

Controlling Lubricant Derived Phosphorous Deactivation of the Three Way Catalysts Part 1: Assessments of Various Testing Methodologies

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ABSTRACT

Prior work by various OEMs has identified the ability of phosphorus-containing compounds to interfere with the efficiency of modern emissions control systems utilized by gasoline-powered vehicles. Considering the growing societal concerns about ecological effects of exhaust emissions, greenhouse gas emissions and related global climatic changes, it becomes desirable to examine the effect of reduced phosphorous (P) deposits in various vehicle makes, models and types of service, over the lifetime of a vehicle's operation.

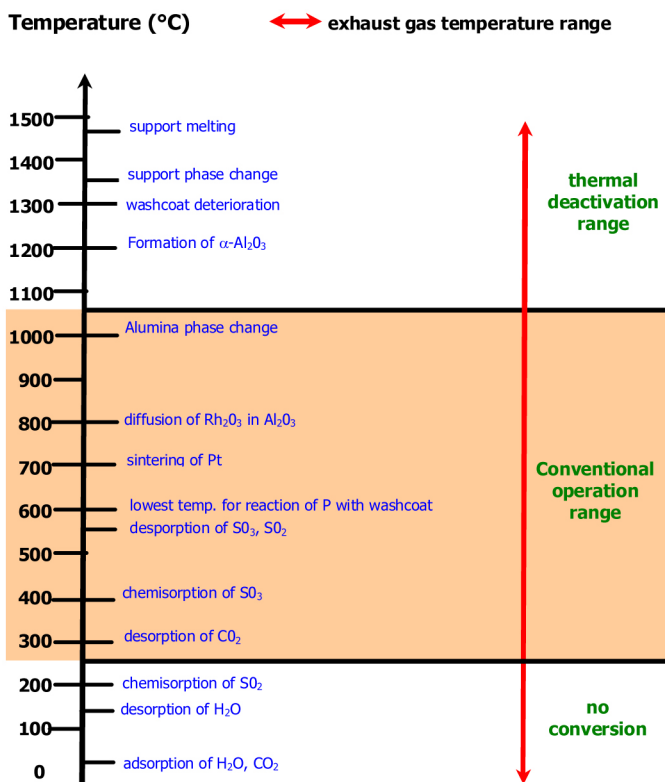
This paper assesses advantages and disadvantages of various methods to examine the path of P transfer throughout exhaust catalytic systems. Test types discussed include examples of bench testing focusing on catalyst compatibility, dyno mileage accumulation and field trial examinations. Results reveal testing challenges encountered with various tests, show measureable differences among oils in phosphorus retention and underscore the beneficial impact of reduced phosphorus exposure on extending catalysts' life and their overall efficiency.

INTRODUCTION

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 (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19).

Since 1994, the International Lubricant Standardization and Approval Committee (ILSAC) oil and American Petroleum Institute (API) specifications for selected viscosity grades have specified a maximum limit on the amount of elemental P allowed in passenger car motor oils. Current GF-4 category oils require less than 0.08% phosphorus by mass and GF-5 retains the 0.08% phosphorus limit while adding an additional phosphorus retention minimum of 79% in the Sequence IIIGB test (ASTM D7320). These limits have been implemented in an effort to minimize phosphorus-derived catalyst poisoning. While they are intended to be an effective way of minimizing catalyst poisoning due to engine oil phosphorus content, they correspondingly constrain the amount of wear and oxidation protection from ZDP additive. Lubricant experts from oil and additive industries, as well as automotive manufacturers, believe that there are ways in which oils can be formulated to minimize their impact on catalyst performance, without reducing the phosphorus content of the oil. In addition, it has been proven (4, 5, and 12) that the deactivation of catalyst performance is not directly related to phosphorus content of the oil only, but rather to the amount of phosphorus that reaches the catalyst. In order to accentuate the volatilized oil poisoning effect on the catalyst, the tests used need to be designed to limit any thermal deactivation of the catalyst ensuring that the volatilized phosphorus mode of deactivation is dominant. The impact of both deactivation mechanisms is primarily a function of catalyst temperature (20). Table 1 provides general trends relating temperature exposure to potential degradation phenomena observed in three-way catalysts (TWC).

Table 1. Temperature Ranges vs. TWC Catalysts' Performance



At the high temperatures reached by TWC as a result of hot exhaust gases and exothermal reactions that take place, the most common thermal deactivation processes are sintering, noble metal alloying, metal-support interactions, and metal losses.

Chemical deactivation of TWC is a result of fuel borne or lubricant borne elements (such as sulfur, calcium, zinc and phosphorous) hindering the reactions that take place within the catalyst. These phenomena can be described as a physical occurrence, where particles tend to build up on the catalyst surface and prevent contact between the substrate and the exhaust gases, or a chemical phenomenon in which molecules directly assault the reactants on the catalyst washcoat and disrupt the chemical reaction.

Presence of P is particularly of concern, because it can react with Ca (also found as part of the engine oil formulation) to form calcium phosphate, which can create a build-up on the catalyst surface. In its volatile form, P has an affinity towards the precious metals in the catalyst washcoat and may disable their ability to react with the exhaust gases. Another theory is that volatile P resides within the porous regions of the washcoat, reducing the catalyst surface area available to interact with the exhaust gasses.

While the theoretical reasons behind phosphorus' impact on catalyst performance are well-researched, it has been difficult

to quantify the exact amount of phosphorous to which the catalyst is exposed as a vehicle accumulates mileage and the catalyst ages, and thereby the damage due to P alone.

In this paper, a detailed discussion of various methods used to chemically deactivate three-way-catalyst via P deposition is reviewed. During the aging process several sets of data are collected which can be used to estimate the actual amount of P to which the catalyst is being exposed (in grams). These calculations are based on inductively coupled plasma mass spectrometry (ICP) oil analysis at the end of a drain interval and records of oil additions and oil consumption. The expected amount of P passing and depositing onto the catalyst via oil consumption and oil volatilization can both be estimated by mass balance. Post-mortem analysis of aged catalysts obtained from several testing methods is done to determine the level of P actually on the catalyst and verify that the estimates based on drain analysis and oil usage records are indeed indicative of the potential catalyst damage.

Pooling results from several different catalyst types, oils and mileage accumulation methods yields a useful correlation in P exposure level calculated by mass balance and actual measured P contamination on the catalyst.

EXPERIMENTAL

As a part of our study to examine various categories of tests sensitive enough to detect P driven deactivation of three way catalysts, we conducted several tests. Three types of these tests are discussed in this paper: field trial, dyno mileage accumulation and catalyst compatibility tests. Tested exhaust systems included four types of modern North American catalyst technologies (2003+) and two types of lubricant formulations.

Oils

In each method of aging, two different 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 formulation tested with the Hyper ZDP™ System represents commercially available ILSAC API GF-4 5W-30 passenger car motor oil whereas the formulation tested with conventional ZDP (pre 2004) represents its predecessor and

provides P retention similar to the many fluids available in the market.

Table 2. Typical Examples of Physical and Chemical Properties of Test Oils

Oil Code	Conventional ZDP	Hyper ZDP™ System
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

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 setup as a measure of P retention and engine durability. While the trial originally started with eight units, four on each oil, two units could not complete the trial.

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. 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

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 optimized to 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 two oil formulations.

Aged Catalysts' Analysis

X-Ray Florescence (XRF)

XRF is the emission of characteristic fluorescent X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental and chemical analysis, particularly in the investigation of aged catalysts. Bulk elemental compositions of catalyst samples taken from the inlet portion of the first brick (when more than one brick) of each of the aged vehicle/catalysis were determined using 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 UniQuant quantitative XRF analysis program.

For some Vehicle+Catalyst types duplicate samples were taken from each side, while for others only a single sample was available. The average phosphorus level across all inlet samples for each unit was considered the best measure of actual phosphorous exposure experienced by that particular catalyst.

RESULTS AND DISCUSSION

For all of the methods studied, drain samples were obtained at each of the mileage/time intervals when the oil was changed. The amount of oil added during the interval or lost from the sump was also recorded. These data were used to estimate P exposure during that interval. Exposure could occur due to volatilization or simply oil consumption/burning. Details of these calculations are in [Appendix A](#). As would be expected, measurement variation and data recording errors can yield odd results: sometimes the estimated phosphorus retention was >100% or the amount of oil loss was negative. These situations would cause the contribution to phosphorus exposure for that interval to be negative, so in these cases the estimated exposure was set to 0. The calculation method here is very simple and differs from other approaches (17), however the results for volatilized phosphorus are virtually identical; the main difference is how much phosphorus comes from burning of the oil.