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Mechanisms of Varnish Formation and Implications for the Use of Varnish-Removal Technology

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Who We Are

EPT: Specialize in resin-based lubricant treatments.

- 20 years experience.
- 1,000 installations.

- Extensive R&D:
    - Advancing the science of lubrication.

Varnish Intro

- "A thin, hard, lustrous, oil-insoluble deposit, composed primarily of organic residue."

- Oil breakdown product.
  - Deposits on surfaces.

- Leads to equipment reliability problems.

- Oil Analysis:
  - Fluid's potential to form varnish assessed by MPC.
  - Quantifies organic residue left on filter patch.

- Formed by thermal/oxidative breakdown of lubricant.

  - ***Free radical*** process.

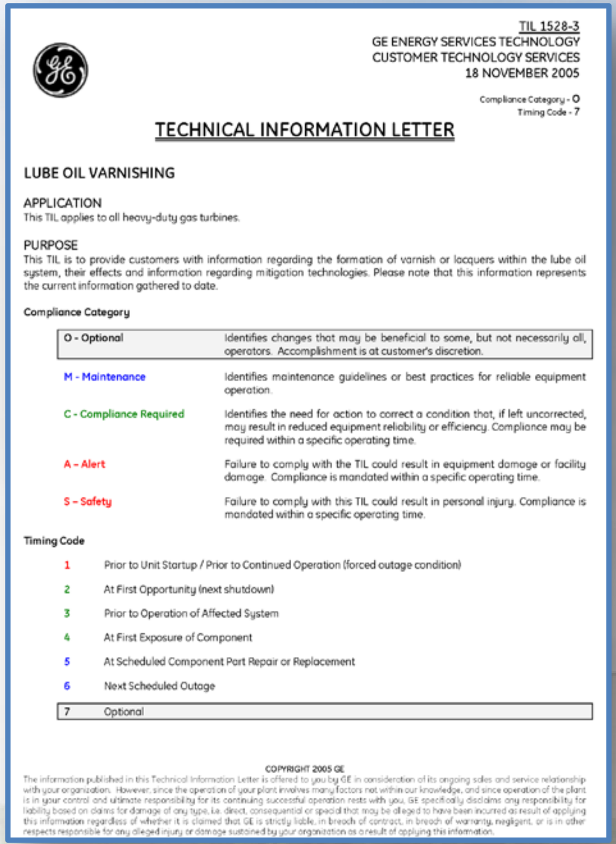
Varnish Problems

Systems affected:

- Turbines
- Compressors
- Molding machines

GE Technical Information Letter:

- *“All (GT) users are expected to have varnish-related problems over time.”*



TIL 1528-3
GE ENERGY SERVICES TECHNOLOGY
CUSTOMER TECHNOLOGY SERVICES
18 NOVEMBER 2005

Compliance Category - O
Timing Code - 7

TECHNICAL INFORMATION LETTER

LUBE OIL VARNISHING

APPLICATION
This TIL applies to all heavy-duty gas turbines.

PURPOSE
This TIL is to provide customers with information regarding the formation of varnish or lacquers within the lube oil system, their effects and information regarding mitigation technologies. Please note that this information represents the current information gathered to date.

Compliance Category

O - Optional	Identifies changes that may be beneficial to some, but not necessarily all, operators. Accomplishment is at customer's discretion.
M - Maintenance	Identifies maintenance guidelines or best practices for reliable equipment operation.
C - Compliance Required	Identifies the need for action to correct a condition that, if left uncorrected, may result in reduced equipment reliability or efficiency. Compliance may be required within a specific operating time.
A - Alert	Failure to comply with the TIL could result in equipment damage or facility damage. Compliance is mandated within a specific operating time.
S - Safety	Failure to comply with this TIL could result in personal injury. Compliance is mandated within a specific operating time.

Timing Code

1	Prior to Unit Startup / Prior to Continued Operation (forced outage condition)
2	At First Opportunity (next shutdown)
3	Prior to Operation of Affected System
4	At First Exposure of Component
5	At Scheduled Component Part Repair or Replacement
6	Next Scheduled Outage
7	Optional

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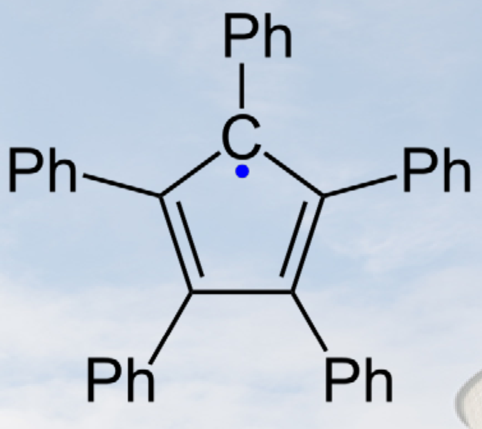
Varnish and Radicals

Thermo-oxidative oil degradation is a radical process:

- Radicals: species with unpaired electron (·).
  - Highly reactive.
- Oil radicals propagate to form polar oxidized compounds.
  - *Varnish precursors*.
- Previous studies:
  - Focus on final varnish deposits.
- This study:
  - Focus on radical intermediates.
  - Measure radicals during oil breakdown.



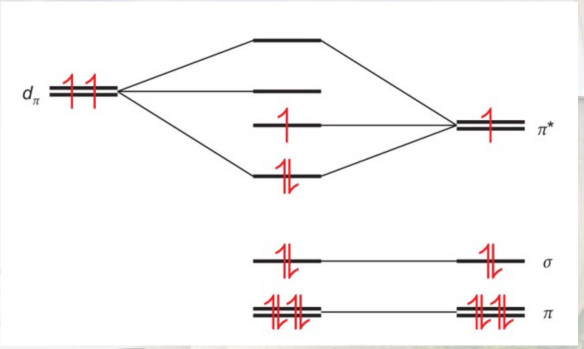


Image Source: Wikimedia, Nature Chemistry

Textbook Oil Oxidation

Textbook mechanism of hydrocarbon oxidation:

- INITIATION – A radical is formed:

  C-H + ·O_2 → C· + H-O_2

- PROPAGATION – One reactive radical becomes many:

  C· + O_2 → C-O-O·

  C-O-O· + C-H → C-O-O-H + C·

  C-O-O-H → C-O· + ·O-H

  Net Reaction: C-H + O_2 → C-O· + ·O-H

  Net Result: 1 radical begets 2 radicals which react with C-H to beget more radicals.

- TERMINATION – Non-radical breakdown products are formed:

  C-O-O-H → O=C-O-H

  C· + ·C → C-C

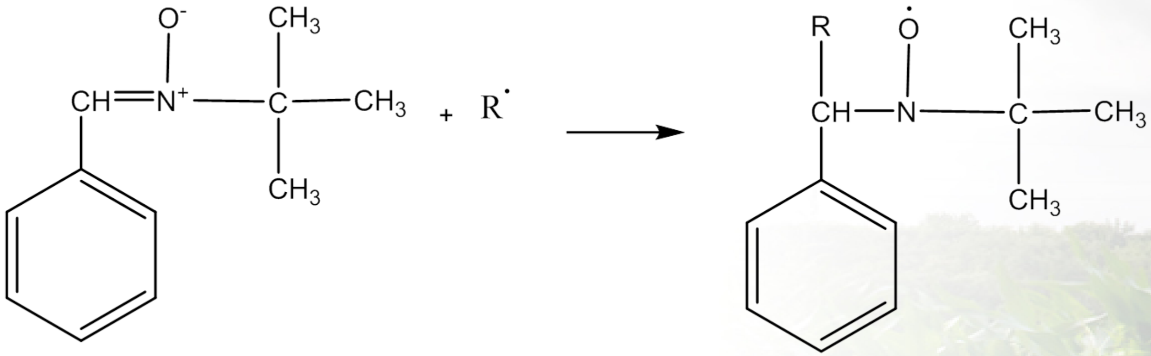
Source: "Chemistry and Technology of Lubricants", 2010.

Radical Detection

- Electron paramagnetic resonance (EPR).
- Reactive radicals short-lived.
  - 1/1,000,000 of a second.
- Short lifetime makes detection difficult.

- Radical traps:
  - React with short-lived radicals.
  - Form stable (long lived) radical adducts.

  - Common radical trap: α-phenyl N-*tert*-butyl nitrone (PBN).

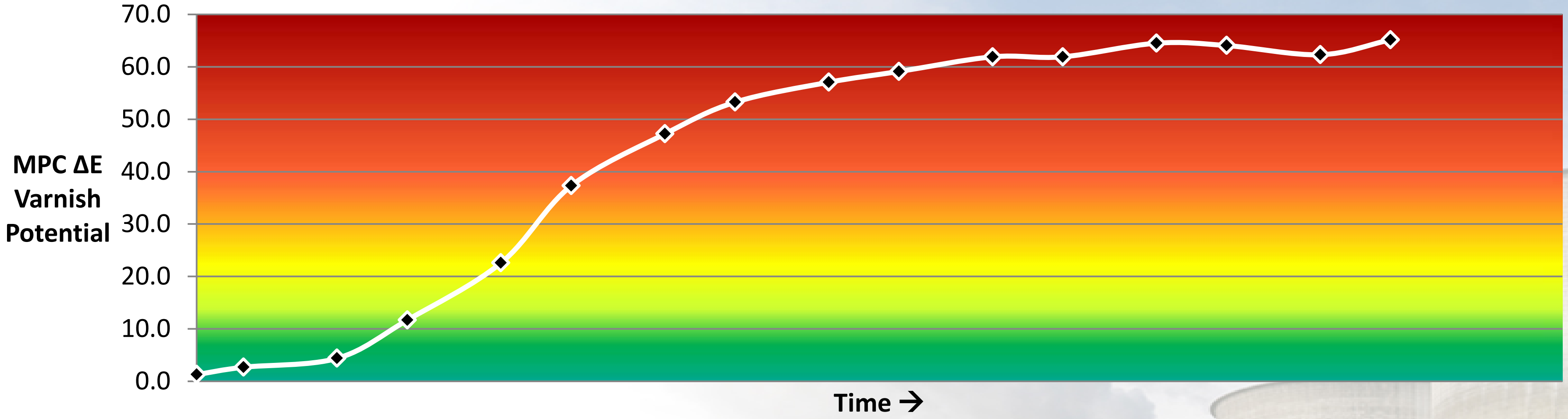


Source: J. Optoelectron. Adv. Mater. 2007, 9, 1010–1013; Bruker.

Oil Breakdown

Lab-Scale Oxidative Degradation of Mineral Oil:

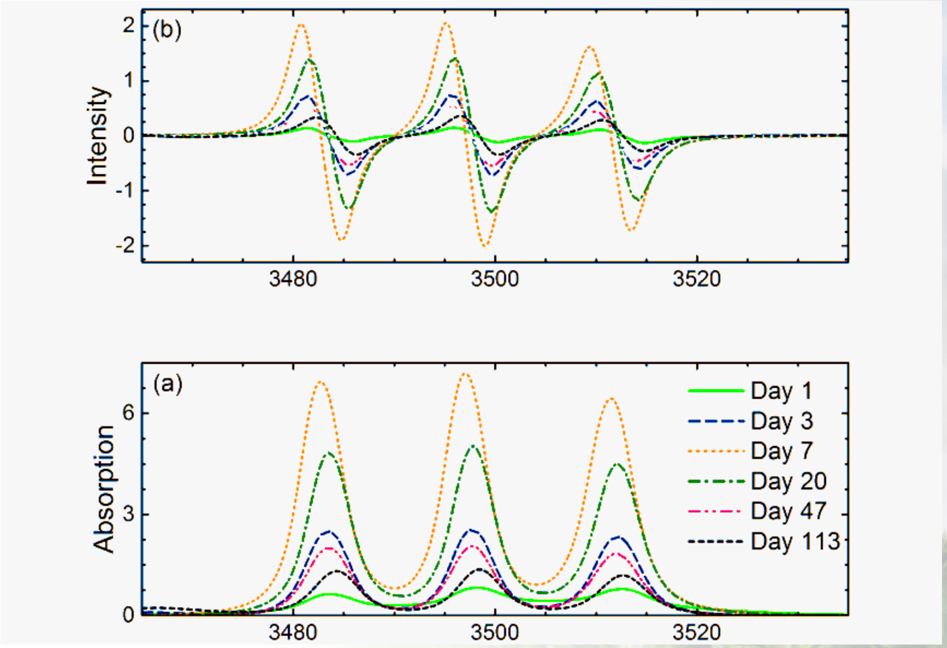
- Monitor patch color (MPC) to assess varnish potential.



Radicals Produced by Oil Breakdown

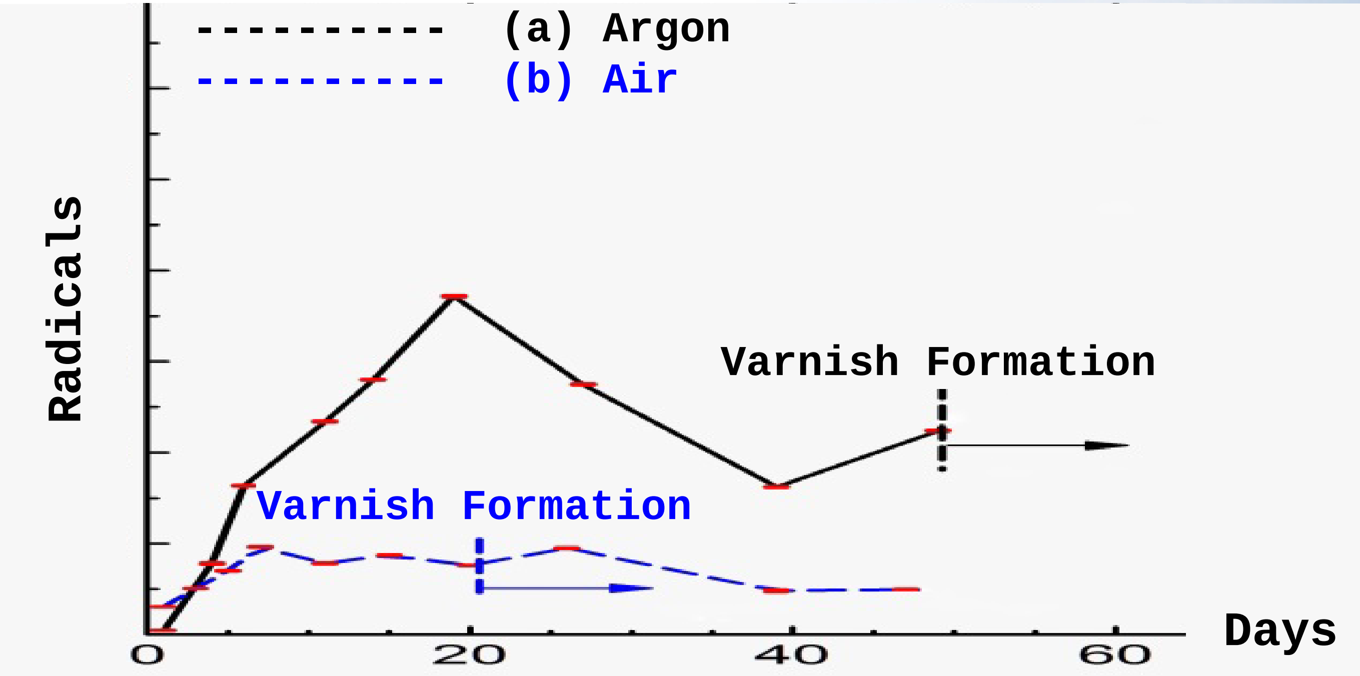
Repeat and monitor radical intermediates by EPR:

- Non-additized Group II base oil with PBN trap subjected to 95°C under:
  - Air atmosphere.
  - Argon atmosphere.
- EPR spectra integrated at regular intervals to quantify radical levels.



Unexpected Results

- Radical levels as a function of time during degradation:



- Unexpected:
  1. Radicals form in absence of O_2.
  2. Higher radical levels observed in absence of O_2.
  3. Varnish (eventually) formed in absence of O_2.

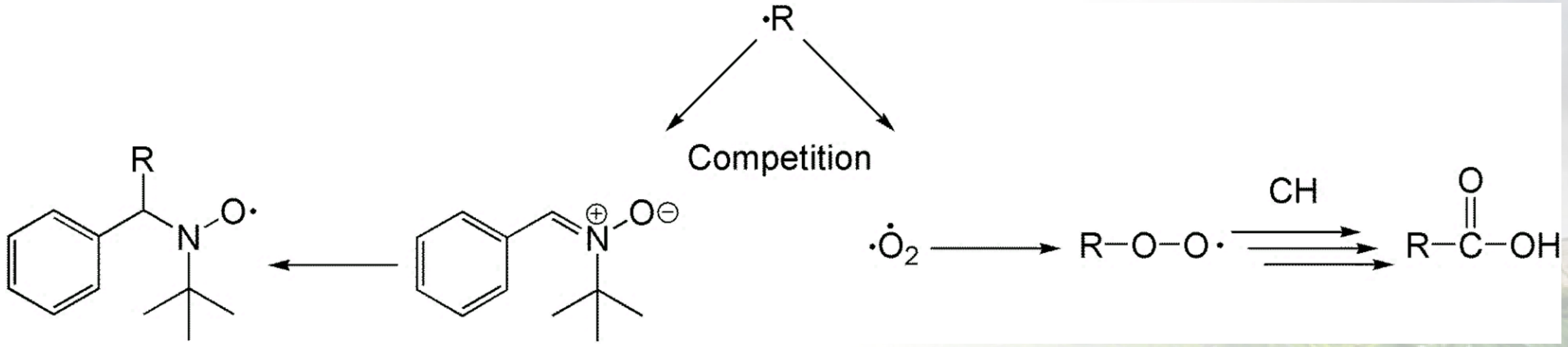
Rethinking Oil Oxidation

1. Radicals form without O_2:
   - Inconsistent with O_2 initiation.
   - Alternative process responsible for initiation.

     $\cancel{R_3C\text{-}H + O_2 \rightarrow R_3C\cdot + \cdot O\text{-}O\text{-}H}$ C-C → C· + C· and/or C-H → C· + H·

     ~~O_2 Initiation~~ Homolytic Cleavage

2. Higher radical levels without O_2:
   - O_2 can trap oil radicals.
   - O_2 competes with PBN to trap radicals.
     - Competition produces non-radical oxidation products.



Rethinking Oil Oxidation

- INITIATION: *radicals form with/without O_2.*

With O_2:
C-C → C· + C·
C-H → C· + H·
C-H + O_2 → C· + H-O_2

Without O_2:
C-C → C· + C·
C-H → C· + H·

- PROPAGATION: *Net radical increase with O_2.*
  No net change without O_2.

With O_2:
C· + O_2 → C-O-O·
C-O-O· + C-H → C-O-O-H + C·
C-O-O-H → C-O· + ·O-H

Without O_2:
C· + C-H → C-H + C·
H· + C-H → H-H + C·

- TERMINATION: *Polar oxidation products form with O_2.*
  - *Without O_2, non-polar hydrocarbons form.*

With O_2:
C-O· + ·O-H → C-O-O-H → O=C-O-H

Without O_2:
C· + ·C → C-C
H· + ·C → C-H

Varnish Without Oxygen?

3. Why did varnish form under argon in our experiment?
    - PBN to blame?
    - PBN and its radical adducts are polar.
    - Without PBN:
        - With O_2 varnish still produced.
        - Without O_2 varnish *NO longer produced*.

- Varnish does not form in the absence of polar species.

Varnish Mitigation

Conclusions from radical breakdown experiments:

- Oxygen is not required to initiate oil breakdown.
- When present, oxygen traps radicals leading to polar varnish precursors.
- Varnish does not form in the absence of polar species.

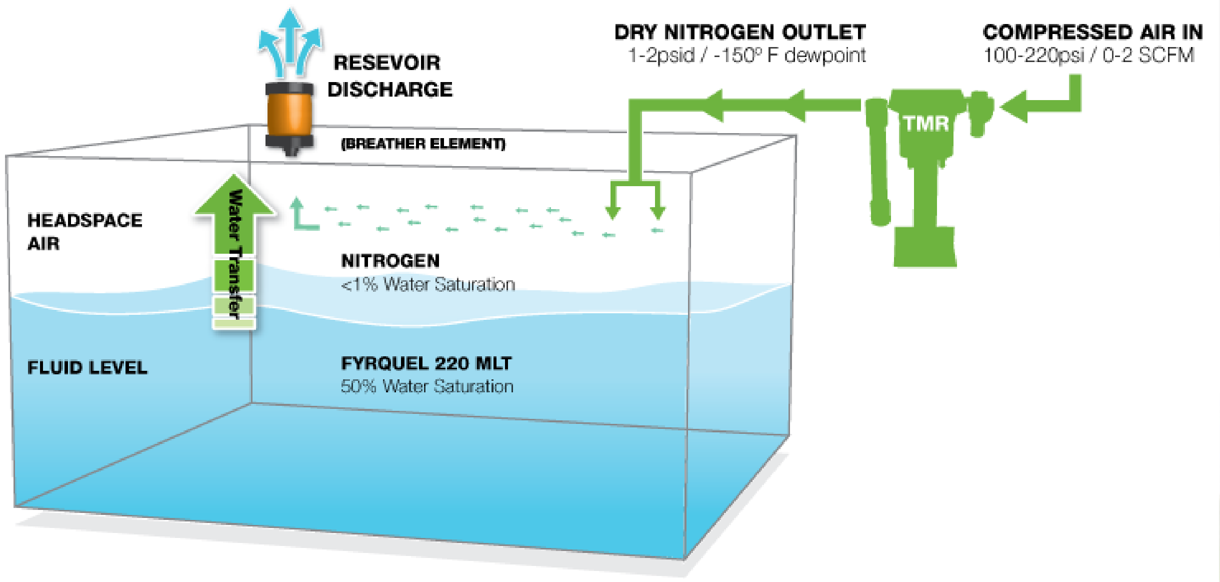
- Prevent varnish by:

1. Preventing formation of polar species.
2. Removing polar species as they form.

1) Prevent Oxidation

Limit formation of polar breakdown products.

- Limit fluid's contact with O_2.
  - Prevents O_2 from trapping radicals.
  - N_2 blanket over fluid reservoirs.
  - Dry N_2 also removes H_2O from oil.



Dry N_2 Blanketing

2) Remove Polar Species

If polar products do form, remove them.

- Use resin-based technology.
  - Removes polar breakdown products.
  - Varnish does not form in absence of polar products.

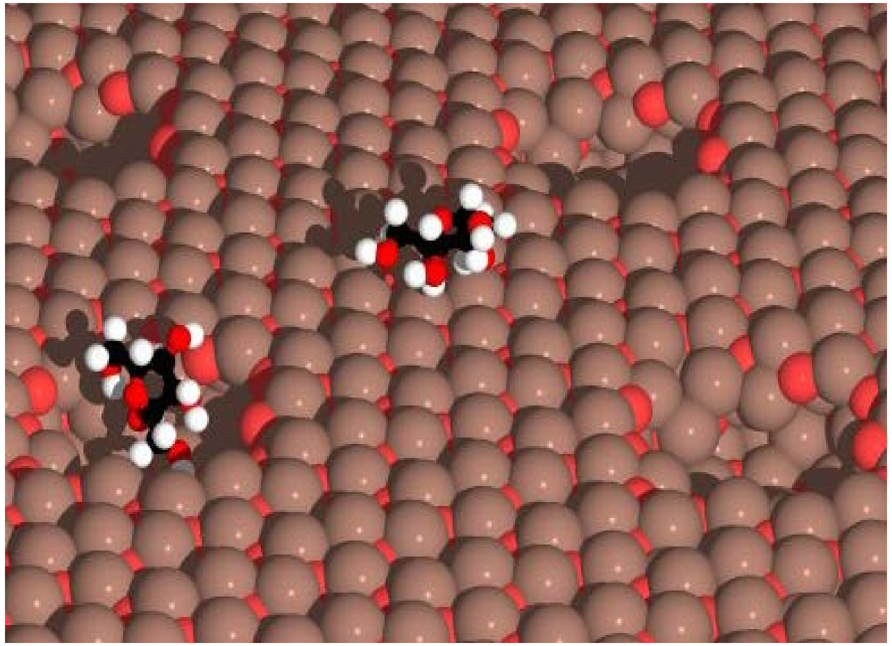
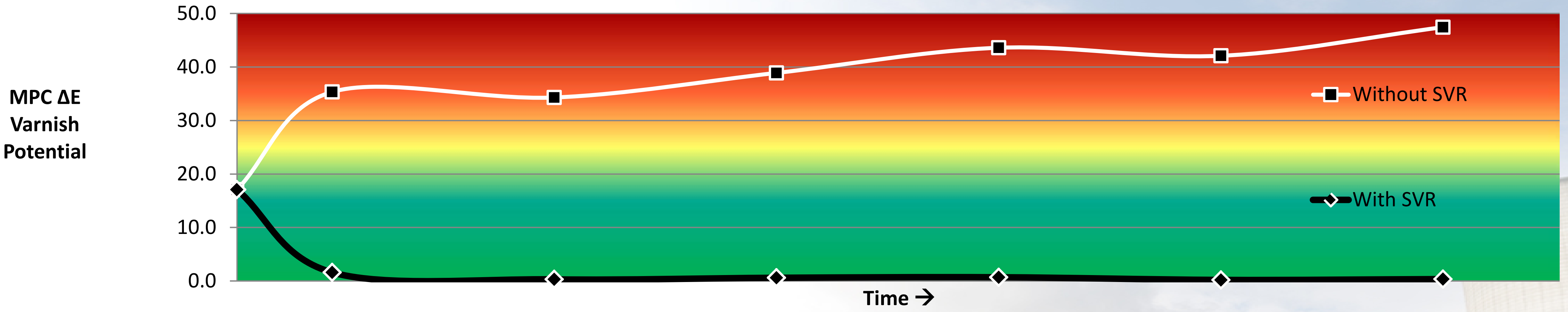


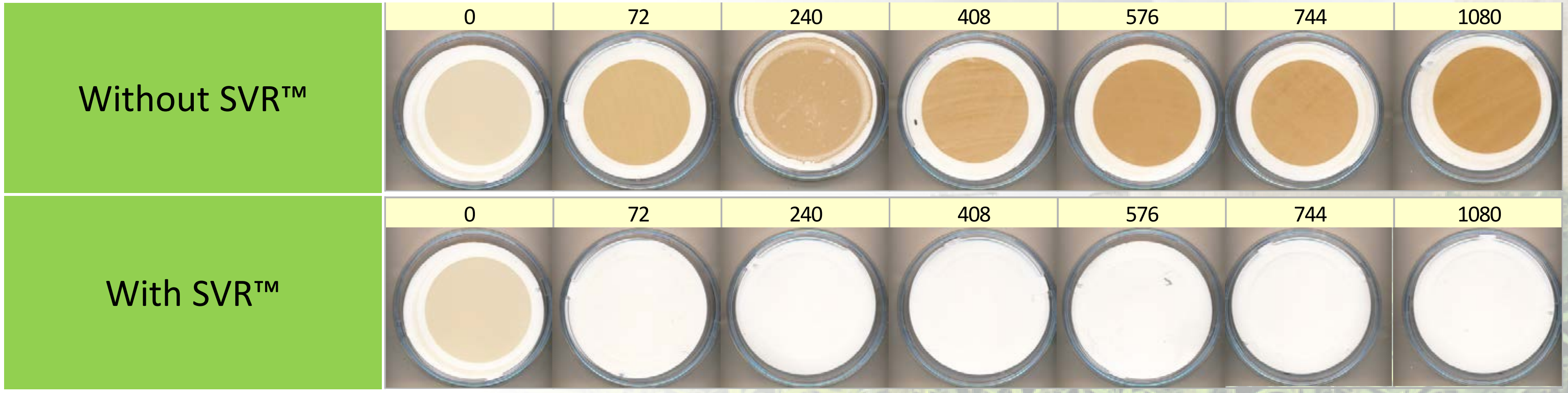
Image Source: Argonne National Laboratory

SVR (Soluble Varnish Removal) Skid

Resin-Based Varnish-Removal

Oil degradations: with & without resin to remove polar breakdown products.





Summary

- Thermo-oxidative lubricant breakdown leads to varnish formation.
  - Radical process.

- EPR study of radical intermediates involved in oxidation revealed:
  - Initiation of breakdown does not require O_2 as previously thought.
    - Oil hydrocarbons form radicals on their own.
  - Role of O_2: trap which promotes radical propagation.
    - Results in O_2 incorporation to form polar breakdown products.
  - Polar products result in varnish formation.

- 2 Strategies to mitigate the risk of lubricant varnishing:
  1. Don't allow polar breakdown products to form:
     - Limit lubricant exposure to O_2 using inert N_2 blanket.
  2. Remove any polar breakdown products which do form:
     - Use resin to remove soluble polar species before they can form varnish.
     - Improve lubricant condition and maintain it even under degrading conditions.

Thank you!