combine (coalesce) to form larger bubbles
Speed and Load Effects on Lubricant & Viscosity Selection

- The most common mismatch of lubricants to a machine application is the selection of the wrong viscosity.

Hydrodynamic Lubrication

- Fluid film lubrication - Surfaces separated by bulk lubricant film, affected by viscosity, load, and speed.
- Mixed film lubricant - Both the bulk lubricant and boundary film play a role.
- Boundary lubrication - Protection essentially dependent on boundary film.

- Boundary Film (antiwear additive protection)
- Bulk Lubricant (viscosity protection)
- Starts, Stops, and Shock Load Conditions
Effect of Lubricant Viscosity on Fuel Consumption

EPA Transient Cycle
(Measured Fuel Consumption, Hot Start)

[Graph showing the relationship between HTHS Viscosity (cP) and Fuel Consumption (lb/hr).]

Diesel EGR Field Test
32 Qt Crankcase = 8 lb Soot

EGR Field Test Used Oil Viscosity
(25,000 mile Drains)

[Graph showing the relationship between Soot (% by weight) and KV @ 100 °C.]

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Soot Thickening Effect on Fuel Consumption
(Lab Dyno Test)

![Graph showing the relationship between soot content and fuel consumption.](image)

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Soot Wear Mechanism in EGR Diesel Engine Tests

- Abrasive Wear by Primary Soot Particles is the Key Wear Mechanism in most diesel engines in particular the engine valve trains.
- Wear can be reduced with Oils that Form Sufficiently Thick Films.

- **Film thickness < soot size**: More abrasive wear
- **Film thickness > soot size**: Less abrasive wear

**ME 690 Alternative Fuels & Advance in IC Engines**
Maintenance Philosophies

- **Proactive Maintenance**
  - Conditions are maintained that avoid the onset of machine wear and component degradation. Conditions are monitored and remedial actions are taken to stabilize healthy operating conditions. Maintenance activities are proactive, i.e. ahead of the first initiation of failure, not in response to.

- **Predictive Maintenance**
  - The progression of failure is monitored using non-destructive instrumentation. Machine repair is scheduled prior to catastrophic breakdown.

- **Preventive Maintenance**
  - Maintenance is scheduled according to historic trends, experience, or reliability data. Typically, operating intervals such as hours, miles, or cycles are used as a basis for maintenance, not machine conditions. Considerable guesswork is involved.

- **Breakdown Maintenance**
  - Maintenance is scheduled in response to operational failure.

### Human Body Parallel to Machine Maintenance

<table>
<thead>
<tr>
<th>Maintenance strategy</th>
<th>Technique needed</th>
<th>Cost per hp per year</th>
<th>Human body parallel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proactive Maintenance</td>
<td>Monitoring and correction of failure root causes, e.g., contamination</td>
<td>$0.10</td>
<td>Cholesterol and blood pressure monitoring with diet control</td>
</tr>
<tr>
<td>Predictive Maintenance</td>
<td>Monitoring of vibration, wear debris</td>
<td>$8</td>
<td>Detection of heart disease using EKG or ultrasonics</td>
</tr>
<tr>
<td>Preventive Maintenance</td>
<td>Periodic component replacement</td>
<td>$13</td>
<td>By-pass or transplant surgery</td>
</tr>
<tr>
<td>Breakdown Maintenance</td>
<td>Large maintenance budget</td>
<td>$18</td>
<td>Heart attack or stroke</td>
</tr>
</tbody>
</table>
**Oil Sampling Guidelines**

- Sample at operating machine temperature.
- Sample within 10 minutes of typical operating conditions.
- Always sample from same point using same procedure.
- For machine requiring frequent oil changes, always sample at same time interval after change.
- Do not sample immediately after oil change or the addition of makeup fluid.
- Analyze within 48 hours of taking sample.

**Drawing Samples from Diesel Engines**

- Diesel Engine’s sampling frequency: 150 Hours
- Samples should be drawn between pump and filter.
Fluid Properties Analysis

- Fluid property degradation contributes to wear and corrosion.
  - Viscosity
  - Lubricity
  - Additive
  - Specific Gravity
  - Oxidation

Oxidation Stability

- Effects of oxidation
  - Oil Darkening
  - Pungent Odor
  - Acidity Increases
  - Viscosity increases

- Acidity greatest with lower temperature oxidation.

- Darkening and increased viscosity greatest with higher temperature oxidation
## Causes of Additive Depletion

<table>
<thead>
<tr>
<th>Causes</th>
<th>Depletion Mechanism</th>
<th>Additives Affected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excessive Heat and Oxidative Reactions (root causes: heat, air (oxygen), moisture, metal particles)</td>
<td>Additives are sacrificed by decomposing reactive compounds.</td>
<td>Antioxidants, oxidation inhibitors, some antiwear additives</td>
</tr>
<tr>
<td>Particle Scratching (root causes: high particle ingestion and wear debris generation)</td>
<td>Surface-active additives attach to polar particles (e.g., dirt and wear debris). When particles are removed through filtration, additives deplete.</td>
<td>Antioxidants, antitrust, rust inhibitors, detergents, dispersants, alkalinity improvers, some VI modifiers</td>
</tr>
<tr>
<td>Water Washing (root causes: water ingestion combined with active water separation)</td>
<td>Some additives dissolve better in water than lubricant base stocks. When water is removed additives go with it.</td>
<td>Rust inhibitors, emulsifying agents, dispersants, some antioxidants and antiwear</td>
</tr>
<tr>
<td>Boundary Layer Lubrication and Abrasive Wear (root causes: loss of film strength and/or suspended abrasive particles)</td>
<td>Surface-active additives attack to free metal surfaces as wear processes remove oxide or antiwear films. The higher the film removal rate, the higher the depletion.</td>
<td>Antioxidants, antitrust, extreme pressure, rust inhibitors</td>
</tr>
<tr>
<td>Diesel Engine Combustion By-Products (root causes: blow-by, vertueling, high sulfur fuels)</td>
<td>Sulfoinic acids neutralize alkalinity improvers. Dispersants suspend soot particles and eventually become overloaded.</td>
<td>Alkalinity improvers, antioxidants, dispersants, detergents</td>
</tr>
</tbody>
</table>

### Viscosity Measurement

- **Absolute Viscosity**: Resistance to flow as affected by shear stress (Centi-poise)
- **Kinematic viscosity**: Resistance to flow as affected by shear stress and specific gravity (Centi-stokes).

**Kinematic viscosity** = Absolute viscosity / Specific Gravity

- Kinematic viscosity of water is 1 cSt
- Absolute viscosity of water is 1 cPs
High Temperature Effects on Oil Viscosity

- Temporary Effect: Raised Oil Temperature reduces resistance to shear and lowers oil viscosity.
- Permanent Effect: Sustained raised temperatures permanently increases oil viscosity
  - Oxidation (Soluble oxide by-products such as sludge)
  - Polymerization
  - Vaporization of lighter oil fractions
  - Specific gravity increases
- Change oil when viscosity increases by 20% or more, or decreases by 10% or more.

FTIR: Fourier Transform Infrared Spectroscopy

- **Evaluates**
  - Oxidation
  - Nitration
  - Sulphation
  - Moisture
  - Soot Buildup
  - Freon
  - Alcohol
  - Glycol
  - Antiwear Additives

IR Absorption by Organic Molecules from vibration affected by
  - Mass of the atoms
  - Chemical Bond Force
  - Spatial Geometry
FTIR: How It Works

- Infrared energy absorbed by a used oil sample is plotted as a waveform spectrum (a wavelength of 10 microns equals a waveform number of 1000, i.e. $\times 100$).
- The new oil spectrum is overlaid above or below the used oil spectrum for easy comparison.
- Properties such as oxidation additive levels, and certain contaminants are evaluated by comparing the two spectrums at specific wave-numbers. These areas are the “Markers” which can show an increase or decrease in a particular property based on a change in the absorption level.

Infra Red Spectra Locations

<table>
<thead>
<tr>
<th>Component</th>
<th>Performance</th>
<th>Approximate Wavenumber</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel soot</td>
<td>Trend only</td>
<td>2000-4000</td>
<td>Broadband absorption</td>
</tr>
<tr>
<td>Oxidation products**</td>
<td>Trend only</td>
<td>1700-1770</td>
<td>Not reference sensitive</td>
</tr>
<tr>
<td>Nitration (nitro oxidation)</td>
<td>Trend only</td>
<td>1630</td>
<td>Not reference sensitive</td>
</tr>
<tr>
<td>Sulphur (sulfate oxidation)</td>
<td>Trend only</td>
<td>7000-8200, 1150</td>
<td>Not reference sensitive</td>
</tr>
<tr>
<td>Diesel fuel*</td>
<td>2% or higher</td>
<td>800</td>
<td>Good reference required</td>
</tr>
<tr>
<td>Water*</td>
<td>0.1% or higher</td>
<td>3400 (proximate levels)</td>
<td>Free/dissolved Interferences</td>
</tr>
<tr>
<td>Antioxidant additive</td>
<td>Trend only</td>
<td>3650</td>
<td>Good reference required</td>
</tr>
<tr>
<td>Antwear additive</td>
<td>Trend only: 935-999</td>
<td></td>
<td>Good reference required</td>
</tr>
<tr>
<td>$\gamma$-oil*</td>
<td>0.1% or higher</td>
<td>880, 1040, 1080</td>
<td>**</td>
</tr>
</tbody>
</table>

*considered “best estimates” ** Carbonyl Products - carbon bonds to single oxygen: 1st Carbonyl Products - carbon bonds to two oxygens: 2nd
FTIR Examples

**Antioxidant Additive**

Critical Region
3650 cm⁻¹

**Base-Stock Oxidation**

Critical Region
1700-1770 cm⁻¹

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**FTIR Examples**

**Fuel Soot**

Tilt Between
2000-4000 cm⁻¹
Indicates Soot Buildup

**Fuel Dilution**

Critical Region
7000-8200 cm⁻¹
Engine Oil Contamination

- **Effect of Water Contamination**
  - **On the oil**
    - Promotes Oxidation – creates slimes and resins
    - Increases conductivity – transformer oil
    - Reacts with oxidation/ rust inhibitors – forms acids and precipitants
    - Causes “Water washing” of additives that are more soluble in water than oil, e.g. anti-rust and anti-oxidant. Other polar impurities are also attracted to water. This eventually leads to a “Chemical Soup” at the bottom of the sump.
Effect of Water Contamination

- On the oil
  - Destroys antiwear additive (ZDDP) – forms hydrogen sulfide and sulfuric acid.
  - Encourages microbial growth
  - Forms non-Newtonian fluids* – Viscosity affects
  - Reacts with VI improvers
  - One drop of water in a gallon of oil at 180F will destroy antiwear additives – control suspended water to below 100 PPM.

* Fluids where viscosity is affected by changes in shear rate

Fuel Dilution

<table>
<thead>
<tr>
<th>Amount of Dilution</th>
<th>Viscosity Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%</td>
<td>SAE 30 ⇒ 20</td>
</tr>
<tr>
<td>7%</td>
<td>SAE 30 ⇒ 10</td>
</tr>
</tbody>
</table>

Change oil when fuel dilution exceeds 2%

Tests for fuel dilution: Viscosity, FTIR, Flash Point (ASTM D92), Paper/Gas Chromatography (ASTM D3524), Steam Distillation
Causes of Fuel Dilution

- Faulty Injector and Cup Seals (Heavy Ends)
- Leaking Fuel Lines (Raw)
- Dribbling Injectors (Heavy Ends)
- Blow-By (Heavy Ends)
- Worn Injector Pump (Raw)
- Leaking Pump Seals (Raw)
- Defective Spray Patterns (Heavy Ends)

*Fuel Conditions in parentheses

Fuel Soot

- Incomplete combustion of fuel
- Low compression
- High fuel/air ratio
- Improper scavenge
- Excessive ring wear/blowby
- Plugged air filter
- Excessive idling
- Cool engine temperatures
- Poor fuel nozzle operation
- Defective turbo operation

Tests for Soot: Pentane Insolubles (ASTM D893), Membrane Filtration, Paper Chromatography, FTIR, Thermogravimetric Analysis (TGA), and ASTM Coagulant/Centrifugation
Ethylene Glycol - Antifreeze

- Boiling point 198°C
- Freezing point -12°C
- 50 - 60% water
- Oxidation inhibitors
  - Potassium
  - Sodium
  - Boron
  \[
  \text{Common Ratio} = \frac{5}{1} \text{ Sodium} : \text{Boron}
  \]
- Causes oil thickening, forms gels/emulsions, restricted oil flow, and poor lubrication

Tests for glycol: FTIR, Spectrographic Analysis, Viscosity, Water Analysis, Reagent Methods (ASTM D2982), Gas Chromatography (ASTM D4291)

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Engine Oils will enable Low Emissions
By Lowering Interference with Aftertreatment

- Metallic ash can plug after-treatment cores
- Certain metals are absorbed onto catalyst sites and prevent the sites from functioning - 'poisoning the catalyst
- With Ultra Low Sulfur fuel, the sulfur from consumed oil becomes a significant sulfur contributor
- Lower the amount of oil 'consumed' in an engine
  - By engine design
  - Less volatile oil, better seal compatibility to minimize leakage, better detergency/oxidative stability to minimize power cylinder deposits and allow engine to function as designed
- Decrease the amounts of metallics and ash forming components in oil
  - This is the major thrust of future oil specifications
Challenges of reducing DEO Sulfur

- Reduction of most effective anti-wear - ZDDP - replacement not certain
- Reduction of most detergents and some types of A/O’s, FM’s and VM’s
- Engine metallurgy and design must take into account these reductions
- Engine durability with revised chemical compositions must be demonstrated
- Proof of performance will be required

New Engines must operate with lower ZDDP and Detergents

- Oils will still be required to pass performance tests
- OEMs see a bigger problem with trucks misfueled with higher sulfur fuel. They believe they can solve fuel misapplication and this will reduce the oil problem
- Many of the 'new' additives have already seen use in the field, although there may be some very new additives which are or will be undergoing field tests - to minimize risks
- New additives require extensive toxicology tests and registration
- Oil costs will be higher due to better base oils and the use of more expensive additives. The cost of crude oil and raw materials continues to increase (Motor oil may finally be more expensive than spring water)
HD Diesel Fuel Efficiency

- Truck Fuel economy is influenced more by tires, aerodynamics, idle time and driver habits than by engine oil
- However oil can influence fuel efficiency of the engine
  - Most Significant influence is High Temperature High Shear viscosity of the oil - a 10W-30 oil will give better fuel efficiency than a 15W-40
  - High soot levels will decrease fuel efficiency
  - A balance is required to achieve good film thickness for bearing and wear performance yet thin enough to give fuel efficiency
  - Better quality base oils with higher viscosity index will help

Engine Durability and Extended Drain Intervals

- In 1994 in the US On-highway diesel fuel sulfur went from an average of 3900 ppm to 400 ppm. This (along with better engine technology) enabled the HDD trucks to go from 12,000 - 15,000 mile drains to 30,000 to 50,000 mile drains. (Two to Three times)
- Despite the lowering of some key components durability should not suffer for the same reasons that drains increased after 1994
- We do not expect the same kind of dramatic drain interval increase in the change to ULSD
### Summary of Lab Tests

<table>
<thead>
<tr>
<th>Test</th>
<th>Recommended Instrument/Method</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Particle Counting</td>
<td>Automatic particle counters using &quot;Pore Blockage&quot;</td>
<td>Avoids optical interferences from air, moisture, and fluid darkness</td>
</tr>
<tr>
<td>2. Viscosity Analysis</td>
<td>Direct reading &quot;absolute viscosity&quot; tests</td>
<td>Avoids errors associated with changing specific gravity, surface tension, and Newtonian properties</td>
</tr>
<tr>
<td>3. Total Base Number</td>
<td>ASTM D4739 test procedure</td>
<td>Avoids interferences from wear metals and weak acids associated with ASTM D2696</td>
</tr>
<tr>
<td>4. Total Acid Number</td>
<td>ASTM D664 or D974</td>
<td></td>
</tr>
<tr>
<td>5. Infrared Spectroscopy (for fuel soot, oxidation, sulfation and nitration)</td>
<td>&quot;Transmission cell&quot; configuration</td>
<td>ATR methods may have too low a signal strength for some fluids and fluid properties</td>
</tr>
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<tr>
<td>6. Moisture Analysis</td>
<td>&quot;Vapor Induced Scintillation&quot; method</td>
<td>Avoids additive interferences</td>
</tr>
<tr>
<td>7. Fuel Dilution</td>
<td>Gas chromatography or flash point, plus viscosity</td>
<td>FTIR for fuel may have interferences from reference mismatch</td>
</tr>
<tr>
<td>8. Glycol Dilution</td>
<td>Spectrographic analysis for potassium, sodium, or boron</td>
<td>Avoid &quot;wet chemistry&quot; techniques</td>
</tr>
<tr>
<td>9. Spectrographic Analysis</td>
<td>ICP emission or spark emission spectrometers</td>
<td>Must have sufficient number of elements to cover the additive and wear metals range</td>
</tr>
<tr>
<td>0. Ferrographic Analysis</td>
<td>Ferrous particle counter plus glass or membrane ferrograms</td>
<td>Bichromatic microscope with image capture ability is helpful</td>
</tr>
</tbody>
</table>
**Lubricating Oils**

- Efforts are being made to increase useful life of lubricating oils as it alone costs approximately 6%–7% of the overall operating costs.
- For using any alternative fuel for large scale usage, it becomes imperative to examine critically the condition of the lubricating oil, and its compatibility with the new fuel being used.
- An exhaustive series of Tribological tests need to be conducted in order to ascertain the comparative performance of the newly developed alternative fuel vis-à-vis mineral fuels.

**Tribological Studies on Lubricating Oil**

- Lubricating oil degradation and ageing because of prolonged, repeated *mechanical, thermal, environmental stresses, depletion of additives and contamination with foreign particles*
- All these factors are inter-related and work synergistically to worsen the oil condition
- Analysis of used lubricating oil is a very effective tool for condition monitoring of an engine. *Oil analysis is also a very powerful technique for failure analysis, diagnostics and preventive maintenance.*
- Density, Kinematic viscosity, Ash content, Water content, Flash point, Pentane and benzene insolubles, IR spectroscopy, SPDS/SCDS, TLC, AAS, and Ferrography for wear debris analysis
Oil Tribology Results

- Factors affecting Engine Oil Performance
  - Oil Thickening
  - Loss of wear protection additives
  - Deposit controls in high temperature and high load conditions
  - Oil Thinning
  - Loss of corrosion protection
  - Low temperature Sludge formation in short engine runs

- *Lube oil analysis can yield information about the engine condition and early detection of the problem.*
- *No single test is sufficient to get a clear picture and several tests are to be exploited for a clear picture.*