

Controlling Lubricant-Derived Phosphorous Deactivation of the Three-Way Catalysts Part 2: Positive Environmental Impact of Novel ZDP Technology

2010-01-2257

Published
10/25/2010

Ewa Bardasz, Elizabeth A. Schiferl, Jonathan S. Vilardo and Thomas T. Curtis
Lubrizol Corp.

Frances E. Lockwood
Ashland Inc.

Thomas R. Smith and Timothy Lee Caudill
Valvoline Company

Copyright © 2010 SAE International

ABSTRACT

Prior technical work by various OEMs and lubricant formulators has identified lubricant-derived phosphorus as a key element capable of significantly reducing the efficiency of modern emissions control systems of gasoline-powered vehicles (1 , 2 , 3 , 4 , 5 , 6 , 7 , 8 , 9 , 10 , 11 , 12 , 13). However, measuring the exact magnitude of the detriment is not simple or straightforward exercise due to the many other sources of variation which occur as a vehicle is driven and the catalyst is aged (1).

This paper, the second one in the series of publications, examines quantitative sets of results generated using various vehicle and exhaust catalyst testing methodologies designed to follow the path of lubricant-derived phosphorous transfer from oil sump to exhaust catalytic systems (1). Data discussed include a survey of TWC technologies used currently by the passenger car and light duty truck market, catalyst compatibility testing, paired vehicle dynamometer tests, field trials and life cycle analysis. Finally, post-mortem analysis of aged catalysts is used to both quantify the level of phosphorus exposure from the oil as well as estimate the loss of performance resulting from phosphorus deposition within the catalyst. Results reveal a significant and beneficial impact of reduced lubricant-derived phosphorus exposure on the life and efficiency of various three-way catalyst technologies

when utilized in numerous vehicle types and driving cycles. A novel statistical model was developed which provides a quantitative measure of the effect of lubricant-derived phosphorous contamination of TWC. The overall environmental benefits of the specific motor oil formulations in this study with the novel ZDP versus conventional ZDP are clearly defined by means of the life cycle analysis (LCA).

INTRODUCTION

Three-way Catalyst Characteristics

The three-way catalyst (TWC) is used in rich-burn or stoichiometric internal combustion engines for simultaneous conversion of oxides of nitrogen (NO_x), carbon monoxide (CO), hydrocarbons (HC), formaldehyde (CH_2O) and EPA classified Hazardous Air Pollutants (HAPs). The three-way catalyst is effective in a wide variety of engine applications and fuels, including natural gas, propane and gasoline.

The currently used three-way catalysts, are generally a multicomponent materials, containing varying concentrations of the precious group metals (PGM) such as rhodium, platinum and palladium, γ -alumina (Al_2O_3), and other metal oxides, some of them acting as chemical promoters also known as oxygen carriers (OC). To achieve a large surface area for catalytic reaction, the internal surfaces of the catalyst are covered with a thin coating of a highly porous material.

**Documents**

Document Sharing Hub

known as the washcoat. The washcoat generally consists of alumina with a large surface area, with other oxides added as structural promoters acting as stabilizers to maintain surface area and others, as chemical promoters. This system becomes the support for the precious metal components (PGM). Catalyst designers use many different technologies to achieve an optimum performance of a catalytic converter for a specific application. Exact catalyst formulations are, as one might expect, closely guarded secrets.

An ability to withstand mild deactivation is built into the design of the catalytic converter. However, severe deactivation could prevent the system from meeting current EPA emissions legislation (14).

Over the last several decades it was well established by the automobile and oil industries that motor oil borne phosphorus (P) originating from antiwear component zinc dialkyldithiophosphate (ZDP) deactivates catalytic converters by forming a variety of metallic phosphates that reduce catalyst efficiency, thus increasing levels of exhaust emissions. In its volatile form, phosphorus has an affinity towards PGM and OC in the catalyst washcoat and may disable their ability to react with the exhaust gases (1,2,3,4,5,6,7,8,9).

Survey of the TWC Technologies

In order to understand the effect of phosphorus poisoning across a range of catalyst types, catalysts from eight (8) top selling 2006-2007 MY vehicles designed to meet current EPA emissions requirements (Tier 2, Bin 2-8) were purchased and analyzed. For vehicles equipped with a close-coupled converter and an underfloor converter, only the close-coupled converter was analyzed. For vehicles with two exhaust banks and a converter in each bank, only one bank converter was analyzed. In all systems, only the first catalyst placed in a converter was analyzed and this catalyst is defined as the light-off catalyst.

In our study, Proton- Induced X-Ray Emission (PIXE) was used as a non-destructive elemental analytical method for obtaining the full composition of all catalysts. PIXE simultaneously measures concentration of all elements in the periodic table from sodium (Na-11) to Uranium (U-92). When compared to electron based x-ray analytical techniques such as energy dispersive spectroscopy (EDS), PIXE offers better peak to noise ratios and consequently much higher trace element sensitivities.

Concentration levels of three typical PGMs and two typical OCs at the inlet of each catalyst type tested are shown in [Figures 1](#) and [2](#).

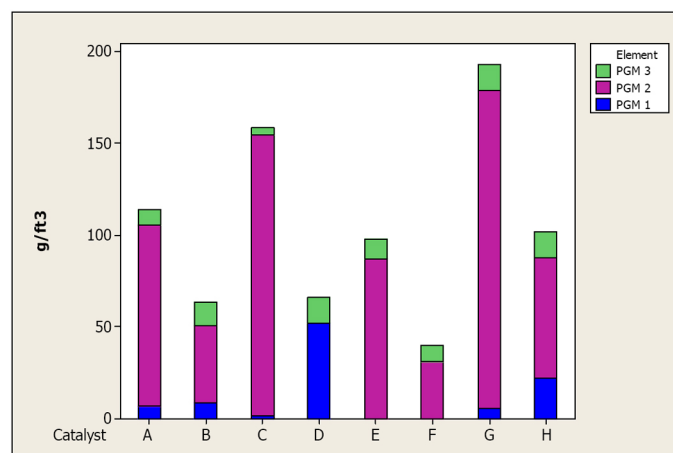


Figure 1. Level of PGM at Inlet of New Catalyst

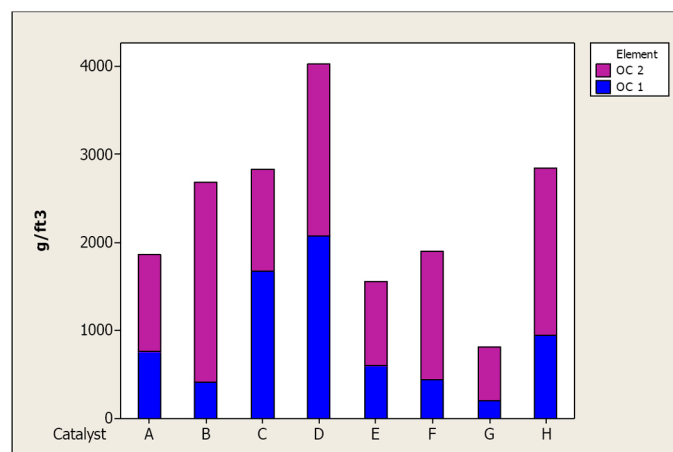


Figure 2. Level of OC at Inlet of New Catalyst

These graphs demonstrate a wide spread in a variety of formulating strategies/cost and robustness of systems. Based on results of our survey, four catalysts A, B, C and D were chosen for further study as they appeared to bracket the range of catalyst element profiles available.

EXPERIMENTAL

Methods for Catalyst Aging

As a part of our study to examine various categories of tests sensitive enough to detect phosphorus driven deactivation of three-way catalysts, we conducted several tests, where catalysts A, B, C and D were exposed to lubricant-derived phosphorous species.

Three types of these tests are discussed in this paper:

- field trial mileage accumulation,
- vehicle dyno mileage accumulation and

- catalyst compatibility tests.

Tested exhaust systems included four (4) modern North American catalyst technologies (2003+) and two types of lubricant formulations.

Test Oils

In each method of aging, two formulations of crankcase oils were used for testing. For purposes of our studies, the only difference in the formulations evaluated was the nature of the ZDP composition. Two different ZDP formulations were evaluated while maintaining equivalent phosphorus levels as follows:

- Hyper ZDP™ System - (HPR) ZDP - patented secondary ZDP with alcohol mixtures balanced to reduce phosphorus volatility while maintaining wear protection
- Conventional ZDP - commercially available secondary ZDP used in various markets globally for passenger car and heavy duty diesel applications.

The lubricant containing HPR ZDP represents commercially available ILSAC API GF-4 SAE 5W-30 passenger car motor oil whereas the formulation tested with conventional ZDP (pre-2004) represents its predecessor and provides phosphorus retention similar to the many fluids available in the market. Thus our study delineates the effect of the different ZDP systems in very similar oil formulations.

Table 1. Typical Examples of Physical and Chemical Properties of Test Oils

Oil Code	Conventional ZDP	HPR ZDP
KV @ 100°C, cSt	8.53	8.44
CCS @ -30 C, cPs	5270	5204
Calcium (ppm)	1624-1675	1648
Phosphorous (ppm)	736-757	760

Field Trial Mileage Accumulation Tests (11,12)

The taxi cab field trial was conducted in New York City over a two year period. Test duration covered 100,000 miles of typical moderate to high temperature driving cycles. Side-by-side field trial performance was conducted using new 2003 Vehicle+Catalyst A system. Oil change interval was selected to be 5,000 miles, typical duration recommended by the vehicle manufacture. Based on extensive past experience, used oil analysis was used as a measure of phosphorus retention and engine durability. While the trial originally started with eight (8) units, four on each oil. One vehicle

using oil with conventional ZDP and one vehicle using oil with HPR ZDP were excluded from the final analysis due to issues beyond the control of the fleet operator which were unrelated to oil performance or ZDP.

Vehicle Dyno Mileage Accumulation Tests

Vehicle mileage accumulation was carried out on the mileage accumulation dynamometers for 50,000 to 100,000-miles. Four 2006 model/catalyst B vehicles and two 2006 model/Catalyst C vehicles were used in this test; half used conventional ZDP and half used HPR ZDP. Since the evaluation of oil additive technology volatility characteristics was the key performance objective of this study, a modified durability driving cycle was used as a mileage accumulation. The Federal Durability test cycle includes a mixture of idle, acceleration, deceleration and cruise driving patterns. Oil samples were taken at the end of each change interval (5,000 miles) for compositional analysis.

Bench Tests: Catalyst Compatibility Testing (10,13)

The engine platform utilized in this oil evaluation test is a General Motors 3.1 L V-6 engine, installed in vehicles such as the 2001-03 Chevrolet Malibu. The aging portion of the test, in which the catalyst degradation takes place, is run as steady state cycle. The test length is 240 hours and the oil sampling occurs every 24 hours. Oil temperature is maintained at 150 °C via external oil heater, and exhaust gas temperature is set ~530°C. The manifold absolute pressure set point optimizes lubricant borne phosphorus transport through the crankcase ventilation system by promoting PCV flow.

This test was used to examine aging phenomena of the 2006 Catalyst D technology upon exposure to the two different ZDP type oil formulations.

Post Mortem Analysis of Aged Catalysts

XRF Analysis

XRF analysis was performed on ‘close-coupled’ bricks divided into inlet 1”, mid 3”, and outlet 1” sections. Each section was ground to a fine powder in a carbide grinding dish and made into pellets. The pellets were examined using the Philips PW2400 XRF Spectrometer and UniQuant5 software.

Surface Area (BET) Measurements

The most widely used technique for measuring surface area is called BET method (Brunauer, Emmett and Teller, 1938). Sample cores, 0.75 inch in diameter by 0.5 inch in length, were taken from the inlet, middle and outlet sections of the aged close-coupled catalysts. 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. The surface area values are reported as m^2/g .

T50 Light-Off Temperature Measurements

The pulsator laboratory reactor system was used to measure aged catalyst light-off performance. The test set-up combusts air and fuel via a combustion furnace set at 800°C for ignition. The pulsator light-off performance of selected catalysts was evaluated at a $\text{SV} = 33,000 \text{ hr}^{-1}$ using sulfur-free fuel with an exhaust gas temperature ramp rate of $10^\circ\text{C}/\text{min}$ and $\lambda = 0.998$. The T_{50} values for HC, CO and NO_x were measured and recorded as the temperature at which 50% conversion efficiency for the monitored component occurred. Lower light-off temperatures indicate better catalyst activity. Light-off evaluations were performed before and after regeneration, where the pulsator is set to run at $\lambda = 0.98$ at 650°C for $\frac{1}{2}$ hour. Results from the separate sections, evaluated before and after regeneration, were averaged and reported.

RESULTS AND DISCUSSION

Traditionally, the emission conversion efficiency or tailpipe output in grams might be used to assess the effect of phosphorus exposure on the catalyst performance after long term aging. However, across such a wide range of engine types, engine calibrations targeting various emission levels, fuel compositions, catalyst characteristics and aging severity, there are simply too many factors other than phosphorus affecting results, relative to the number of vehicles tested. In fact, getting enough data to evaluate lubricant-derived phosphorus impact using a ‘whole vehicle’ approach would be a cost prohibitive exercise. Instead, our study pursued another unique approach. We focused on information obtained from post mortem analysis of the aged catalysts. It provided a rich source of data to isolate the effect of phosphorus deactivation alone in opposition to other catalyst technology related parameters such as, PGM, OC, surface area, etc.

Post Mortem Analysis of Aged Catalysts from Field Trials, Dyno Mileage Accumulation and Bench Testing

Post mortem analysis of aged catalysts included decanning, followed by taking samples along the length of the catalyst for XRF, BET and T50 assessments. Driver side and passenger side samples of the catalyst were analyzed for some models. Figures 3 and 4 show the comparison between the single new result and the multiple aged results for inlet samples only. Note that slightly different methods/labs were used to make the measurements, but that in general there is good agreement for all but Catalyst C. For that model, the aged catalysts had very low levels of the OC elements, making the aged catalyst sample very different from both the

new counterparts as well as other catalysts. The difference among the aged results represents between (part-to-part) and within variation (sample-to-sample).

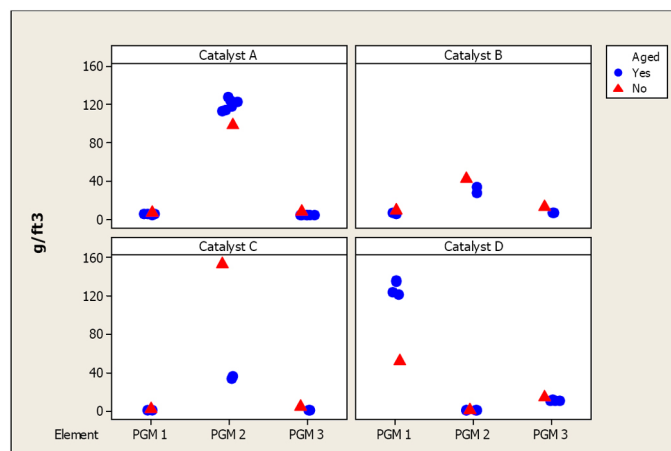


Figure 3. Catalysts A, B, C & D: Levels of PGM at Inlet, Aged versus New

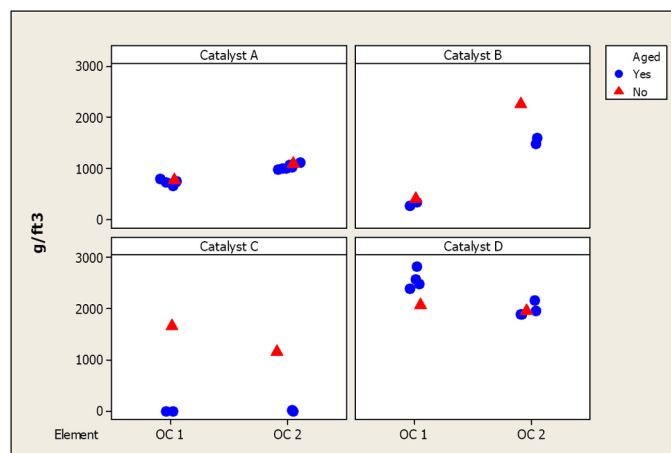


Figure 4. Catalysts A, B, C & D: Levels of OC at Inlet, Aged versus New

Results from all aged samples are in Figures 5 and 6 and show that for some vehicles, the level of PGM varies with distance from the inlet of the TWC. For Catalyst A the level of PGM 2 is highest at the inlet and 0 at the outlet; for Catalyst D, PGM 1 decreases from front to back. The levels of the two OC components did not vary greatly with distance from inlet for any catalyst.