Low Volatility ZDDP Technology: Part 2 - Exhaust Catalysts Performance in Field Applications

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ABSTRACT

Phosphorus is known to reduce effectiveness of the three-way catalysts (TWC) commonly used by automotive OEMs. This phenomenon is referred to as catalyst deactivation. The process occurs as zinc dialkyldithiophosphate (ZDDP) decomposes in an engine creating many phosphorus species, which eventually interact with the active sites of exhaust catalysts. This phosphorus comes from both oil consumption and volatilization. Novel low-volatility ZDDP is designed in such a way that the amounts of volatile phosphorus species are significantly reduced while their antiwear and antioxidant performances are maintained.

A recent field trial conducted in New York City taxi cabs provided two sets of “aged” catalysts that had been exposed to GF-4-type formulations. The trial compared fluids formulated with conventional and low-volatility ZDDPs. Results of field test examination were reported in an earlier paper (1). As a part of our current examinations, Federal Test Procedure (FTP-75) emissions tests were conducted. Emissions data collected showed a statistically significant difference in 50% hydrocarbon (HC) efficiency light-off time, on low impact ZDDP as compared to conventional ZDDP, and an even greater effect on nitrogen oxides (NOx) and carbon monoxide (CO) emissions due to a reduction in the phosphorus-derived catalyst deactivation.

INTRODUCTION

ZDDP is a key antiwear agent and has been used in crankcase lubricants for more than 50 years. ZDDP operates by forming a wear protecting layer on metallic surfaces in an operating engine. However, while ZDDP decomposes, the phosphorous can enter the exhaust stream, either by oil consumption or volatilization, and interact with the catalyst washcoat to form phosphorus species. Two types of phosphorus compounds have been identified: 1) a porous overlayer of zinc, calcium and magnesium phosphates on the catalyst washcoat surface and 2) aluminum and cerium phosphates within the washcoat (2). Presence of such phosphorus compounds reduces TWC efficiency for the reduction of HC, CO and NOx emissions.

This phenomenon is particularly important because over the past two decades, the U.S. Environmental Protection Agency (EPA) has steadily increased the amount of driving miles required to warranty the catalytic converter from 50,000 miles to 120,000 miles or 10 years. Over the same period, EPA has also reduced the acceptable levels of HC, CO and NOx emissions that can be emitted from an automobile’s tailpipe. These factors are forcing lubricant formulators to develop crankcase oils with decreasing concentrations of conventional ZDDP (3-9) or introduce low volatility ZDDP technology.

The objective of this program was to determine the effects of two crankcase lubricants on catalyst efficiency of six sets of catalysts after 100,000 miles of taxi service. Evaluations were conducted by operating the test vehicle on a 48-inch chassis dynamometer over the Federal Test Procedure (FTP-75) driving cycle. Details of the test program are given in the experimental section.

EXPERIMENTAL

Six 2003 NY Taxi Ford Crown Victoria (4.6L-2V V8) cabs each accumulated 100,000 miles over a two-year period on a typical taxi-cab service schedule.
Mileage accumulation included moderate to high temperature driving cycles. Oil change interval was selected to be 5,000 miles, the typical duration recommended by the vehicle manufacture. Three of the vehicles accumulated mileage using conventional ZDDP engine oil (Oil 1); the other three vehicles were run using experimental low-volatility ZDDP engine oil (Oil 2). Table 1 provides the cab numbers and corresponding oil characteristics (1).

Two SAE 5W-20 viscosity grade ILSAC GF-4, API SM oils were used in this study. Both oils were formulated using ExxonMobil EHC group II base oils and an olefin copolymer (OCP) viscosity modifier. Typical analysis of these oils is given in Table 1. The only difference in composition of these oils was the type of ZDDP technology used. Oil 1 contained conventional ZDDP, while Oil 2 was formulated with a newly developed low volatility ZDDP technology.

Table 1. Oil properties and assigned cab numbers (1).

<table>
<thead>
<tr>
<th>Oil Code</th>
<th>Oil Designation</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>KV @ 100°C, cSt</td>
<td>Conventional ZDDP</td>
<td>8.53</td>
<td>8.44</td>
</tr>
<tr>
<td>CCS @ -30 C, cPs</td>
<td>Low-Volatility ZDDP</td>
<td>5270</td>
<td>5204</td>
</tr>
<tr>
<td>Calcium (ppm)</td>
<td></td>
<td>1673</td>
<td>1648</td>
</tr>
<tr>
<td>Phosphorous (ppm)</td>
<td></td>
<td>776</td>
<td>742</td>
</tr>
<tr>
<td>Cab Numbers</td>
<td></td>
<td>025,208, 022,370, 675, 410</td>
<td></td>
</tr>
</tbody>
</table>

Note: The Ca and P numbers are considered within normal component, blending and measurement variation.

Catalysts Systems

The dual exhaust catalyst system, shown in Figure 1, contains one close-coupled and two underbody catalysts per bank (6 catalysts per vehicle). All six cabs/catalyst systems were manufactured and assembled in the same time frame.

![Figure 1. 2003 Ford Crown Victoria Catalyst System](image)

The two close-coupled catalysts are 55 in³ in volume with 900/2.5 substrate density/wall thickness. The close-coupled catalysts have a zoned washcoat with an average Pt:Pd:Rh ratio of 2:12:1 and a total load of 73 g/lft³. The four underbody catalysts are 50 in³ in volume with 400/8.5 substrate density/wall thickness. The underbody catalysts have a Pt:Rh ratio of 3:1 and a total load of 12 g/lft³.

Exhaust Emissions Measurements

The aged catalyst systems were removed from the vehicles and sent to Southwest Research Institute in San Antonio, Texas for vehicle emission testing. The catalysts were tested in random order; three of the catalysts were tested twice. The aged oxygen sensors were sent to Ford Motor Company for inspection. The oxygen sensors from all six cabs appeared visually similar with no excessive deterioration observed on either oil.

A 2004 Ford Crown Victoria, supplied by Ford Motor Company, was used to evaluate all six catalyst systems. This ‘slave’ vehicle had approximately 4,000 miles of vehicle aging using baseline (conventional ZDDP) crankcase lubricant. The stock oxygen sensors from the slave vehicle were used for all testing to isolate the emission impact of the two oils on the catalysts. In addition to the six aged systems, the stock catalyst system from the 4K miles slave vehicle was also tested as a baseline comparison for the 100K miles systems.

The catalyst systems were instrumented, as shown in Figure 2, for exhaust sampling and temperature measurements. Exhaust sample probes were installed in front of the close-coupled catalysts (feedgas), between the close-coupled and underbody catalysts (midbed) and after the underbody catalysts (tailpipe). The left and right bank sample probes were connected together with T-pipes at the feedgas (FG), midbed (MB) and tailpipe (TP) exhaust emission measurement test points. Thermocouples (1/8") were installed in similar locations as the exhaust probes, as well as within the catalysts bricks, to determine catalyst midbed temperatures.

![Figure 2. Catalyst System Instrumentation](image)

Vehicle testing utilized the Federal Test Procedure (FTP-75) drive cycle. A US06 cycle was run as a prep cycle prior to the FTP cycles in order to stabilize the catalyst systems by removing any sulfur present from mileage accumulation. The vehicle speed versus time for the 3 Bags of the FTP-75 cycle are shown in Figure 3.
X-Ray Diffraction (XRD) Measurements

X-ray diffraction (XRD) data were collected on the right-side close-coupled catalysts (R-Brick1) from cabs 625 and 675, both of which accumulated mileage using the conventional ZDDP engine oil and cab 410, which accumulated mileage using the low-volatility ZDDP engine oil. For these experiments washcoat was scraped from the inlet (first 0.5 inches) of a core sample. Thin layer XRD specimens were prepared by mounting the scraped washcoat on flat, off-axis-cut (zero background) quartz plates using Vaseline. The diffraction patterns were collected using a Scintag PAD-V X-ray diffractometer using copper Kα X-rays scanning from 5 to 86 degrees 2θ.

Raman Spectroscopy Measurements

Spectra were collected using a Renishaw 1000 Raman Microscope with 488 nm laser excitation, with the frequencies ranging from 100-1800 cm⁻¹ or 100-2200 cm⁻¹. Cross-sections of all six catalyst inlets from the left-side close-coupled catalyst (L-Brick1) were examined. Spectral data were obtained primarily as maps, although some individual spectra were obtained for cab 675. In addition to catalyst inlets, cross-sectional areas ~15 mm below the surfaces of conventional oil cabs 208 and 675 and low-volatility oil cabs 370 and 410 were examined.

Surface Area (BET) Measurements.

Sample cores, 0.75 inch in diameter by 0.5 inch in length, were taken from the inlet, middle and outlet sections of the left-side close-coupled catalysts (L-Brick1) from all six cabs. Measurements on the inlet section from all the catalyst systems were saturated and no useful information could be obtained. Thus, the middle and outlet sections were used for the surface area and pulsator index ratio (IR) experiments. The pulsator IR experiments are explained in the next section.

Surface area measurements, by the standard BET method, were conducted to determine the internal surface area of the washcoat. This method is based on nitrogen adsorption at liquid nitrogen temperatures. Samples were evaluated on a Micromeritics Accelerated Surface Porosimetry (ASAP) 2400 analyzer after an initial degas at 350°C for two hours. The surface area values are reported as m²/g.

Pulsator Index Ratio (IR) Measurements

The pulsator laboratory reactor is a test rig, which combusts air and fuel via a combustion furnace set at 800°C for ignition (10). Computer feedback control allows for a precise A/F setpoint and modulation which is used to generate the desired combustion constituents from burned fuel.

The pulsator index ratio (IR) of a catalyst is the ratio of the rear oxygen sensor (after the close-coupled catalyst) signal and the front oxygen sensor (before the closed-coupled catalyst) signal. The IR is an indicator of the catalyst’s transient oxygen storage.

Chassis Dynamometer Setup

The Ford Crown Victoria was tested on a Horiba 48-inch single-roll chassis dynamometer. This dynamometer electrically simulates inertia weights up to 15,000 lb over the FTP, and provides programmable road load simulation of up to 200 hp continuous at 65 mph. The dynamometer settings for the Crown Victoria are given in Appendix 2. The fuel used during testing was a single batch of Hallermann Tier II EEE emissions certification gasoline.

POST-MORTEM CATALYST ANALYSIS

X-Ray Florescence (XRF) Measurements

Bulk elemental compositions of both close-coupled catalysts from the left-side (L-Brick1) and right-side (R-Brick1) from all six cabs were determined using X-ray fluorescence (XRF) spectroscopy. Each catalyst brick was cut lengthwise (parallel to the flow direction) into quarters. One quarter of each catalyst was evenly divided into inlet, middle, and outlet sections. Each section was then ground into a fine powder using a carbide ring and puck grinding dish. Pellet specimens, prepared from the ground catalyst powders, were analyzed using a Panalytical PW2400 WDS XRF spectrometer and a UniQuantitative XRF analysis program.
characteristics and is a measure of the monitorability of a catalyst for OBD (On-Board Diagnostics).

The pulsator index ratio of each catalyst was measured at an exhaust gas temperature of 500°C in iso-octane fuel. The space velocity was 66K hr⁻¹. A modulation of λ (A/Fnetual / A/Fstoich) ±0.014 (A/F ±0.2) cycling at a frequency of 1 Hz was applied during testing. A λ-sweep was performed over the range of λ = 0.999 to λ = 1.002 in order to determine the control UEGO setpoint where the maximum pulsator index ratio occurred (usually λ≈1.001). The recorded pulsator index ratio for each sample was determined at the maximum IR setpoint. The voltage signals from oxygen sensors placed in front of and behind the catalyst sample were recorded at a rate of 20 Hz for 5 minutes.

Four sets of data were collected for each catalyst. These raw oxygen sensor voltages were then converted to a pulsator path length index ratio, which was averaged and recorded. Higher index ratio values indicate a catalyst has worse oxygen storage and release characteristics.

RESULTS AND DISCUSSION

Exhaust Emissions Analysis

Results gathered for standard regulated emissions of THC, CO, and NOx, along with THC Light-Off Time will be discussed in the paper. Initially, the focus was on the THC light-off time. It was expected that as ZDDP interacts with the active sites of the catalysts, the light-off time will increase. The light-off time is defined as the length of time it takes the efficiency of the catalyst to get to >50% immediately after the start of an FTP-75 cycle.

Figure 4 shows the efficiency over time for all of the FTP-75 cycles run on all of the catalyst systems including the one stock (4K mile) baseline catalyst system which was evaluated prior to the 100K mile catalyst systems. While the number of FTP-75 tests differs slightly across cars, the catalyst systems exposed to the low-volatility ZDDP (Oil 2) have on average a faster THC light-off time than those which used the conventional ZDDP (Oil 1). The average light-off time differences, while small in magnitude and less than expected, are significantly different at the 95% confidence level. Better than expected light-off times are attributed to use of the 900/2.5 close-coupled catalyst substrates, which have low bulk densities and high geometric surface areas.

Directionally, the light-off time benefit with low-volatility ZDDP may have a larger magnitude on standard 400/6.5 substrates which have higher bulk density and lower geometric surface areas.

Since the light-off time does not reflect the overall efficiency, the sum of the area under the THC efficiency curve between 20 and 40 seconds was used to better quantify the difference between the oils; larger areas are associated with faster light-off and better catalytic performance. These results are shown in Figure 5. The difference between the oils is greater than the variations within consecutive FTP cycles for a single vehicle or between FTP tests for all vehicles using the same oil.

![Figure 5: Integrated area between 20-40 seconds of the FTP cycle. Greater area implies faster light-off and better catalytic performance.](image)

Modals traces of Bag 1 emissions (THC, CO, NOx) for cumulative feedgas, midbed and tailpipe emissions are shown in Appendix 3. As expected, the feedgas emissions are very similar for all the systems evaluated since one slave vehicle was used for the testing. In addition to the slight improvement in THC light-off time already discussed, a larger emission benefit for both CO and NOx is observed at the midbed location which also carries through to the tailpipe location. This type of CO/NOx benefit throughout the warmed-up portion of the FTP cycle has been seen in other studies. It is well known that CO and NOx catalytic performance is dependent on oxygen storage capacity (OSC). The use of low-volatility ZDDP allows for less phosphorus to reach the catalyst and hence, less poisoning of the oxygen storage capacity (OSC) components (e.g. ceria).

Loss of phosphorus from volatilization was calculated by measuring the phosphorus content of the used
engine oil at each oil change. The total phosphorus exposed to each cab’s exhaust system was estimated from the volatilized phosphorus and oil consumption data collected during the study. This is summarized in Table 2. Note that one cab (410) experienced very high oil consumption, leading to higher total phosphorus exposure than would be expected for Oil 2.

Table 2. Summary of the Estimated Phosphorus Exposure

<table>
<thead>
<tr>
<th>Oil - Cab</th>
<th>Consumed oil phos (g)</th>
<th>Volatilized phos (g)</th>
<th>Total phos exposure (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil 1-025</td>
<td>3.8</td>
<td>10.53</td>
<td>14.3</td>
</tr>
<tr>
<td>Oil 1-208</td>
<td>5.0</td>
<td>9.90</td>
<td>14.9</td>
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<tr>
<td>Oil 1-675</td>
<td>2.9</td>
<td>11.49</td>
<td>14.4</td>
</tr>
<tr>
<td>Oil 2-022</td>
<td>4.9</td>
<td>4.99</td>
<td>9.9</td>
</tr>
<tr>
<td>Oil 2-370</td>
<td>2.8</td>
<td>5.97</td>
<td>8.8</td>
</tr>
<tr>
<td>Oil 2-410</td>
<td>7.3</td>
<td>5.86</td>
<td>13.2</td>
</tr>
</tbody>
</table>

Plots of catalyst efficiency vs. phosphorus exposure suggest some interesting trends. Figure 6 shows the Bag 1 NOx catalyst efficiency vs. the total phosphorus exposure. For all of the cabs, except cab 675, a higher amount of estimated phosphorus exposure results in lower (worse) catalyst efficiency for NOx. In fact, if cab 675 is omitted, the difference on average is about 10.3 percentage points. Post-mortem analysis on cab 675 offered some insight on the observed high NOx efficiency with high phosphorus exposure and will be discussed in a later section of the paper.

Figure 6: Bag 1 NOx Catalyst Efficiency vs Total Phosphorus Exposure.

Catalyst Post-Mortem Analysis

After completion of vehicle testing, the catalysts were sent to Ford Motor Company for post-mortem analysis. X-ray fluorescence (XRF), x-ray diffraction (XRD), Raman spectroscopy, surface area measurements, and pulsator index ratio (IR) experiments were conducted on the close-coupled catalysts from all six cabs. One goal of the post-mortem analysis was to attempt to provide insight into the better than expected performance of cab 675 which accumulated mileage on the conventional ZDDP oil. Recall that the poorer than expected results from cab 410, run on low-volatility ZDDP oil, was attributed to high oil consumption (Table 2 and Figure 8).

X-Ray Fluorescence Analysis

Only the close-coupled catalysts from each cab were analyzed since phosphorus is known to preferentially poison on the front section of the first brick in the system. This is shown graphically in Figure 7 for the left-side close-coupled catalysts (L-Brick1) from all six cabs.

Note that all of the cabs that accumulated mileage on the low volatility oil had lower phosphorus amounts on the catalyst inlet which reflects the lower total phosphorus exposure to the catalyst. A catalyst phosphorus capture efficiency was calculated from the total phosphorus exposure (consumed+volatilized) and the amount of phosphorus observed on the inlet portion of the catalyst from XRF analysis. The capture efficiency was very similar for all the cabs, regardless of oil used, and ranged from 18-24%. This range of catalyst phosphorus capture efficiency (less than 30%) has been observed previously for fully-combusted ZDDP components (12).

The XRF results were also compared to the type of phosphorus exposure. For this evaluation, the XRF results from the left-side (L-Brick1) and right-side (R-Brick1) close-coupled catalysts were averaged. It appears that P on the inlet is most correlated with
volatilized phosphorus (Figure 8) but not consumed oil phosphorus (Figure 9).

Figure 8. Average phosphorus on inlet section of close-coupled catalysts versus exposure to volatilized phosphorus.

Figure 9. Average phosphorus on inlet section of close-coupled catalysts versus exposure to consumed oil phosphorus.

X-Ray Diffraction Analysis

X-ray diffraction (XRD) experiments were conducted on the right-side closed-coupled (R-Brick1) inlet section from cabs 675 and 025, both run on conventional ZDDP oil, and on cab 410, run on low volatility ZDDP oil, to determine the phosphorus compounds. Recall that cab 675 had better than expected catalytic activity (Figure 6). The XRD patterns for both conventional cabs are shown below in Figure 10. In addition, the diffraction patterns of the ground substrate and a fresh catalyst of the same washcoat and pgm loading as that of the cabs are shown.

Figure 10. XRD patterns from the inlet section of the right-side close-coupled catalyst (R-Brick1) from Cabs 025 and 675, both run on oil blended with conventional ZDDP.

The sharp Pd peaks indicate coarsening of the Pd particles due to thermal aging for both cabs compared to the fresh sample where the precious metal particles are too fine to produce an XRD pattern. Diffraction peaks that are present exclusively in the XRD patterns at 20.3, 21.5 and 22.9 degrees correspond well with aluminum phosphate. Other unidentified peaks are most likely attributed to other phosphate compounds, but could not be positively identified. However, the XRD patterns from the inlet section of conventional oil cabs 025 and 675 are nearly identical and do not help explain the difference in observed catalytic activity between the two cabs. The XRD spectrum for cab 410, run on low volatility ZDDP oil, was very similar to that of the patterns for the conventional oil cabs indicating both oils produced similar phosphorus species on the catalyst.

Raman Spectroscopy Analysis

Raman and optical spectroscopy were used to examine the inlet section of the left-side close-coupled catalyst (L-Brick1) from conventional ZDDP containing oil cabs 675 and 206 and low-volatility ZDDP containing oil cabs 370 and 410. All of the catalyst inlet cross-sections showed the presence of a brittle, white overlayer that completely covered the washcoat. This overlayer is shown optically for conventional oil cab 675 (Figure 11a) and low-volatility oil cab 410 (Figure 11b).
A Raman spectrum is shown in Figure 12 from cab 675 illustrating the components detectable on the catalyst surface at two different locations. In Figure 12 the square, circle and plus symbols identify the AlPO₄, Ca₁₉Zn₁₂(PO₄)₁₄ and CePO₄ peaks, respectively. The main contaminants observed are Ca₁₉Zn₁₂(PO₄)₁₄, CaCO₃, cerium and aluminum phosphates, combustion by-products (e.g. carbon), and what appear to be pyrophosphates in the vicinity of 1050 cm⁻¹.

The presence of Ca₁₉Zn₁₂(PO₄)₁₄ is different from what has been previously observed in dozens of customer-aged catalyst spectra (13). For those samples, α-CaZn₂8(PO₄)₅ was usually the calcium-zinc phosphate species observed. Ca₁₉Zn₁₂(PO₄)₁₄ is essentially the saturation composition for Zn₁₂(PO₄)₂ in β-Ca₃(PO₄)₂ when the ratio of calcium to zinc is greater than 9:1 (14). Since there is less ZDDP, and thus less zinc present here, the presence of Ca₁₉Zn₁₂(PO₄)₁₄ is reasonable. Raman spectra obtained from cross-sectional areas below the inlet surfaces of conventional oil cabs 208 and 675 and low-volatility oil cabs 370 and 410 did not yield additional information to differentiate the catalysts from one another and did not explain the better vehicle emissions performance observed for cab 675.

**Surface Area (BET) and Pulsator Index Ratio (IR) Analysis**

Surface area and laboratory pulsator index ratio (IR) experiments were conducted on the left-side close-coupled catalyst (L-Brick1) from all six cabs to further assess the improvement in CO and NOx emissions that were observed on the vehicle (Appendix 3, Micbed Traces).

The surface area of a catalyst can be deteriorated (decreased) by two methods:

1) thermal degradation which causes sintering and collapse of the washcoat pores and
2) poisoning where the pores can be blocked or washcoat and/or OSC materials can form inactive compounds (e.g. aluminum or cerium phosphate).

To reduce the phosphorus impact on surface area and OSC measurements, cores were taken from the outlet section of the left-side close-coupled catalysts (L-Brick1) which did not contain phosphorus (Figure 7).
Figure 13 contains data comparing the catalyst outlet surface area and pulsator IR results. For good catalyst performance a high surface area and low IR are desired. A low IR indicates that transient oxygen storage capacity is very active and the catalyst can release and store oxygen during A/F transients, thus maintaining high CO/NOx performance. Note the very good correlation ($R^2 = 0.99$) between surface area and IR for the outlet section of all the cabs. This data supports the better than expected emissions performance for cab 675, run on conventional ZDDP, due to its very high surface area and low IR value. It is also interesting to note the poorer performance for cab 410 (low-volatility ZDDP) and cab 025 (conventional ZDDP). Even at the outlet, which contains no phosphorus, the surface area is very low and IR very high indicating more thermal damage than the other cabs. This could be due to a different driving cycle for these cabs.

![Surface Area (BET) Measurements vs. Phosphorous](image1)

**Figure 14.** Comparison of surface area and phosphorus amount (XRF) of mid-section of left-side close-coupled catalysts (L-Brick1).

**CONCLUSIONS**

Improvements in TWC efficiencies (associated with Low Volatility ZDDP) are linked to:

- Lowered amount of volatile P species deposited at the catalyst inlet face (30% reduction)
- At similar oil consumption rates, the lower amount of volatilized phosphorus exposed to the catalyst with low volatility ZDDP resulted in lower degradation of the oxygen storage capacity (OSC) and improved CO/NOx performance.
- One cab (675), using conventional ZDDP oil, maintained high surface area and catalytic performance despite being exposed to similar amounts of phosphorus. Extensive post-mortem analysis did not identify the presence of different phosphorous compounds. One postulation is that cab 675 experienced milder thermal deterioration.
- One cab (410), using oil formulated with low volatility ZDDP had much higher than expected overall oil consumption which will likely override any improvements due to the low volatility ZDDP.
- Observed a strong association between phosphorus amount on the catalyst and surface area. All of the low volatility ZDDP cabs had less phosphorus on the catalyst compared to the conventional ZDDP cabs.
- Vehicle and laboratory experiments showed enhanced CO/NOx performance when oxygen-storage activity and high catalyst surface areas were maintained. In addition, laboratory experiments demonstrated the
relationship between lower phosphorus amounts and higher catalyst surface areas.

NYC taxi trial conducted with GF4, 0.07% P lubricants demonstrated that cabs using oils blended with Low Volatility ZDDP typically (after excluding two suspect cabs [410 and 675]):

- Had on average 46% less volatile P than Conventional ZDDP
- Maintained excellent antiwear/antioxidancy performance [1]
- Had statistically improved THC light-off time
- Had on average 10% lower NOx emissions
- Had lower CO emissions (detailed in Appendix 3).

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Emission testing was carried out at Southwest Research Institute in San Antonio, Texas.

REFERENCES


CONTACT

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ADDITIONAL SOURCES

CFR, Title 40, Part 86

DEFINITIONS, ACRONYMS, ABBREVIATIONS

BET – Brunauer, Emmett, Teller (Catalyst surface area measurement)

CO – Carbon Monoxide

HC – Hydrocarbon

IR – Index Ratio

NOx – Nitrogen Oxides

OSC – Oxygen Storage Capacity

RH / LH – Right Hand (Passenger-Side) / Left Hand (Driver Side)

XRF – X-Ray Fluorescence

XRD – X-Ray Diffraction

ZDDP – Zinc dialkyldithiophosphate
### APPENDIX 1. Analysis Method for Exhaust Constituents

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<tr>
<th>Constituent</th>
<th>Analysis Method</th>
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<tr>
<td>Total Hydrocarbon</td>
<td>Heated Flame Ionization (bag, modal)</td>
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<tr>
<td>Methane</td>
<td>Gas chromatography (bag only)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>Non-Dispersive infrared (bag, modal)</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>Non-Dispersive infrared (bag, modal)</td>
</tr>
<tr>
<td>Oxides of Nitrogen</td>
<td>Chemiluminescence (bag, modal)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Magnetopneumatic (modal only)</td>
</tr>
</tbody>
</table>

#### APPENDIX 2. Dynomometer Setup

- a coefficient: 25.58 lbs
- b coefficient: -0.4616 lb/mph
- c coefficient: 0.02825 lb/mph²
- Equivalent Test Weight: 4000 lbs

### APPENDIX 3. BAG 1 CUMULATIVE FEEDGAS EMISSIONS

- THC Collection point: Engine Out
- CO Collection point: Engine Out
- NOx Collection point: Engine Out

#### Emission Graphs
- Emission vs. Time
- Average across all FTPs
- Data points for different conditions
APPENDIX 4.

FTP Test Start Dates for Catalysts:

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dates</th>
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<tr>
<td>Oil 1-025</td>
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</tr>
<tr>
<td>Oil 1-208</td>
<td>6/13/05, 7/18/05</td>
</tr>
<tr>
<td>Oil 1-675</td>
<td>5/10/05, 6/27/05</td>
</tr>
<tr>
<td>Oil 2-022</td>
<td>8/8/05</td>
</tr>
<tr>
<td>Oil 2-370</td>
<td>8/4/05</td>
</tr>
<tr>
<td>Oil 2-410</td>
<td>8/22/05, 9/6/05</td>
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