STATUS REPORT

THE DEVELOPMENT OF RAPID AGING AND POISONING PROTOCOLS FOR DIESEL AFTERTREATMENT DEVICES

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Rapid Aging and Poisoning Protocols

- An accelerated test protocol which simulates longer mileage field-service for evaluating durability and understanding mechanisms of deterioration.

- Benefits include:
  - More understanding of processes and mechanisms
  - More rapid product development
  - Verification of application early in life cycle
  - Testing for uncommon situations
  - Research basis for new materials or applications
Development of Rapid Protocols

- **ACCELERATED ENGINE OR BENCH PROTOCOL**
  - Compare performance changes
  - Compare material changes
  - Evaluate application and develop protocol
  - High mileage or engine bench aged catalysts
  - Extensive material characterization

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Current Research Focuses

• Current research was developed through extensive discussion with engine, auto and catalyst companies.
  – Diesel oxidation catalysts - Phosphorous poisoning
  – Lean NOx traps - High temperature lean-rich thermal aging
  – Diesel particulate filters - Ash effects on performance
  – Selective catalytic reduction catalysts - Aging and poisoning of combined DPF-SCR

• Catalysts from Engelhard and Delphi
• Substrates from NGK and Dow

• This research is supported by DOE OFCVT Fuels Technology Program and our program managers are Kevin Stork, Dennis Smith, and Steve Goguen

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Catalyst and DPF Holder Assemblies

CATALYST CAN

CATALYST BRICK

DPF CAN

DPF BRICK

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Engine Bench Setup

- Syringe Pump
- Drive Motor
- DOC
- Exhaust Sampling
- Exhaust HC Injection
- Hatz Engine
- Throttle Controller
# Summary of DOC Poisoning Effects

<table>
<thead>
<tr>
<th>Deactivation Method</th>
<th>Methodology</th>
<th>Field-Service Equivalence</th>
<th>Performance Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus/Sulfur Adsorption (Cerium and Aluminum Phosphates)</td>
<td>Injecting into Intake Manifold</td>
<td>Normal Bus Operation</td>
<td>Hydrocarbon Oxidation</td>
</tr>
<tr>
<td>Dense Soot Overlayer</td>
<td>Mixing Lube-Oil with Fuel</td>
<td>Excessive Lube-Oil Consumption</td>
<td>Carbon Monoxide and Hydrocarbon Oxidation</td>
</tr>
<tr>
<td>Zinc Phosphate Glaze</td>
<td>Injecting into Exhaust Manifold</td>
<td>Not Observed (Poor Oil Control?)</td>
<td>Carbon Monoxide Oxidation</td>
</tr>
</tbody>
</table>
Phosphorus Exhaust Chemistry

- Zinc sulfate
- Phosphoric acid

Electrospray MS Intake manifold injection poisoning

• Representative of fuel and intake manifold injection poisoning
  • Phosphoric acid (H₃PO₄)
  • Zinc sulfate (ZnSO₄)
UT Bench-Flow Reactor for LNT Aging

GAS MIXTURES USED FOR LNT AGING

<table>
<thead>
<tr>
<th>CONDITION</th>
<th>TIME, sec.</th>
<th>O₂, %</th>
<th>CO₂, %</th>
<th>H₂O, %</th>
<th>NO, ppm</th>
<th>CO, %</th>
<th>H₂, %</th>
<th>N₂, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>EVALUATION LEAN</td>
<td>20</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>1000</td>
<td>0</td>
<td>0</td>
<td>bal</td>
</tr>
<tr>
<td>EVALUATION RICH</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>1.3</td>
<td>bal</td>
</tr>
<tr>
<td>AGING LEAN, 800°C*</td>
<td>158*</td>
<td>0</td>
<td>5</td>
<td>10</td>
<td>1000</td>
<td>0</td>
<td>0</td>
<td>bal</td>
</tr>
<tr>
<td>AGING RICH, 800°C*</td>
<td>22*</td>
<td>3*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>6*</td>
<td>2*</td>
<td>bal</td>
</tr>
</tbody>
</table>

* TIMES AND CONCENTRATIONS VARY SLIGHTLY WITH TARGET AGING TEMPERATURE

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Deterioration of Hi-Temp LNTs as Function of Temperature and Number of Aging Cycles

% NOx REDUCTION

NUMBER OF AGING CYCLES

T=704°C
T=825°C
T=953°C
T=1058°C

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Mechanisms of Deterioration for Hi-Temp LNTs

AGING TEMPERATURE, C

EVALUATION TEMPERATURE

AGING TEMPERATURES

400 500 600 700 800 900 1000

BARIUM TRANSFORMATION
BARIUM AGGLOMERATION
POTASSIUM MIGRATION AND LOSS
PLATINUM SINTERING

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LNT Material Changes

PARTICLE SIZE DISTRIBUTION OBTAINED FROM TEM

POTASSIUM MIGRATION TO INTERFACE

BARIUM AGGLOMERATION

TRANSFORMATION OF BaCO₃ (TO BaAl₂O₄)

BARIUM AGGLOMERATION TRANSFORMATION OF BaCO₃

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Temperature Profile During LNT Thermal Aging

Maximum temperatures in LNT vary axially during thermal aging.

Aging time and temperature are needed to extract deactivation kinetics.

Temperature varies during aging cycling.
Future Plan for LNT Aging

• Continue aging and characterization
  – Barium / Potassium (high-temperature LNTs)
  – Barium (low-temperature LNTs)
• Extract rates for aging mechanisms
  – Performance loss (global deactivation)
  – PGM sintering and NOx storage media agglomeration/loss
  – Applicable temperature ranges
• Model deactivation with simple kinetics
DPF Plan and Progress

- **Plan**
  - Study confounding issues of phosphorous, ash, and soot
  - Evaluate performance and microstructure analysis

- **Progress**
  - Received samples
  - Performed first tests
  - Blended lube oil into fuel to increase ash loading rate
  - Performed light-off and forced regeneration

- **See DEER poster for more information:**
  - B.G. Bunting and C.G. Li, “The Development of a Small Engine-Based Accelerated Ash Loading Protocol and Application to a New Substrate Material”, DEER 2006, Tuesday, 9/22/06
SCR Aging and Poisoning

- Research just starting
- Inputs from industry gathered so far
  - Focus on zeolite-based SCR
  - Topics of concern
    - Aging of SCR during active DPF regeneration
    - Phosphorous poisoning of SCR catalyst
SCR Aging and Poisoning Concept

- Engine Exhaust
- Fuel Injection
- NH₃ or Urea Injection
- DOC+DPF
- SCR
- Lube Oil and ZDDP
- High Temperature Aging
- Accelerated Poisoning
- NOx Reduction Performance

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Conclusions

• Rapid aging and poisoning protocols require three tasks
  – Develop rapid cycle based on application
  – Compare performance changes to field-aged catalysts
  – Compare material changes to field-aged catalysts

• Rapid aging and poisoning protocols provide an understanding of the processes taking place
  – Extensive materials characterization
  – Kinetic modeling of deactivation mechanisms

• General schemes can be applied to other situations

• It is difficult to obtain field-aged catalysts (hint! hint!) 😊
Upcoming References

• DOC poisoning

• General

• LNT aging