Exhaust Phosphorous Chemistry and Catalyst Poisoning

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Background

- Zinc dialkyldithiophosphate (ZDDP) is added to lube oil for oxidation, corrosion, and wear protection
- Phosphorous content in lube oil is being reduced but not eliminated
- Phosphorous is a well documented catalyst poison
- Most phosphorous is found in front of catalyst and affects light-off
- Various ways have been used to study phosphorous poisoning
  - Long mileage, increased oil consumption, doped fuel, doped lube oil, doped exhaust, direct impregnation
- Phosphorous chemistry is complex and depends on method of introduction and other materials present
  - Surface glazes, fluffy coatings, or bulk washcoat compounds can form

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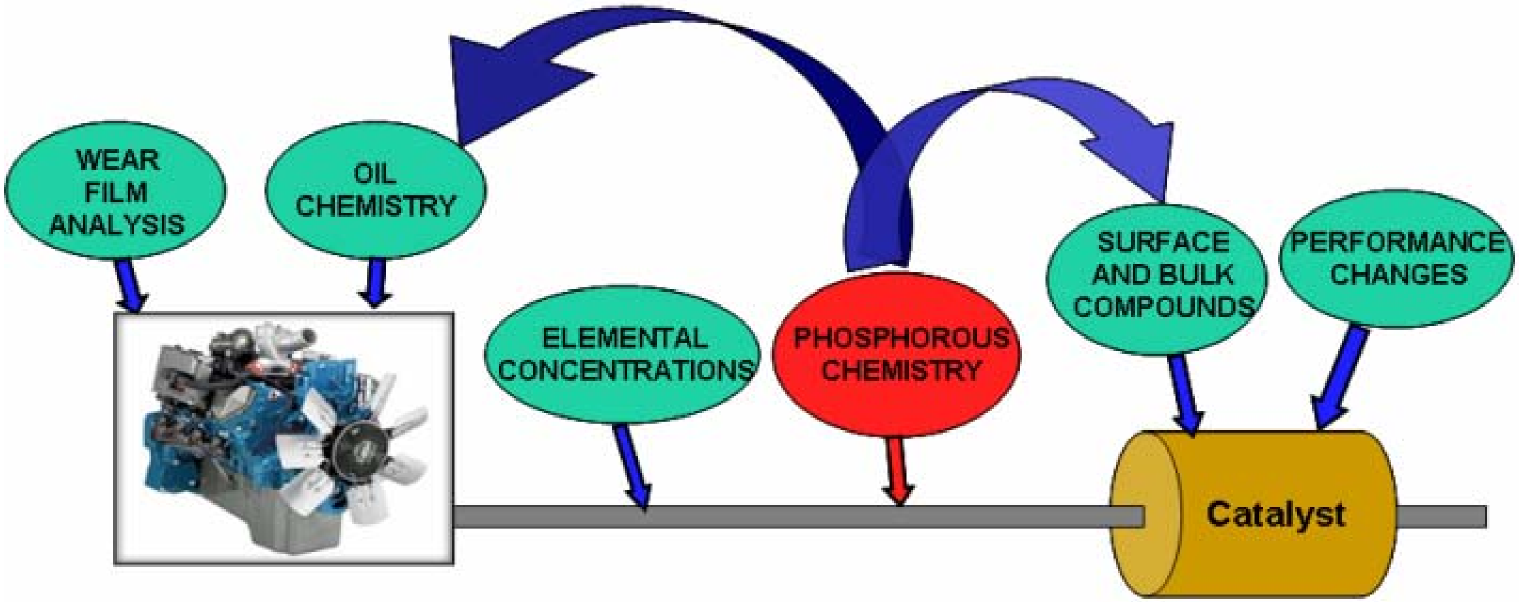
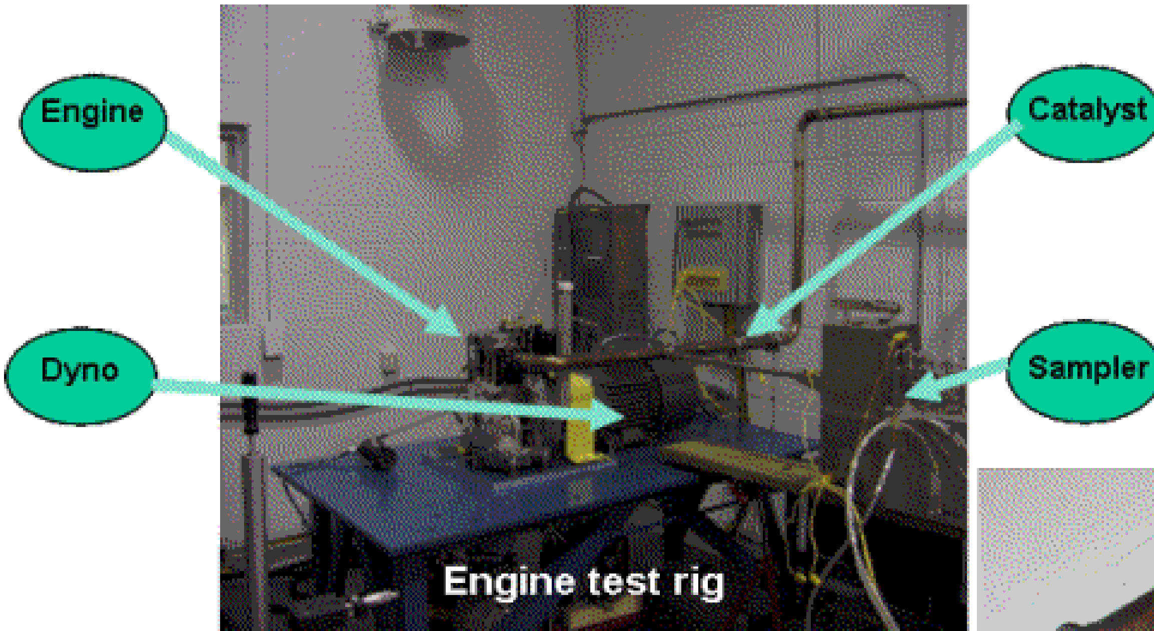
Lube Oil-Related Measurements



Exhaust phosphorous chemistry measurements can provide a link between additive chemistry, engine related effects, and catalyst effects.

Experimental Set-Up



Engine test rig

Catalyst and holder

Materials Used

- Engine
  - Hatz 500 cc single cylinder DI diesel
- Lube oil and ZDDP additives
  - Supplied by Lubrizol
- Fuel
  - DESE fuel, 3 ppm sulfur
- Catalyst substrates
  - Supplied by NGK
    - Cordierite, 200 cpsi, 12 mil, 2” dia x 3” long
- Catalyst washcoating
  - Supplied by Engelhard Corporation
    - Diesel oxidation catalyst (high PM, alumina, ceria)
    - Model catalyst similar to commercial diesel formulations

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Different Pathways Were Used for Introduction of Phosphorous

FORM OF PHOSPHOROUS	LOCATION OF INTRODUCTION	INTRODUCTION MAY REPRESENT
NONE	NONE	BACKGROUND
ZDDP+LUBE OIL	SPRAYED INTO INTAKE MANIFOLD	COMPRESSOR OR VALVE SEAL LEAKS, CLOSED CRANKCASE VENTILATION
ZDDP+LUBE OIL	SPRAYED INTO EXHAUST MANIFOLD	BLOWN TURBO SEAL
ZDDP+LUBE OIL	DISSOLVED IN FUEL	BURNING OF USED LUBE OIL OR RING LEAKS

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An Accelerated Rate of Poisoning Was Used

- Fully formulated HD lube oil + additional ZDDP
  - Doped to 0.5 grams phosphorous per 50 cc
  - ≈ 1% phosphorous vs. ≈ 0.1% normal
  - ≈ 10 times normal concentration
- Oil added at 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

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General Catalyst Test Procedure

- Break in catalyst 4 to 6 hours, variable load cycle
- Two engine light-off tests (2 hours each)
- Poison with 0.5 grams phosphorous equivalent (1 hour)
- Repeat engine light-off test
- Continue poisoning and light-off tests

- Materials and bench performance characterizations on used catalyst
  - SEM, Electron microprobe, XRF, bench performance

- Exhaust impinger sample during poisoning
  - Electrospray mass spectrometry

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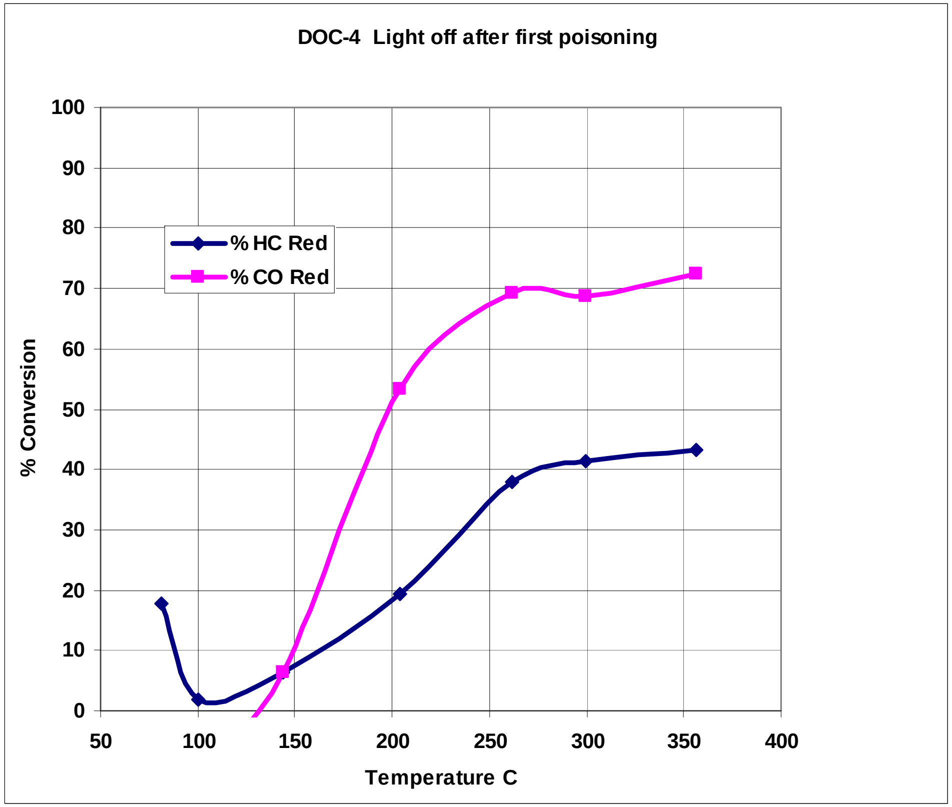
Engine-Based Light-Off Test Procedure

- Temperature increasing
- 7 throttle positions, 0 to full load
- ≈80, 100, 140, 205, 260, 300, 360 deg.C
- Stabilize 15 minutes per position
- Engine out and catalyst out emissions
- Calculate percent reduction for HC and CO
- Find temperatures for 50% CO reduction and 30% HC reduction



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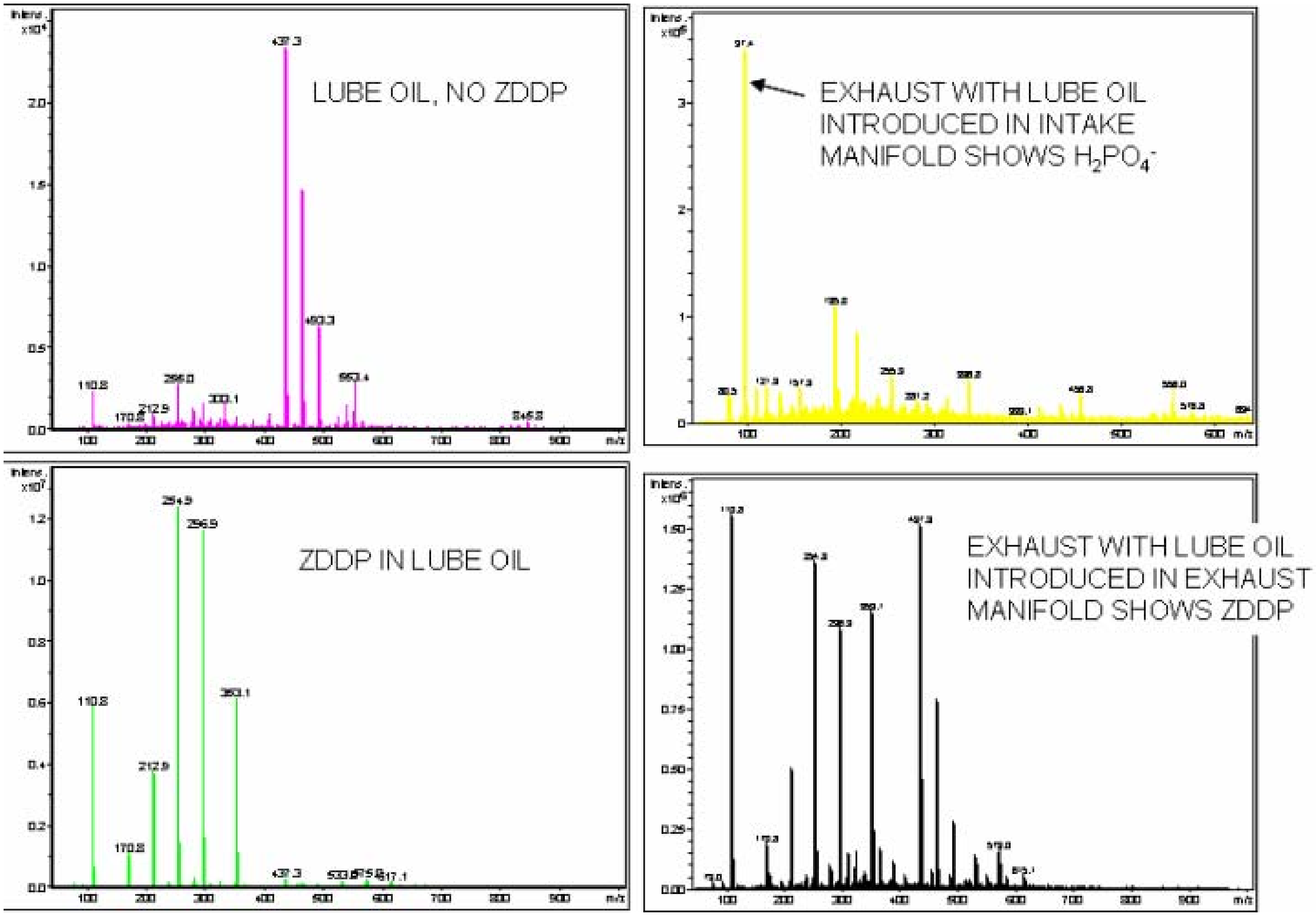
Electrospray Mass Spectroscopy



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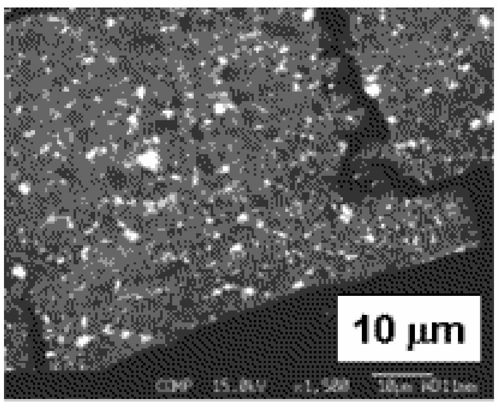
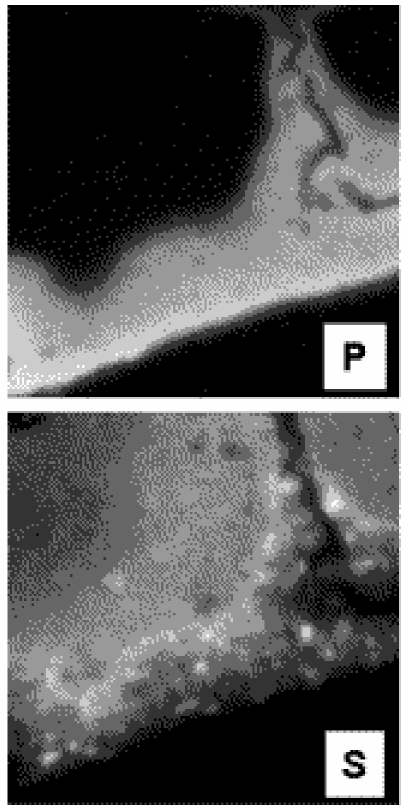
Electrospray Findings

- ZDDP which did not pass through combustion was found in the form of ZDDP or ZDDP fragments in exhaust
- ZDDP which did pass through combustion was found in the form of $H_2PO_4^-$ in exhaust

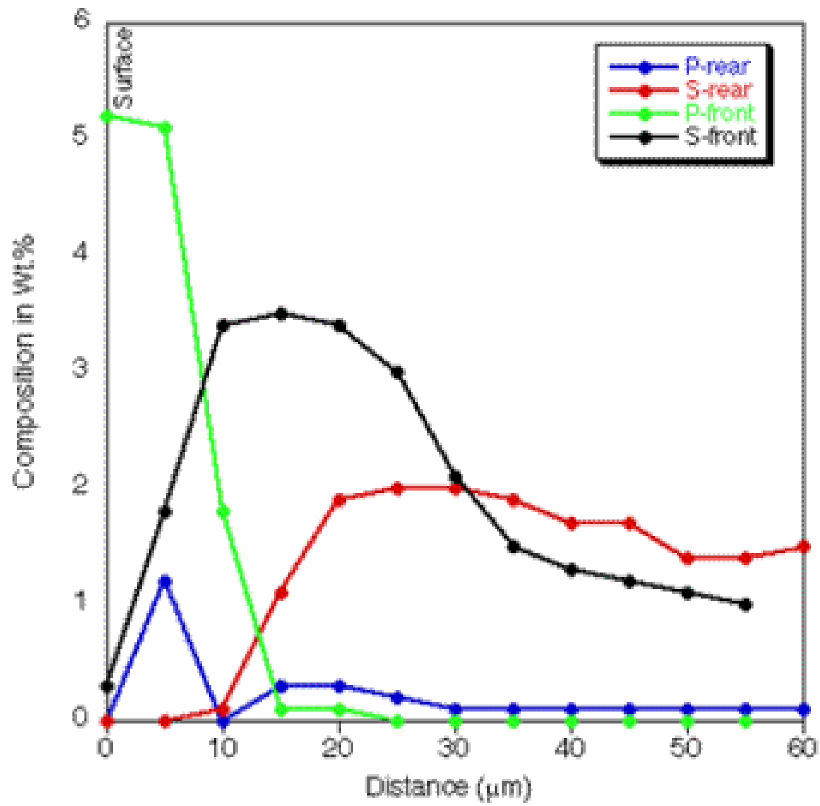
DOC #1, oil and ZDDP injected into intake manifold – phosphorous and sulfur diffused into catalyst surface



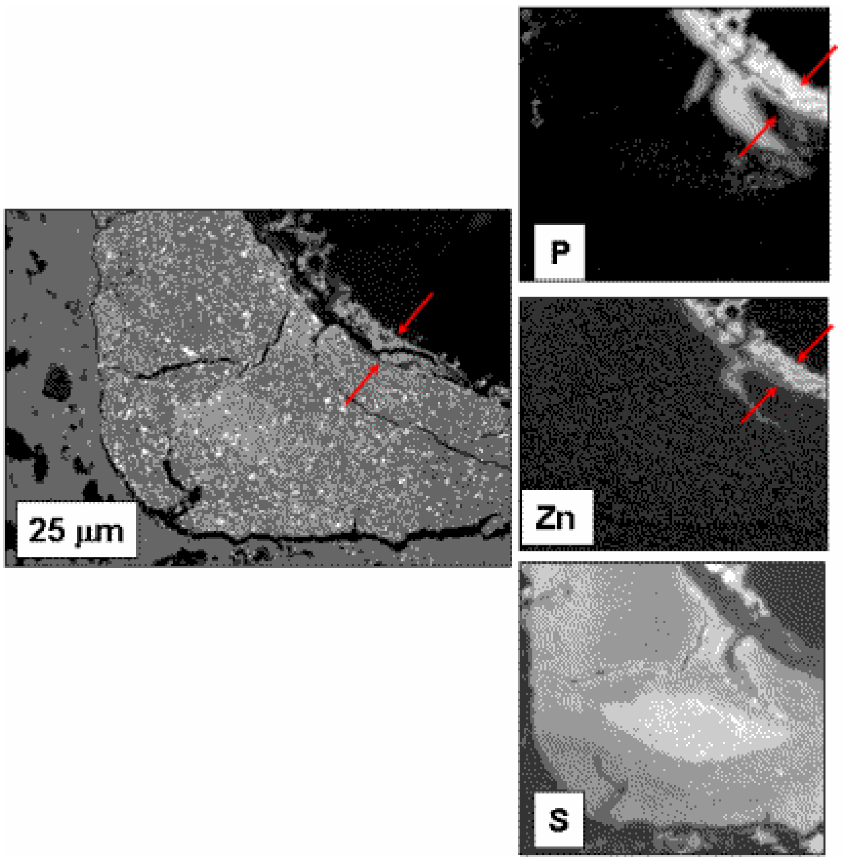
Washcoat cross section

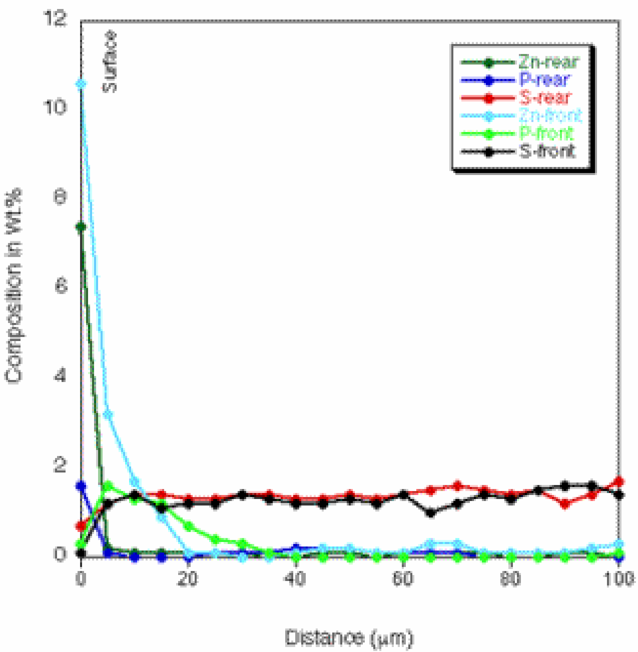


No zinc found



DOC #2, Oil, and ZDDP Injected into Exhaust Manifold – Zinc Phosphate Glaze





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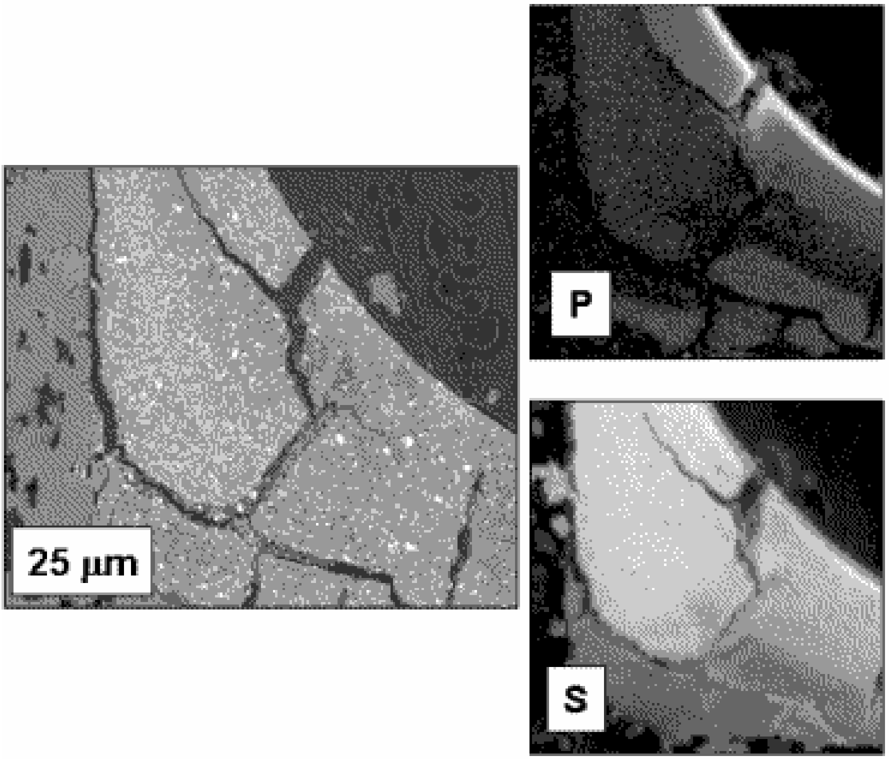
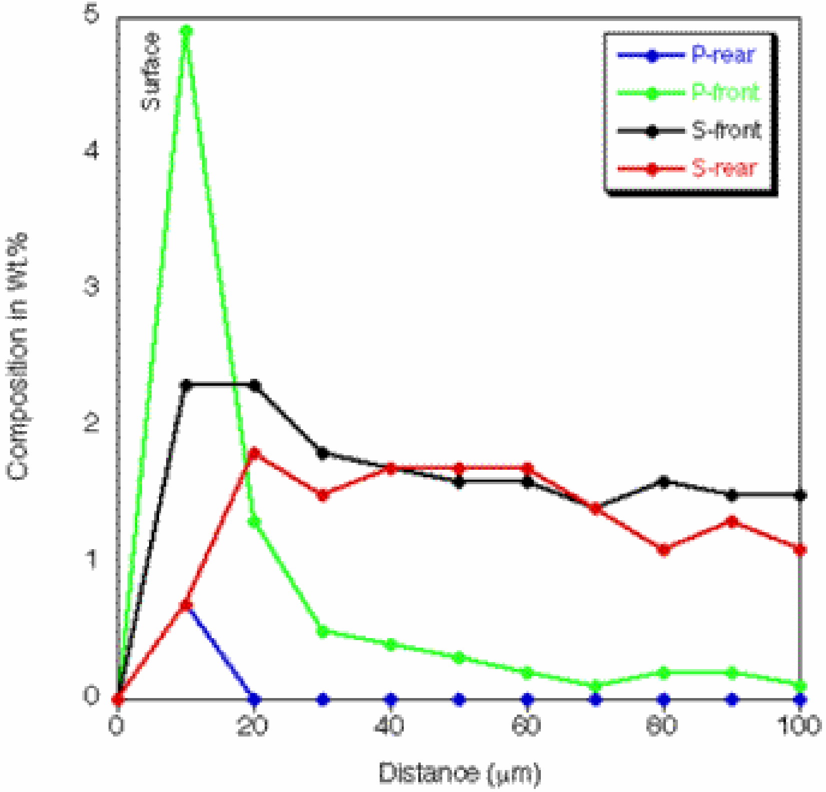
DOC #4, oil and ZDDP dissolved in fuel – phosphorous and sulfur diffused into catalyst surface



No zinc found



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XRF Analysis of Poisoned Catalysts - Phosphorous Uptake Ranged from 11 to 23%

CATALYST	S, wt%	P, wt%	Zn, wt%
NEW	0.00	0.01	0.00
INTAKE MANIFOLD INJECTION	0.79	0.34	0.00
EXHAUST MANIFOLD INJECTION	0.78	0.64	0.22
DISSOLVED IN FUEL	1.22	0.33	0.00
ZDDP DOPED LUBE OIL	2.40	1.12	1.15

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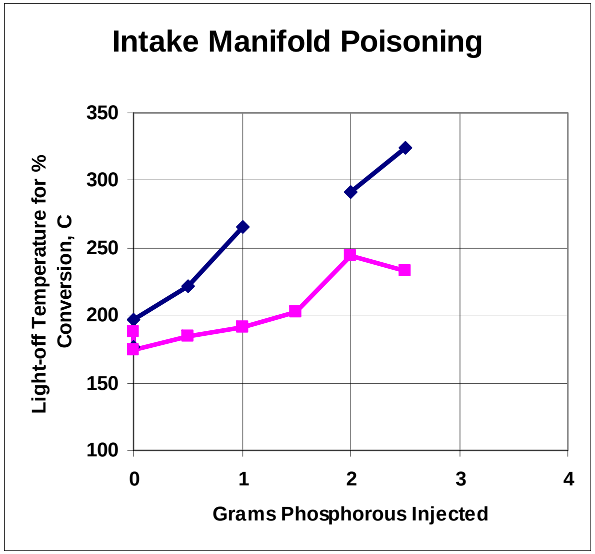
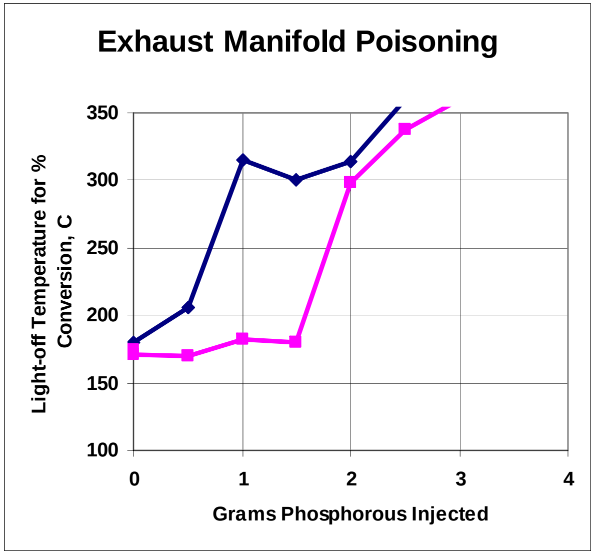
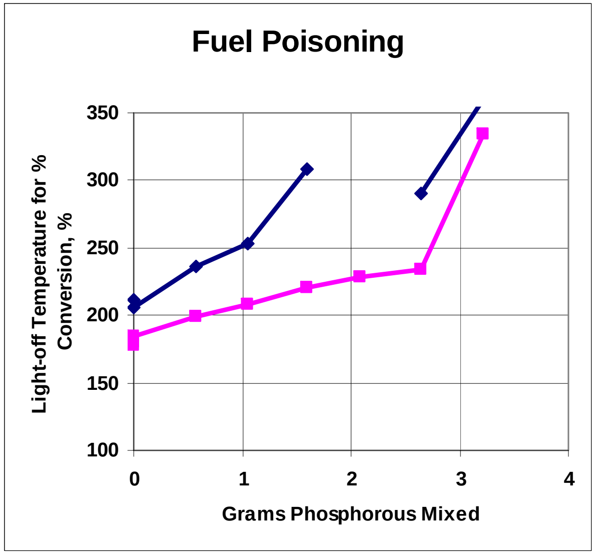
Loss of Light-Off Performance with Phosphorous Injection as Measured on Engine

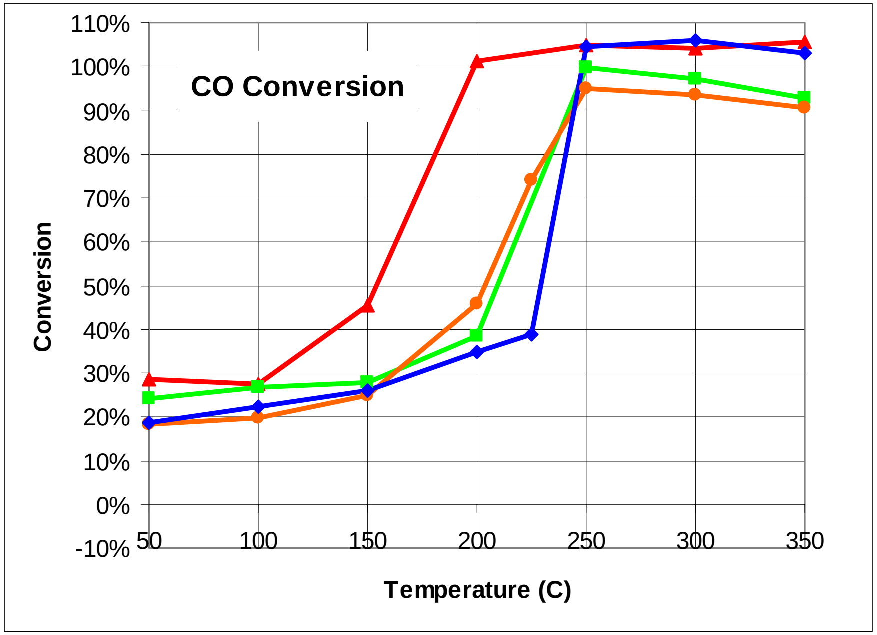


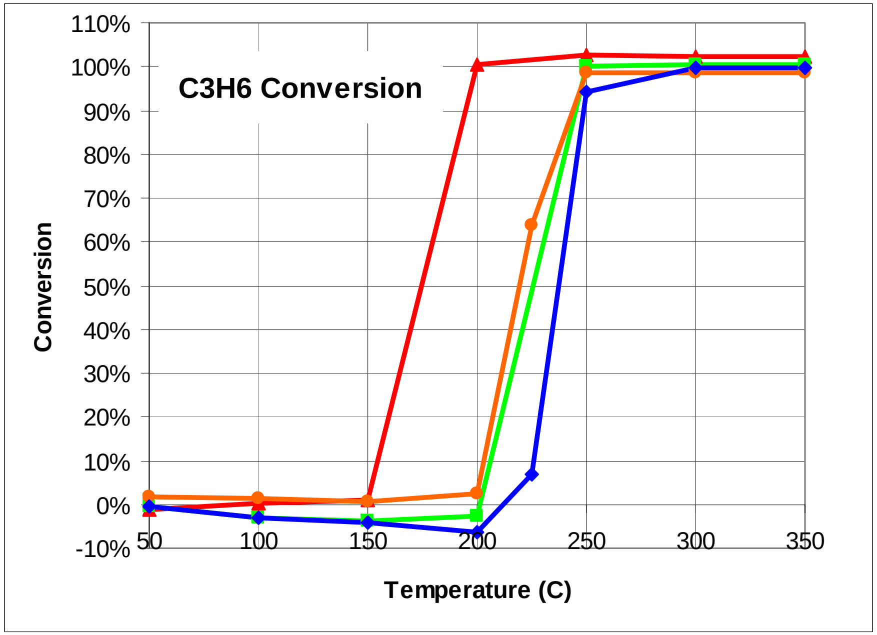




Blue = temperature for 50% CO light-off
Pink = temperature for 30% HC light-off

Bench Reactor Tests of Poisoned Catalysts Also Showed Loss of CO and HC Light-Off Performance





Red = new
Green = intake mfd
Orange = exhaust manifold
Blue = fuel

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Summary - Key Findings

- Phosphorous form and chemistry in exhaust varies with method of introduction
  - Phosphorous passing through combustion is found in exhaust as phosphoric acid
  - Phosphorous added after combustion is found as raw ZDDP or ZDDP fragments
- Catalysts poisoned with phosphoric acid exhaust show phosphorous and sulfur absorption, but no zinc
- Catalysts poisoned with ZDDP exhaust show phosphorous and sulfur absorption combined with a zinc / phosphorous surface glaze
- Phosphorous is concentrated at the front and surface of catalyst, sulfur is more uniform
- Poisoning methods show similar loss of catalyst performance in our CO and HC light-off tests

Future Work

- Continue studies
  - Lube formulations
  - Catalyst formulations
  - Methods of introduction
  - Different duty cycles
  - Further analytical work
- Compare to field aged samples as available

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