Development of Rapid Aging and Poisoning Methods for the Verification of Combustion Engine Aftertreatment Devices

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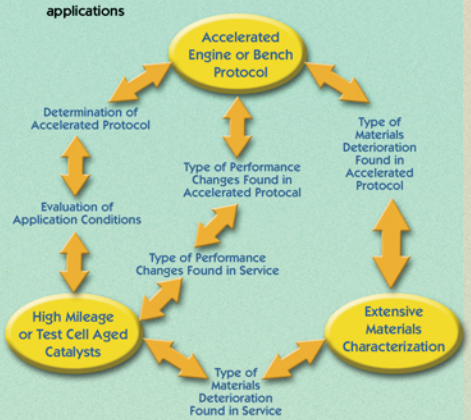
Rapid aging and poisoning protocols

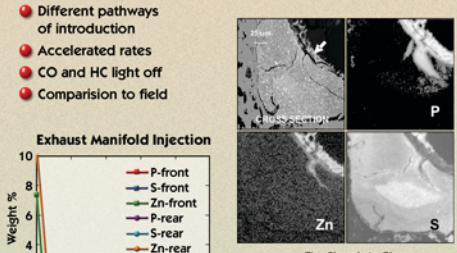
- An accelerated test protocol which simulates longer mileage field service. Benefits include:
  - More complete understanding of processes and mechanisms
  - More rapid product development
  - Verification of application early in life cycle
  - Testing for uncommon situations
  - Research basis for new materials or applications



Diesel Oxidation Catalysts

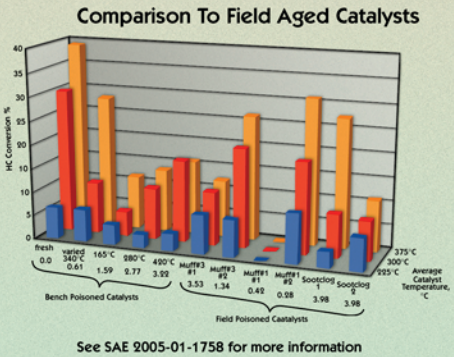
Lab Simulation of aging

- Different pathways of introduction
- Accelerated rates
- CO and HC light off
- Comparision to field



Zinc Phosphate Glaze

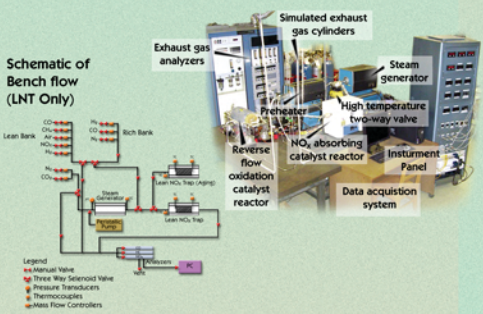
Exhaust manifold introduction of ZDDP



See SAE 2005-01-1758 for more information

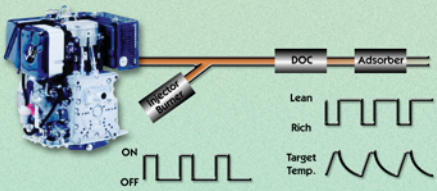
UT Bench Reactor System

– Performance evaluations and aging



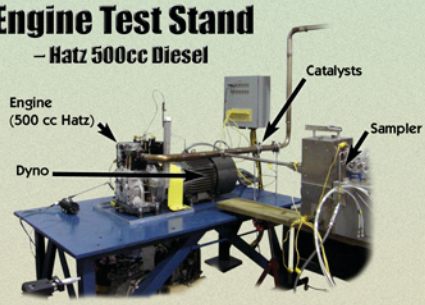
Lean NOx Traps

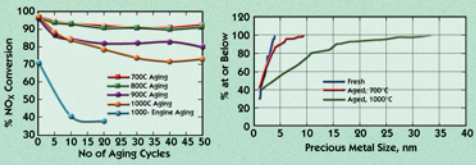
– High-temperature lean/rich thermal aging



Engine Test Stand

– Hatz 500cc Diesel





Catalyst and Holder

– Use small cores cut from larger catalysts

Calyst brick is 2" diameter x 3" length

Diesel Particulate Filters

- Extension of oxidation catalyst work to include effects of ash and soot
- FY 2006

Determining the Combustion Product of Zinc Dialkyldithiophosphate Using Electrospray Mass Spectrometry

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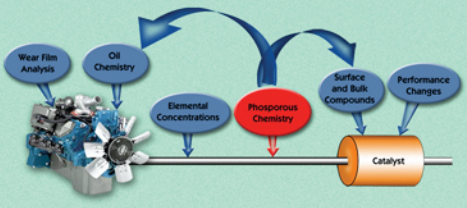
Introduction

Phosphorous in diesel exhaust is derived via the consumption of engine oil containing a phosphorous-based additive, such as zinc dialkyldithiophosphate (ZDDP). These oil additives are introduced for the purpose of engine wear control. Phosphorous present in the engine exhaust can interact with the exhaust emissions catalyst and lead to the loss of performance through masking the catalyst surface or chemical reaction with the catalyst wash coat. To monitor the catalyst poisoning process, lube oil containing ZDDP was added at an accelerated rate through a variety of engine pathways to simulate various types of engine wear or oil disposal processes. In all cases, the phosphorous, detected by negative-ion electrospray mass spectrometer, was found in the exhaust with the form varying according to the method of introduction.

Lube Oil Additive Related Measurements



Can exhaust phosphorous chemistry measurements provide a link between additive chemistry and catalyst reactions?

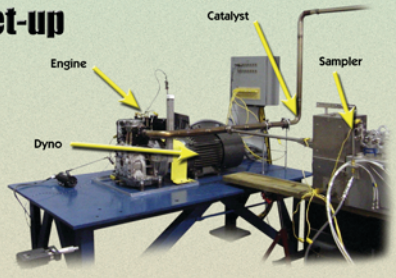
Accelerated Catalyst Poisoning Procedure

- Fully formulated lube oil + additional ZDDP
  - Doped to 0.5 grams phosphorous per 50 cc
  - ≈1% phosphorous vs. ≈0.1% normal
  - ≈10 times normal concentration
- Oil consumption 50 cc/hour
  - Syringe pump + air atomization or dissolved in fuel
  - ≈7% of fuel rate vs. ≈ 0.1% normal
  - ≈70 times normal consumption rate
- Combined rate of poisoning ≈700 times normal field service

Collection and Analysis of Exhaust Samples

- Collection of the diesel exhaust was accomplished by impinging the exhaust into a water solution
- Ammonium hydroxide was added to an aliquot of the solution to yield a final pH of 10.
- Aliquot infused into an electrospray ionization mass spectrometer operated in negative ion mode.
- Data was acquired by scanning the mass spectrometer from 50 to 2000 Daltons and averaging 1000 scans to generate the final spectrum.

Experimental Set-up



Discussion

During the catalyst poisoning phase of an engine-test procedure for each lube oil introduction method, exhaust impinger samples were collected and analyzed by electrospray mass spectrometry. Electrospray ionization mass spectrometry parameters were optimized through analysis of

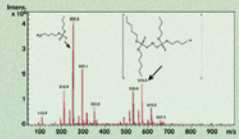
- Oil standards
- Oil and ZDDP mixtures
- Phosphoric acid
- Zinc sulfate
- P_2O_5

Three introduction points were evaluated: exhaust manifold, intake manifold, and diesel fuel. From these data, we concluded that P_2O_5 did not form at any of the three introduction points.

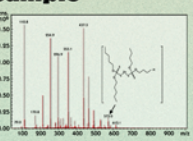
When ZDDP was introduced at the exhaust manifold, the original compound was found in the exhaust. When ZDDP was introduced into either the intake manifold or the diesel fuel, phosphoric acid and zinc sulfate formed in the exhaust. From these data, we demonstrated that the introduction point of ZDDP influenced the chemical state of the emitted phosphorous at the exhaust emission point. Microscopy of the catalyst surface indicated that ZDDP introduced into the exhaust manifold formed a zinc phosphate glaze on the surface. The two other introduction methods showed phosphate in the catalyst wash coat with no zinc present.

In summary, electrospray ionization mass spectrometry in negative ion mode was successfully used to map the combustion products of ZDDP from various introduction points within a diesel engine.

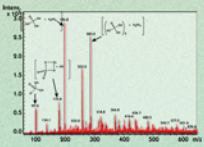
ZDDP Standard



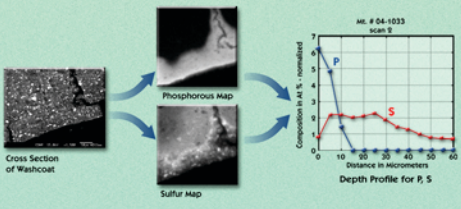
Exhaust Manifold Sample



Low Temperature Intake Manifold Sample



Phosphorous and Sulfur in Washcoat of Poisoned Catalyst – intake manifold introduction



Conclusion

- ZDDP molecules do not decompose when introduced into the exhaust stream.
- ZDDP forms phosphoric acid and zinc sulfate when injected into the fuel or intake air stream and subjected to combustion processes.
- Phosphorus pentoxide did not form at any of the three introductions points.
- Microscopy indicated introduction of ZDDP into the exhaust manifold resulted in a zinc phosphate glaze on the catalyst surface. The two other introduction methods showed phosphate in the catalyst wash coat with no zinc present.

Future Work

- Phosphorous poisoning and phosphorous exhaust chemistry
  - Complete study of three methods of phosphorous introduction
  - Characterize aging rates and aging mechanisms
  - Conduct additional studies with other catalysts or lube oil formulations
  - Compare to field samples