



# Lubricant Degradation Modes

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## Agenda

- Major Lubricant Degradation Modes
    - Oxidation
    - Thermal Degradation
    - Microdieseling (Cavitation)
    - Electrostatic Spark Discharge
    - Additive Depletion
    - Contamination
  - Tests for Identifying Lubricant Degradation Modes
  - Mitigating Lubricant Degradation
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# Major Lubricant Degradation Modes

Oxidation

Thermal Degradation

Microdieseling (Cavitation)

Electrostatic Spark Discharge

Additive Depletion

Contamination

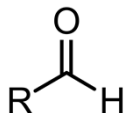
# Oxidation

- Conditions for Oxidation
  - Air / Oxygen
  - Elevated Temperature
  - Catalyzed by Metals - iron and copper

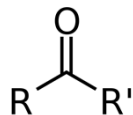


- Oxidation By-products

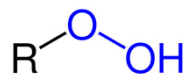
- Aldehydes



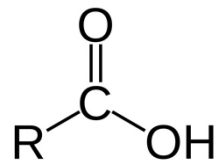
- Ketones



- Hydroperoxides

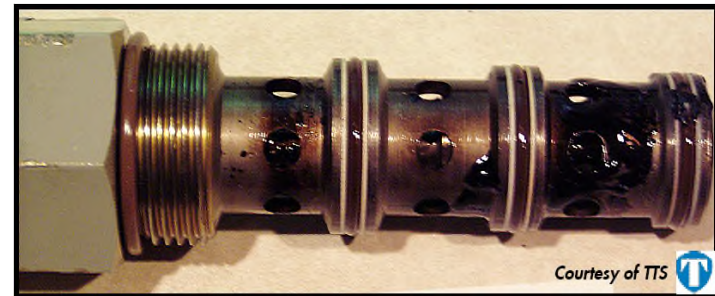


- Carboxylic Acids



## Oxidation

- Progression of Oxidation
  - Initiation – Production of Free Radical
  - Propagation – Production of Additional Free Radicals
  - Termination – Depletion of Antioxidant Additives
- Signs of Oxidation
  - Sludge and Varnish
  - Viscosity Increase
  - Acid Number Increase





## Thermal Degradation

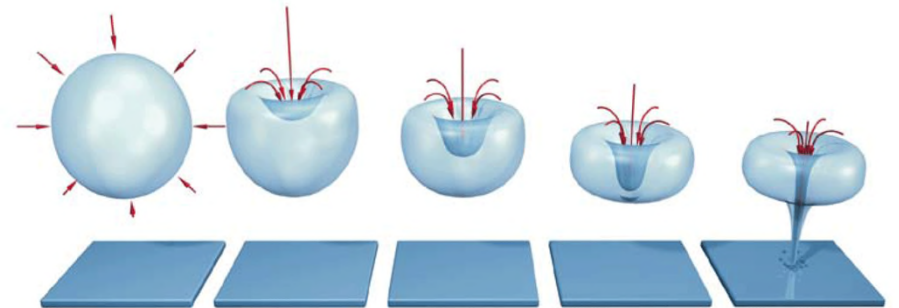
- Conditions for Thermal Degradation
    - Elevated Temperature
    - Lack of Oxygen
  - Thermal Cracking
    - Temperatures Above 200°C (~400°F)
    - Base Oil Molecules Crack into Smaller Molecules
  - Signs of Thermal Degradation
    - Lacquer and Carbonaceous Deposits
    - Viscosity Decrease
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## Microdieseling (Cavitation)

- Vapor bubbles in the fluid form in low-pressure regions and are collapsed (imploded) in the higher-pressure regions of the oil system
- Localized temperature can reach  $1000^{\circ}\text{C}$  ( $>1800^{\circ}\text{F}$ )
- Results on localized thermal degradation
- Forms varnish from coke, tars, and resin



Jet pressure can reach 2,000,000 psi





## Electrostatic Spark Discharge (ESD)

- Electrostatic charge develops when dry oil passes through tight clearances
- Often occurs in filter elements
- Can also occur in oil reservoirs
- Often characterized by a ticking or clicking sound
- Temperatures in excess of  $10,000^{\circ}\text{C}$  ( $>18,000^{\circ}\text{F}$ )
- Immediate thermal degradation
- Formation of free radicals
- Signs of ESD
  - Viscosity Increase
  - Sludge and Varnish



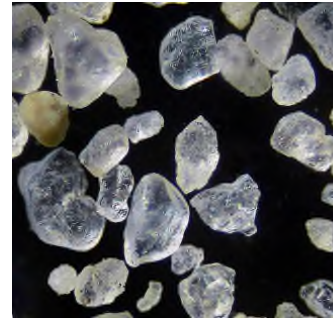


## Additive Depletion

- Many additives are sacrificial components of an oil formulation
  - Antioxidants are depleted as oxidation occurs
  - Antioxidants protect the base oil from becoming oxidized
  - Once antioxidants are depleted, base oil oxidation begins
  - Surface active additives become attached to metal surfaces
    - Rust inhibitors, antiwear, and extreme pressure additives
    - Zinc Dialkyl Dithiophosphate (ZDDP) is an antiwear additive that also has antioxidant characteristics
  - Antifoam additives can be removed in fine filters
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# Contamination

- Solids
  - Environmental Contaminants
  - Wear Metals
- Liquids
  - Water
  - Fuel
  - Coolant
- Gases
  - Air
  - Natural Gas



## Appearance of Water in Oil

Dissolved Water- Oil appears bright and clear. Water can only be removed by vacuum dehydration.



Emulsified Water- Very small droplets dispersed in oil. Oil viscosity may go up and appear cloudy and milky. Tiny amounts of detergent engine oil can contaminate industrial oils.

Free Water- Large drops that readily settle out.

# Tests for Identifying Lubricant Degradation Modes

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## Oxidation

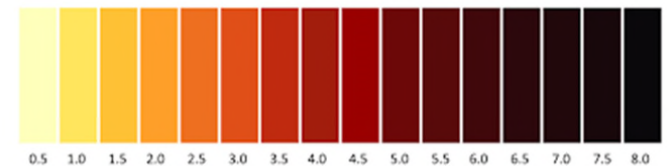
- Viscosity (ASTM D445) – An increase in viscosity can be an early sign of oxidation. Limits should be set to trigger a warning if the viscosity deviates more than 5% from the original value.
- Total Acid Number (ASTM D974) – An increase in the acidity (acid number) of the oil is also an indicator of oxidation. The measured value must be compared to the TAN value for the new oil. An increase of 0.3 mg KOH/g is an indicator of the presence of free radicals or oxidation products.
- Elemental Analysis (ASTM D4951) – an increase in the concentration of iron and/or copper in in-service oil is an indicator of the presence of oxidation catalysts.



# Tests for Identifying Lubricant Degradation Modes

## Measuring Oxidation

- Fourier Transform Infrared (FTIR ) Analysis – FTIR is a powerful tool for diagnosing lubricant degradation. When compared to the spectrum on new oil, it can show an increase in oxidation products. Used with gas engine oils to determine oxidation and nitration.
- Color (ASTM D1500) – Oxidation typically causes an oil to darken. While not a direct indicator of oxidation, a change in color may be a result of oxidation.
- Membrane Patch Colorimetry (ASTM D7843) – Insoluble contaminants are extracted from an in-service oil sample onto a 0.45 micron nitrocellulose patch, and the color of the patch is analyzed by a spectrophotometer. A darker color indicates oxidation and varnish precursors.



## Tests for Identifying Lubricant Degradation Modes

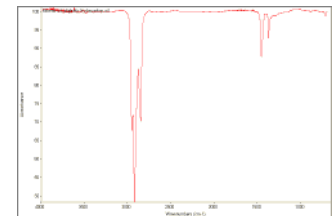
### Measuring Oxidation

- RULER (ASTM D6971) – Remaining Useful Life Evaluation Routine by linear sweep voltammetry measures the remaining Aminic and phenolic antioxidants in an in-service oil sample. It is compared to a baseline of the new oil.
- RPVOT (ASTM D2272) – The Rotary Pressure Vessel Oxidation Test measures the oxidation life of the sample under conditions of elevated temperature, pressurized oxygen, with copper and water present. The value obtained for in-service oil is compared to the value for new oil. If the RVOPT value for an in-service oil sample is less than 25% of the value for the new oil, action should be taken. This may be a full or partial oil change or the addition of an antioxidant additive concentrate.

# Tests for Identifying Lubricant Degradation Modes

## Thermal Degradation

- Viscosity (ASTM D445) - A decrease in viscosity can be a sign of thermal cracking. Limits should be set to trigger a warning if the viscosity deviates more than 5% from the original value.
- Flash Point (ASTM D92) – The flash point of an in-service oil can decrease if the product has undergone thermal cracking. This is especially significant for heat transfer oils that operate at sustained high temperatures.
- Color (ASTM D1500) – Rapid darkening of oil that operates at temperatures over 200°C (~400°F) may suggest thermal degradation.
- FTIR Analysis – Analysis of deposits from oils that have undergone thermal degradation can be identified. The analysis is helpful to differentiate between deposits formed by oxidation and thermal degradation.





## Tests for Identifying Lubricant Degradation Modes

### Microdieseling / Cavitation

- FTIR Analysis – FTIR analysis of the deposits created by microdieseling can aid in identifying it as the mode of degradation.
- Visual Examination of Components – Cavitation often results in severe wear on components such as pump impellers. Examination of those components can be a good way to determine if cavitation has occurred, and with it the phenomenon of microdieseling in the oil.



## Tests for Identifying Lubricant Degradation Modes

### Electrostatic Spark Discharge (ESD)

- FTIR Analysis – Again, FTIR analysis can help to identify the mode of degradation by the analysis of the by-products of the degradation. The presence of soot particles in an industrial oil (turbine or hydraulic oil) is a telltale sign of ESD.
- RULER (ASTM D6971) – The RULER test measures the decrease in aminic and phenolic antioxidants in the oil. A rapid decrease in antioxidants can be suggestive of ESD.
- Dissolved Gas Analysis (DGA ASTM D3612) – Acetylene, ethylene, and methane are often produced when lubricants are exposed to temperatures above 700°C (~1300°F) and are thermally cracked. DGA showing those gases is suggestive of ESD.
- Filter Element Inspection – As noted previously, ESD often occurs in filter elements. Examination of filter elements will often reveal burned or damaged spots where ESD has occurred.

## Tests for Identifying Lubricant Degradation Modes

### Additive Depletion

- FTIR Analysis – Again, FTIR analysis can provide an indication of the decrease in concentration of certain types of additives in a lubricant. Antioxidants, rust inhibitors, antiwear and extreme pressure additives all have their own unique FTIR fingerprint. When the peaks related to a specific additive decrease in analyses performed over time, that is an indication that the additive is becoming depleted.
- RULER (ASTM D6971) – As previously described, the RULER test is designed to monitor the decrease in aminic and phenolic antioxidants over time. It provides a good way to monitor the depletion of those additives.
- RPVOT (ASTM D2272) – This test is used to monitor the decrease in oxidation stability over time. That decrease in performance is directly attributable to depletion of the antioxidant additives in the product.

# Tests for Identifying Lubricant Degradation Modes

## Contamination

- FTIR Analysis – FTIR analysis can identify the presence of some foreign materials in a lubricant. Water and glycol coolants have unique FTIR signatures. Contamination with a product containing a different base fluid type can be identified. Even soot can be identified by FTIR.
  - Elemental Analysis (ASTM D4951) – Elemental analysis can detect environmental contaminants, additive elements that are foreign to the product formulation, and wear metals.
  - Viscosity (ASTM D445) – Contamination of compressor lubricants with the gas being compressed can cause a decrease in the viscosity of the lubricant. Contamination of engine oil with fuel can also cause a viscosity decrease.
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# Mitigating Lubricant Degradation



## Mitigating Lubricant Degradation

### **Oxidation**

- Control lubricant temperature – adding a heat exchanger to reduce the product bulk temperature will reduce the rate of oxidation and extend service life
- Reduce oxygen/air exposure – repair air leaks that introduce air into the oil

### **Thermal Degradation**

- Reduce lubricant temperature – keeping the bulk oil temperature below 200°C (~400°F) can reduce the rate of thermal degradation

### **Microdieseling (Cavitation)**

- Eliminate air introduction – repairing air leaks on the suction side of pumps can stop cavitation from occurring
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## Mitigating Lubricant Degradation

### Additive Depletion

- Monitor additive concentration using in-service oil analysis
- Change oil when additives become depleted

### Contamination

- Install a desiccant filter breather on an oil reservoir to prevent ingress of moisture and environmental contaminants
  - Maintain engines to prevent the ingress of fuel or coolant into engine oil
  - Make certain the correct lubricant is added the equipment
  - Use the correct product to reduce wear of equipment components
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## Questions

- Please post your questions using the Q&A function.
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## **Future Webinars**

February 18, 2022

Grease Reimage

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