



Evolutionary Trends in Additive Technologies: Environmentally Superior ZDP

Additives 2007: Applications for Future Transport



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Outline

- Technology Drivers:
 - Increased performance severity
 - Emissions regulations / Aftertreatment devices
 - Increasing elemental constrains
- Novel ZDP technology:
 - Overall field performance
 - Exhaust catalyst and emissions performance
- Summary



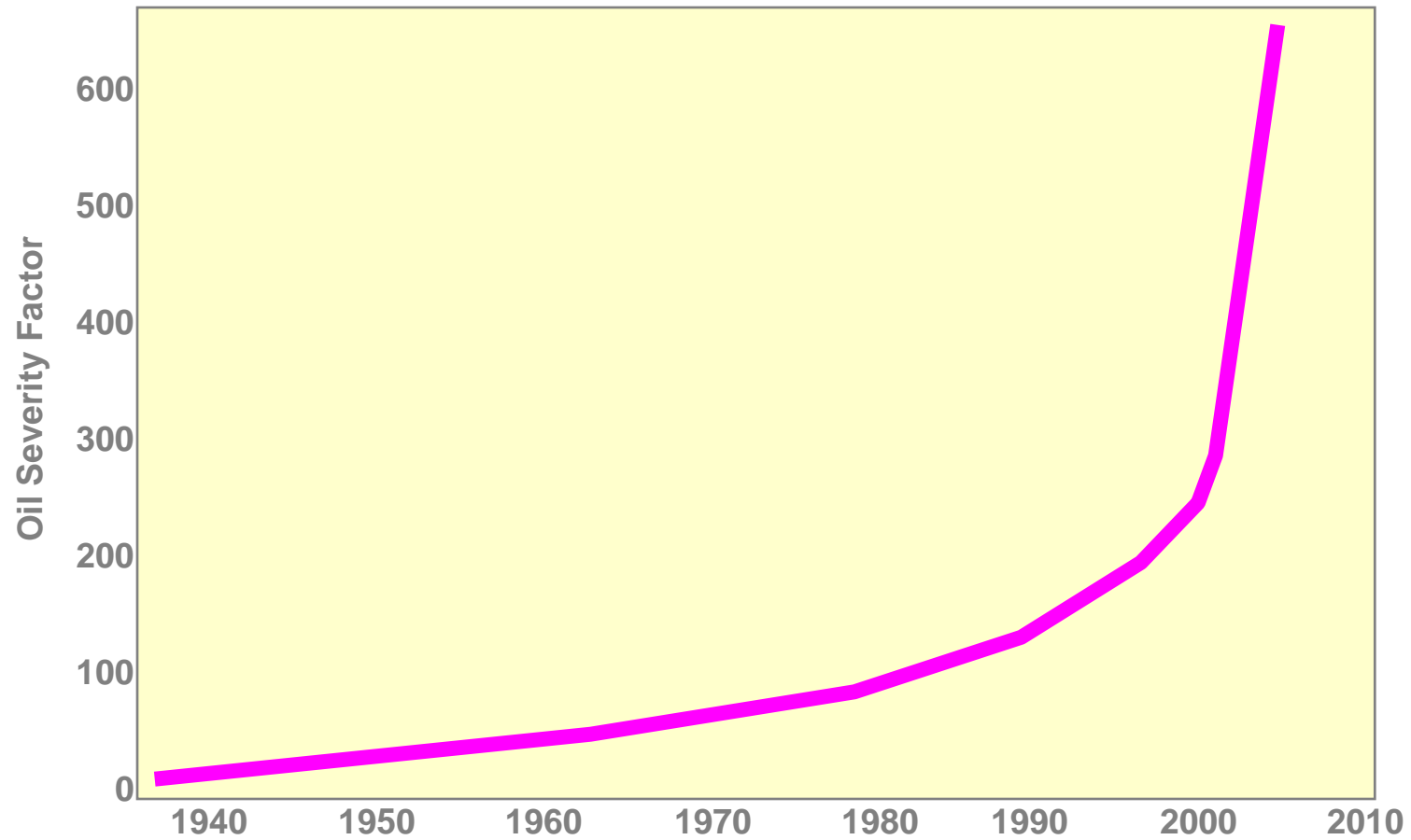
Technology Drivers



Challenges & Opportunities

- Emission regulations are driving change globally
- Base Oil quality/supply changing, viscosity grades changing
- Changes in fuels,
 - Biofuel becoming more prevalent in Europe
 - Push to use E85 in North America
- 2010 to 2012 we will be in the midst of overlapping upgrades ---GF-5, ACEA 2010, PC-11, AP Upgrades.
- Chemical and physical property changes are narrowing our formulating flexibility

Historical Oil Severity Factor Trends



Contributing Factors to Increased Oil Severity Trend Include:

- Extended oil drain intervals
- Potential issues related to use of EGR impact on TBN levels and increased corrosion
- Increased oil temperatures from higher power density engines and smaller oil sumps
- Increased contaminant levels like soot - need for soot-induced antiwear protection

Overall Picture for Transportation Industry

- Keeping the oil longer, exposing it to a harsher environment, and restricting the use of multifunctional components like ZDP to address emissions requirements
- Advancements in engine design and lubricant technology have enabled our industry to meet these challenging times



Global Emissions Regulations Impact on Formulation Strategies



Light-Duty Emissions

	Euro IV Jan. '05	Euro V Mid.' 08	US Tier 2 Bin 5 Jan. '04-'07
PM	0.025 (g/km)	0.005 (g/km)	0.010 (g/mile) or 0.006 (g/km)
NOx+HC	0.30 (g/km)	0.25 (g/km)	n/a
NOx	0.25 (g/km)	0.20 (g/km)	0.07 (g/mile) or 0.04 (g/km)
HC	n/a	n/a	0.09 (g/mile)
CO	0.50 (g/km)	0.50 (g/km)	4.2 (g/mile) or 2.6 (g/km)

Aftertreatment Technology and Lubricant Interactions

	Application	Solution	Concern
Euro IV / V	Passenger Car Heavy Duty Diesel	LNT / DPF SCR / DPF	S/P/Ash S/P/Ash
GF-4 / GF-5	Passenger Car	TWC	P
API CJ-4	Heavy Duty Diesel	DPF	S/P/Ash

Work is ongoing to validate which elements are detrimental to some systems, the effects of phosphorus on TWC is well documented

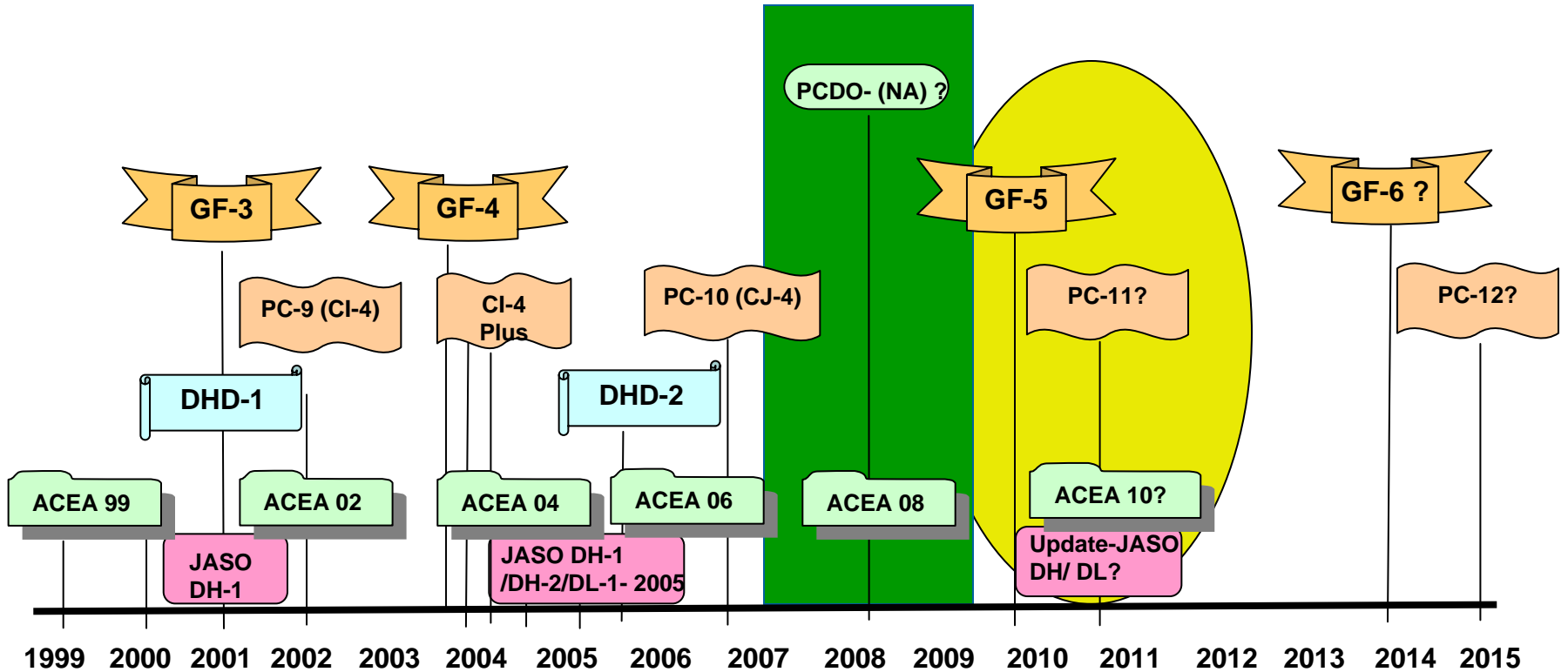
Can ZDP's be optimized for emissions to help mitigate phosphorus deactivation of TWC?

Primary Performance Effects of Elemental Restrictions

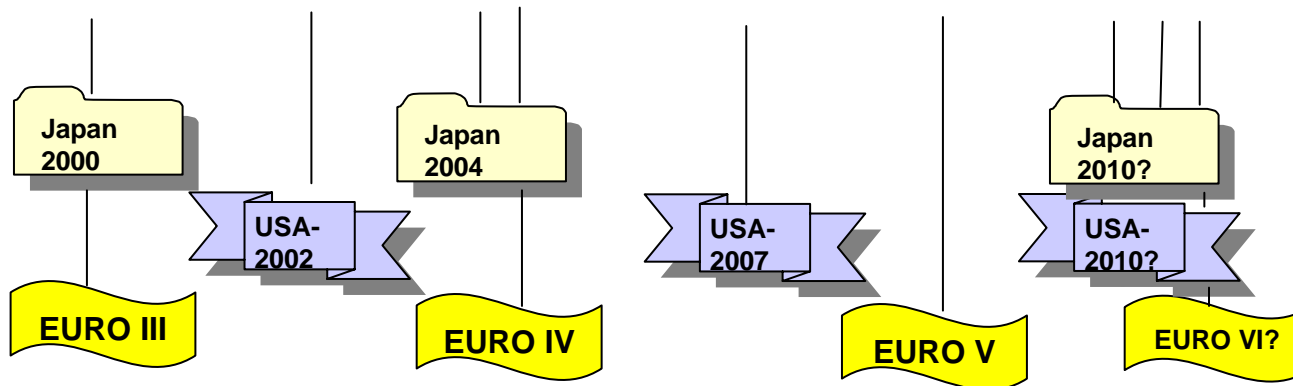
Chemical Restraint	Formulation Restraint	Concern
Sulphur	ZDP	Wear Oxidation
	Detergents	Piston Deposits Corrosion
	Base Oil	Capacity Flexibility
Phosphorus	ZDP	Wear Oxidation
Ash	Detergents	Piston Deposits Corrosion, Drain Intervals
	ZDP	Wear Oxidation

The elements that are targeted for restriction form the very basis of today's lubricants for over 50 years

Lubricant Specifications



Emissions Regulations





Environmentally Friendly ZDP Technology



Emissions-Friendly ZDP

- ZDPs control wear, oxidation and corrosion
- ZDPs can also impact TWC through phosphorus volatilization
- Lubrizol's low volatility ZDP is designed to minimize volatile phosphorus species that can exit the engine and accumulate on catalyst active sites, reducing their effectiveness.

ZDP properties, including volatilization depend on the starting alcohols, higher MW alcohols tend to volatilize less

ZDP Type	R-Group Chain Structure
Short-Chain Primary	$ \begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \\ \\ \text{C} \end{array} $
Short-Chain Secondary	$ \begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} - \end{array} $
Medium-Chain Secondary	$ \begin{array}{c} \text{C} \\ \\ \text{C} - \text{C} - \text{C} - \\ \quad \\ \text{C} \quad \text{C} \\ \\ \text{C} \end{array} $
Long-Chain Primary	$ \begin{array}{c} \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \\ \quad \quad \\ \text{C} \quad \quad \text{C} \end{array} $

Lubrizol Modes of ZDP Decomposition

The starting alcohol can impact the type of ZDP decomposition, thermal leads to formation of a protective antiwear film

- Thermal
- Hydrolysis
- Chemical:
 - ✓ oxidation
 - ✓ acidic
 - ✓ nitration

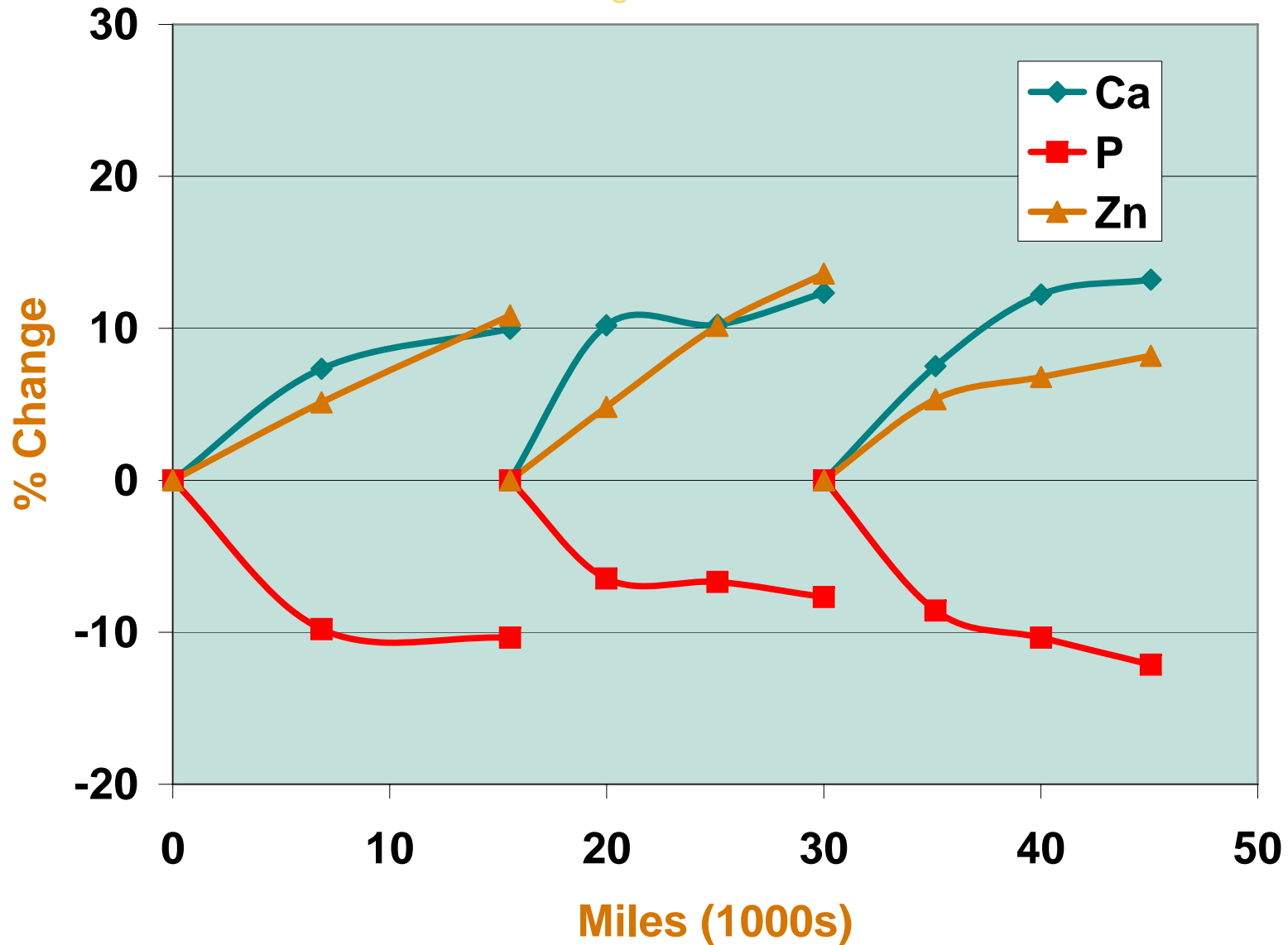
LV-ZDP is made with an optimized mixture of alcohols that minimizes volatility while maintaining the traditional performance of conventional ZDP

ZDP Decomposition Products

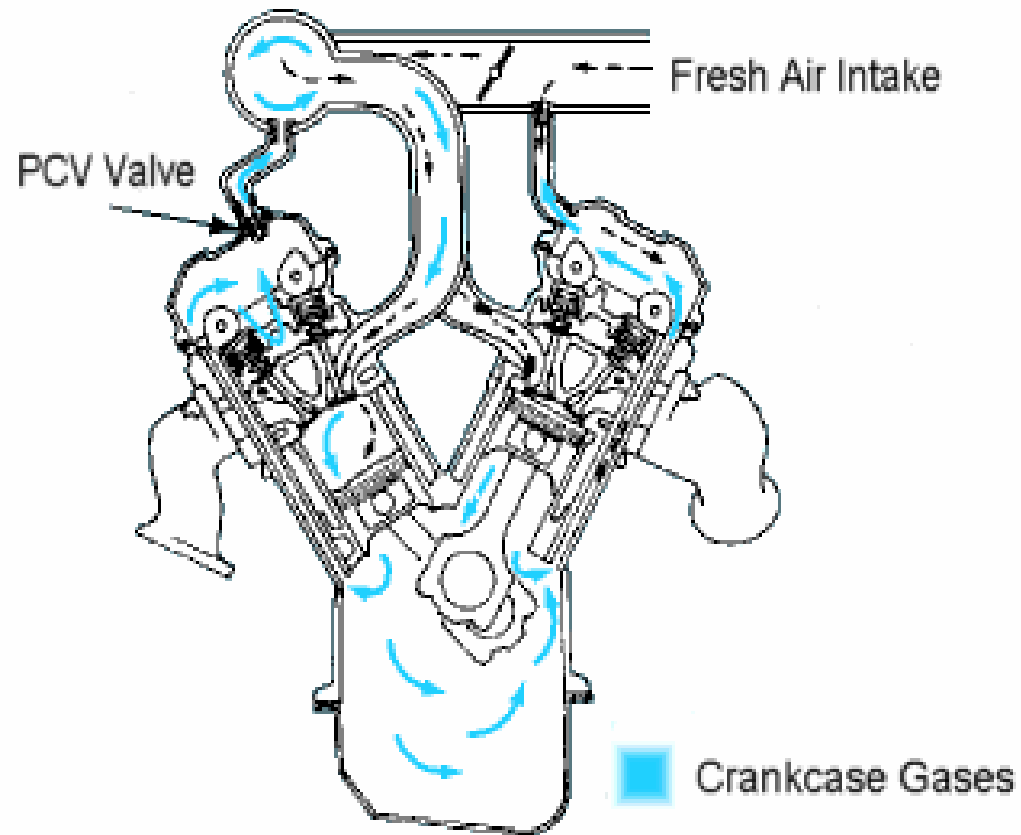
Basic ZDP	$(RO)_2P(O)SH$	$(RS)_3P(O)$
$[(RO)_2P(S)S]$	$(RO)_2P(S)OR'$	$(RS)_2P(O)OR'$
$(RO)_2P(S)SH$	$(RO)_2P(O)OR'$	RSH
$(RO)_3(S)$	$(HO)_3P(O)$	H_2S
$[(RO)_2P(S)OH]_2S$	$[(RO)_2P(S)]_2S$	RS_xR'
$(RO)_2P(S)OH$	$Zn_2P_2O_7$	Olefins
$(RO)_2P(S)SZn(OH)$	$Zn_3(PO_4)_2$	ROH

Field Drain Analysis

% Change in Elements



Positive Crankcase Ventilation



Summary

- ZDP properties including volatility, depend on starting alcohols
- ZDP decomposes into numerous species, many contain phosphorus
- Catalyst poisoning is a complex process involving
 - **Decomposition**
 - **Volatilization**
 - **Oil Consumption (minor)**
- Catalyst poisoning may be reduced with engine design, changes in catalysts technologies, and modifications in ZDP alcohol backbone structure that minimizes phosphorus volatility without sacrificing other performance attributes

New York City Taxi Cab Test - Description

- Vehicles: 2003 T2B7 Ford Crown Victoria 4.6L V8 taxis
- Test duration: 100,000 miles
- Oil change interval: 5,000 miles
- Service: moderate to high-temperature urban driving
- Two oils: ILSAC GF-4, 5W-20, 0.076% P
 - 1) Conventional ZDP
 - 2) Low-volatility ZDP (LV-ZDP)
- Evaluations:
 - EOT engine parts inspection
 - Used oil analyses
 - Aged catalyst FTP emission efficiency tests at SwRI
All catalyst systems evaluated with slave vehicle
 - Post mortem aged catalyst analysis

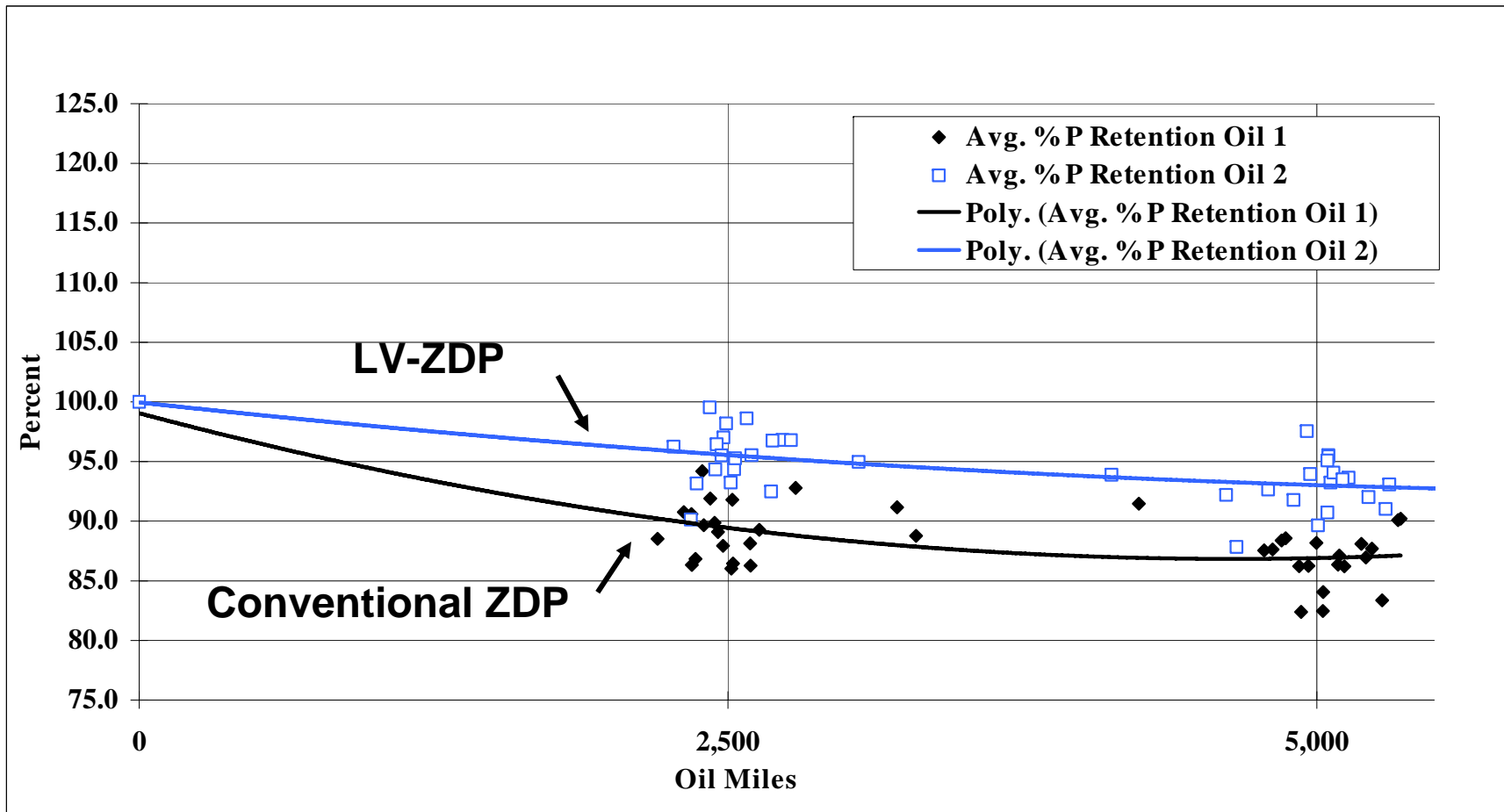
Performance Comparison of ZDP Additives

- Extensive engine inspections at EOT indicate both types of ZDP technologies provide excellent oxidation control, wear protection and sludge/varnish cleanliness.
- Used oil analysis of wear metals and oil condition indicated equivalent performance of the two test oils.

Used Oils Analysis @ 100K miles

Fluid Performance	LV-ZDP vs. Conventional ZDP
% P Loss	Better
Pentane insolubles	Equivalent
C=0	Equivalent
RONox	Equivalent
MRV-35, CCS	Equivalent
Wear metals	Equivalent
TAN/TBN crossover	Equivalent
% Viscosity increase	Equivalent

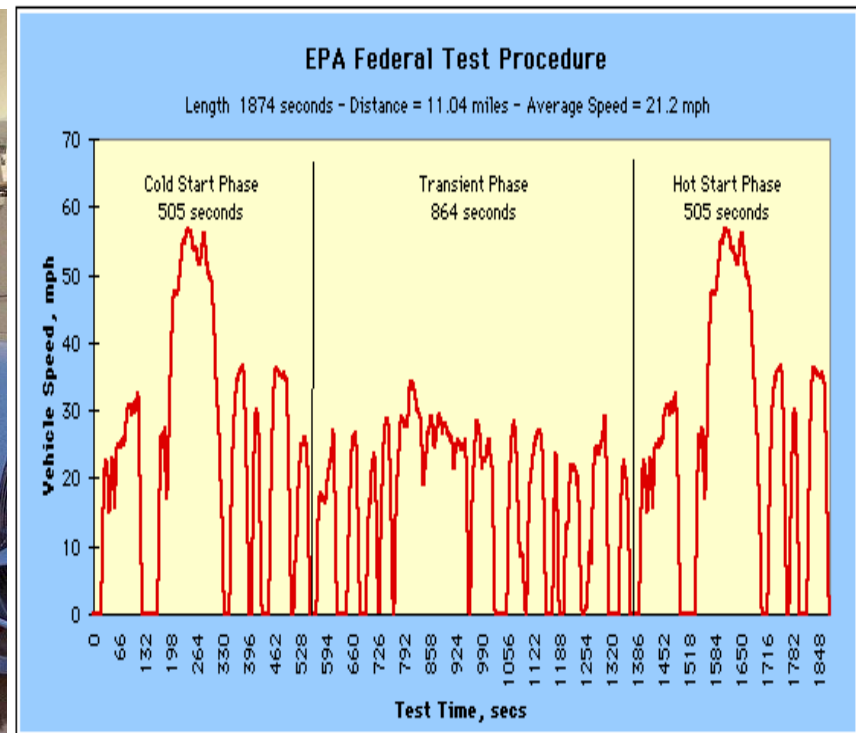
% Phosphorus Retention in Oil Drains: Phosphorus Retention of Conventional ZDP is 50% lower than Phosphorus Retention of LV-ZDP



Crown Victoria: Exhaust System Light-Off Catalyst (right side)

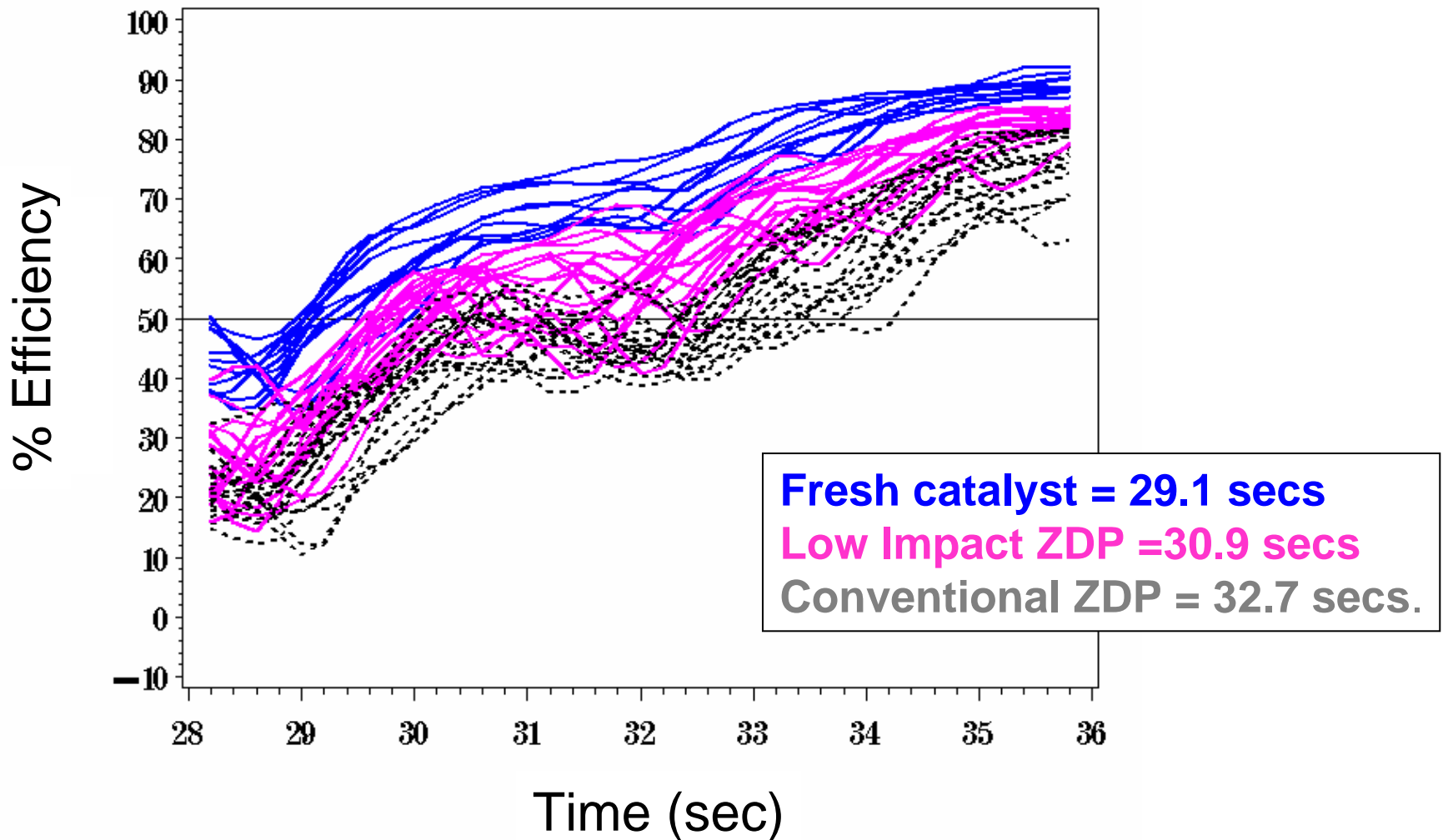


Used Catalyst Efficiency Assessments: FTP-75

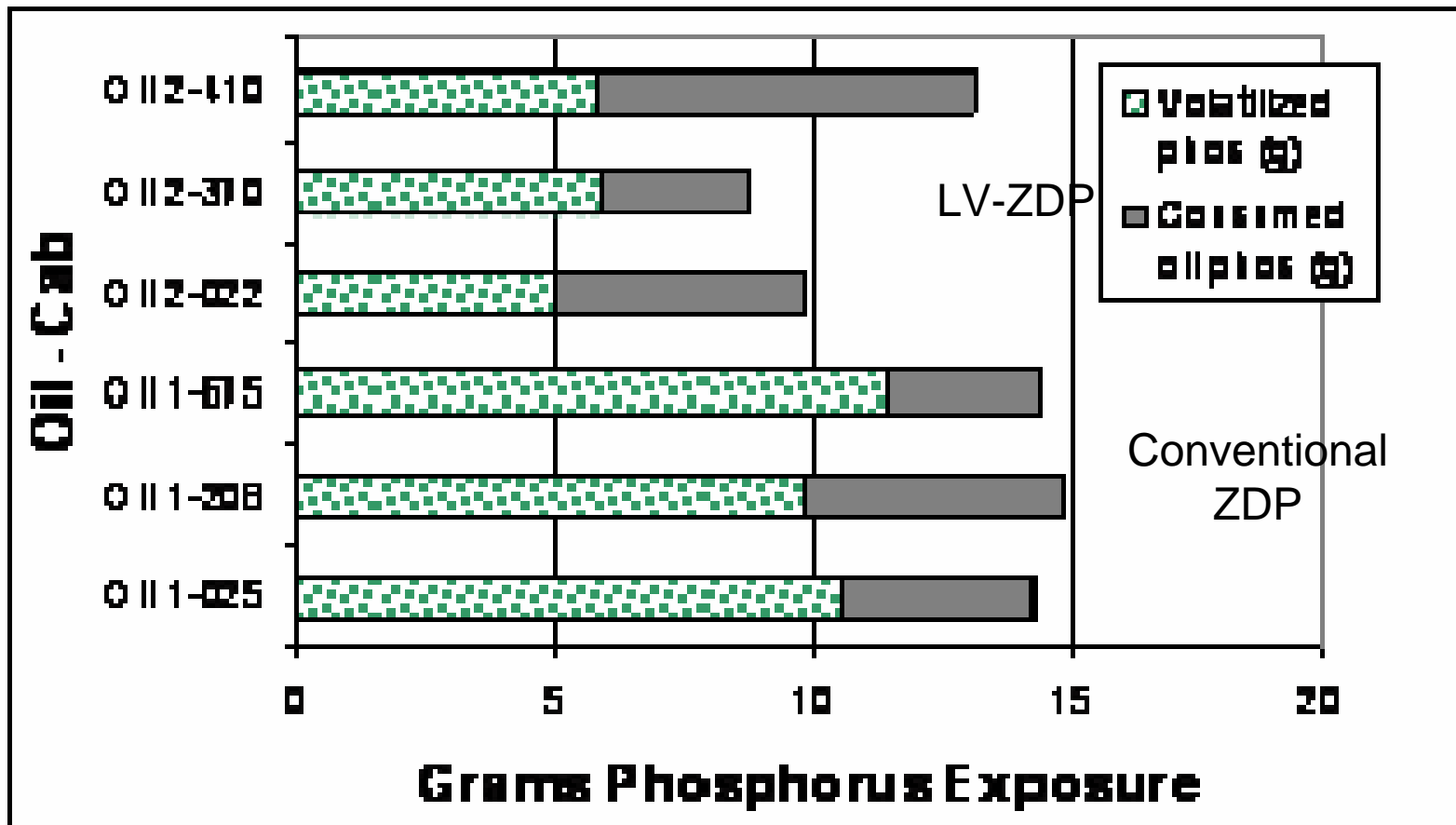


Data Examined: CO, **NO_x**, THC, and **THC Light-Off Time (Bag 1)**

Positive Effect of Low Impact ZDP on THC Light-Off Cat Efficiency: Observed Statistically Significant Differences

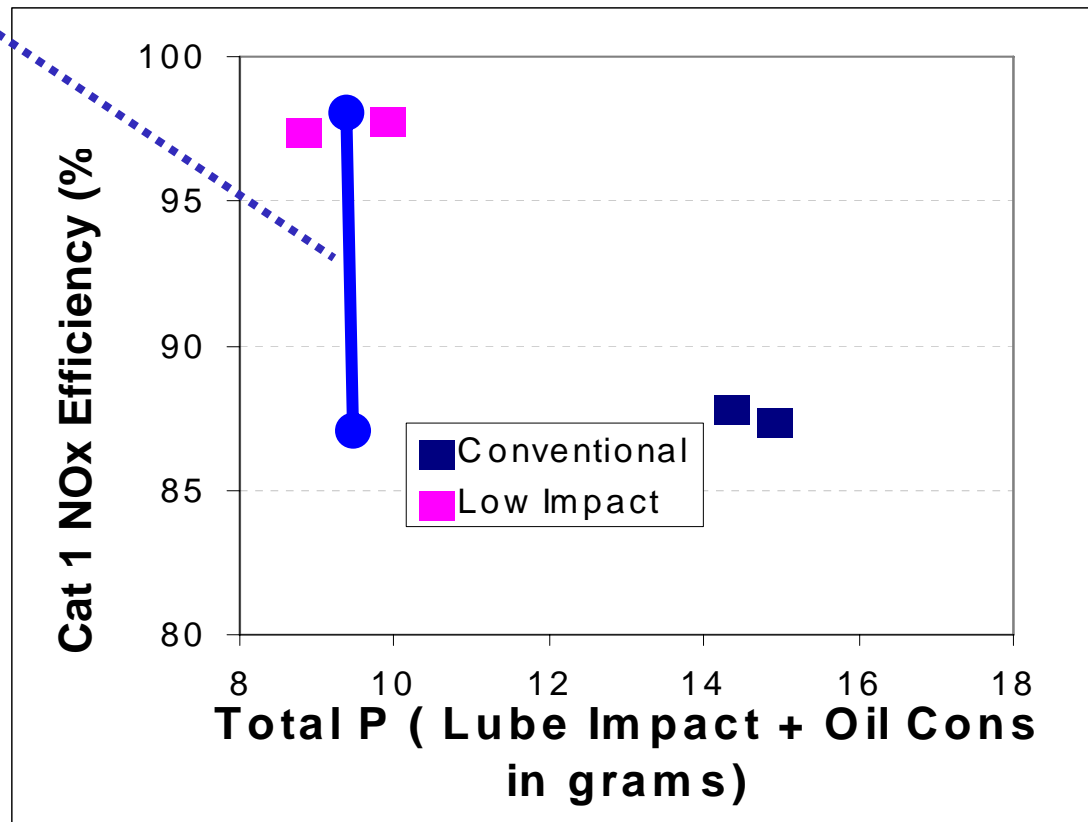


Maximum Amount of Phosphorus (grams) Catalysts Could be Exposed to from OC and Volatility



Statistically Significant Improvements in NOx Efficiency Related to P Exposure Over FTP Cycle

10.3 percentage point difference

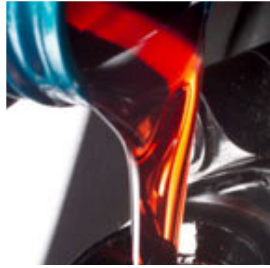


Field Test Summary

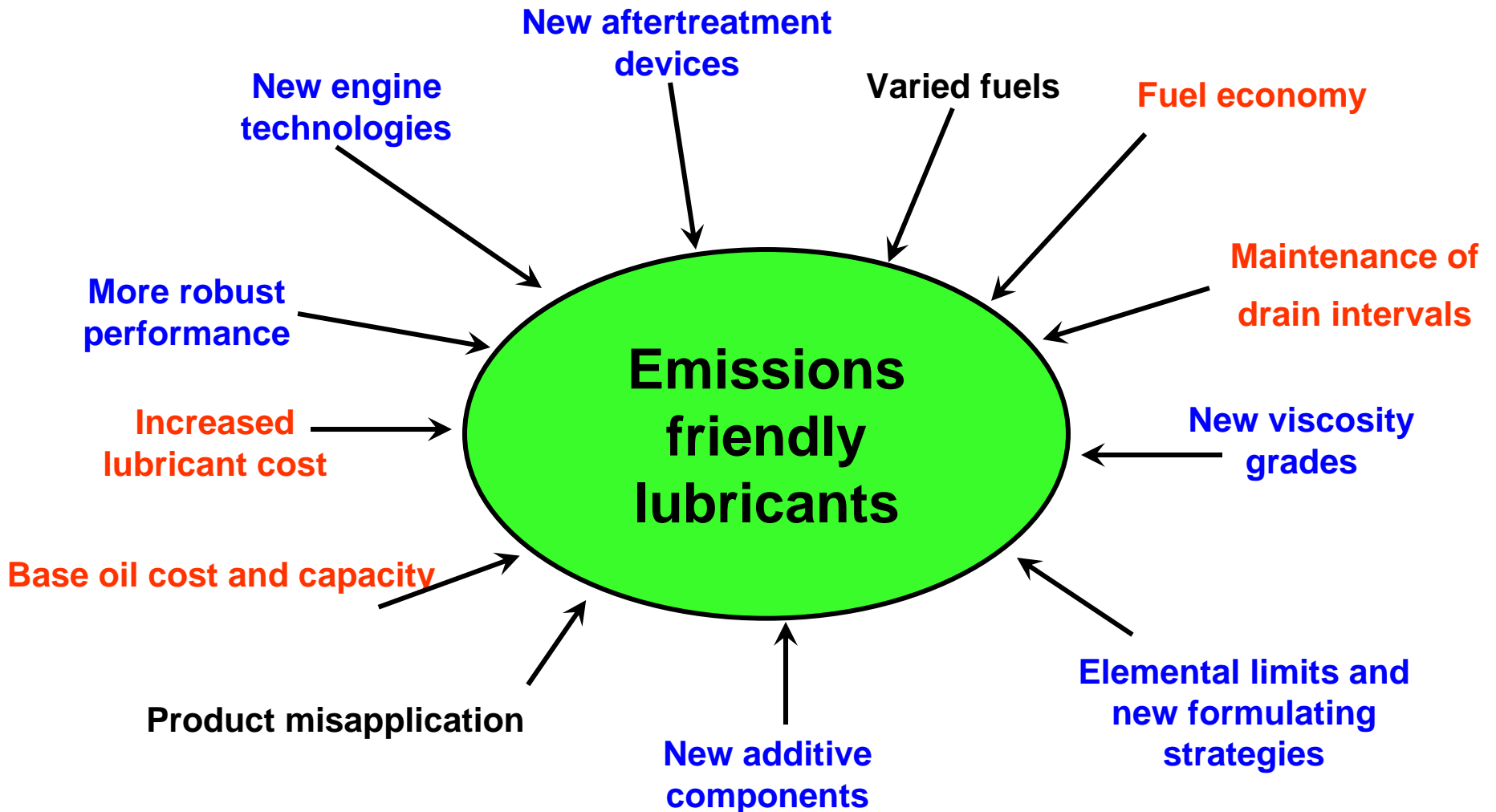
- New York City taxi trial conducted with 0.076 % P, GF-4 fluids demonstrated that Lubrizol's environmentally superior ZDP:
 - Keeps P in crankcase oil
 - Maintains excellent antiwear/antioxidancy performance in the field
 - Deposits less P on the catalyst, resulting in statistically significant
 - » Improved THC light-off time
 - » Lowered NOx emissions



Conclusions



Challenges for Future Engine Lubricant Technologies



Summary

- The use of exhaust aftertreatment will result in a significant change in lubricant design and application
- Future aftertreatment compatible lubricants will require a fine balance to maintain
 - Engine and emissions systems durability
 - Oil drain intervals and fuel economy
- Significant advancements in ZDP technology have been made to establish prototypes meeting these demands.

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