
Phosphorus Volatility Bench Test

ESCIT Meeting

May 4th , 2006

Afton Chemical

Richmond, VA

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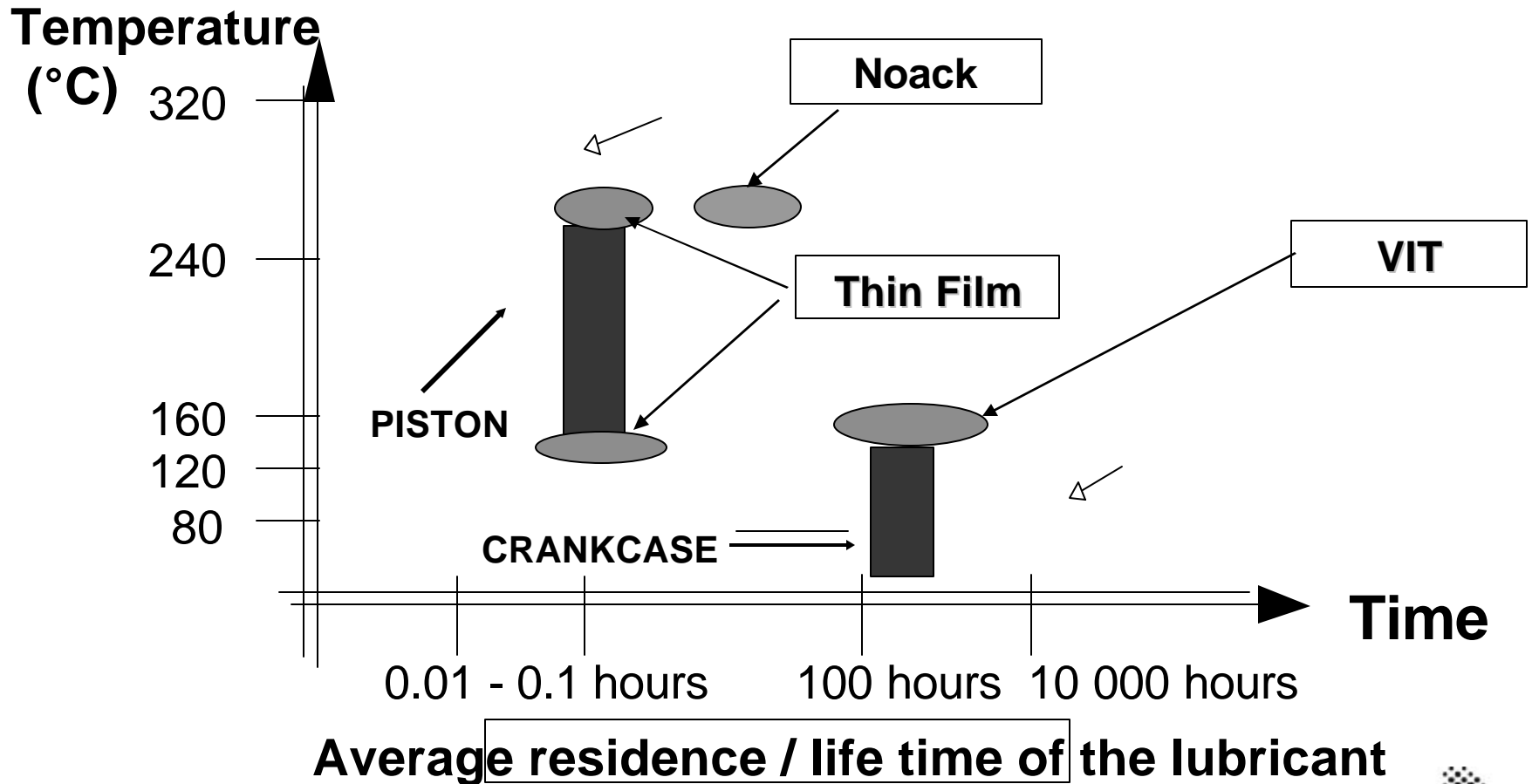
Phosphorus volatility

- Contamination of exhaust gas catalysts might be due to
 - entrainment of oil or
 - to the evaporation of P containing additives or of their degradation products
- Volatilization of P containing additives might also reduce the protection against wear
- Two procedures for the evaluation of phosphorus losses due to evaporation from formulated oils (0.03 % P in Euro IV oil) have been used:
 - over a *thin film* at 150 and 250°C for 10 minutes
 - from the *bulk* at 160°C



Test Procedure for Measuring Phosphorus Volatility

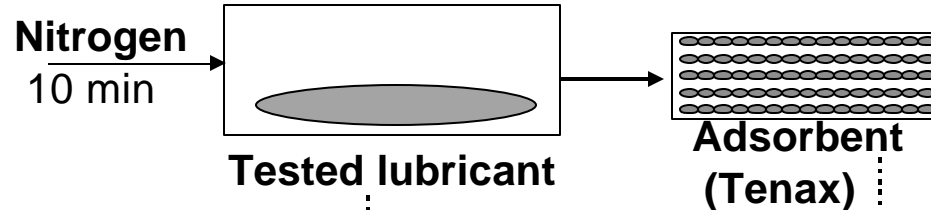
Defining appropriate test conditions (**exposure**)



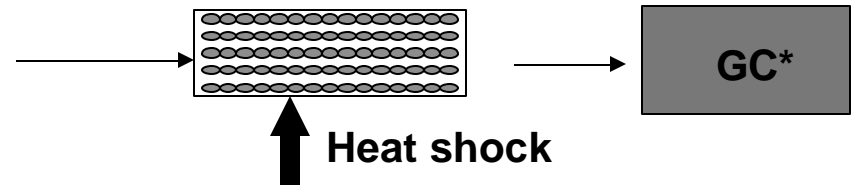
Thin film N₂ stripping: experimental details

Step

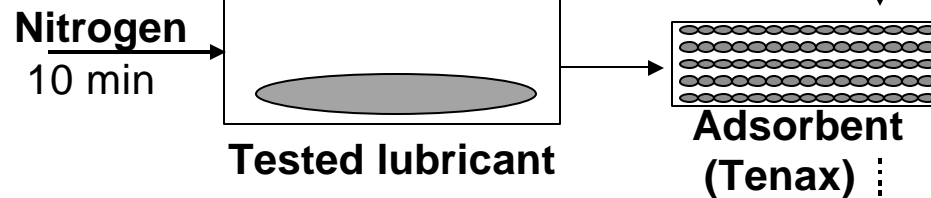
1) Stripping and adsorption
150°C



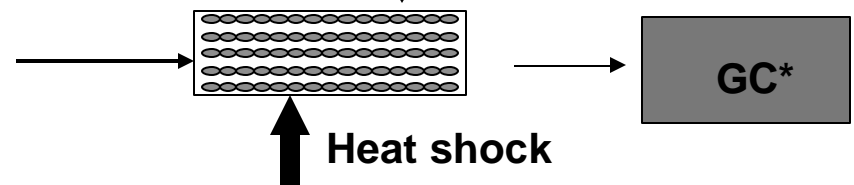
2) Desorption and analysis



Stripping and adsorption
250°C



3) Desorption and analysis



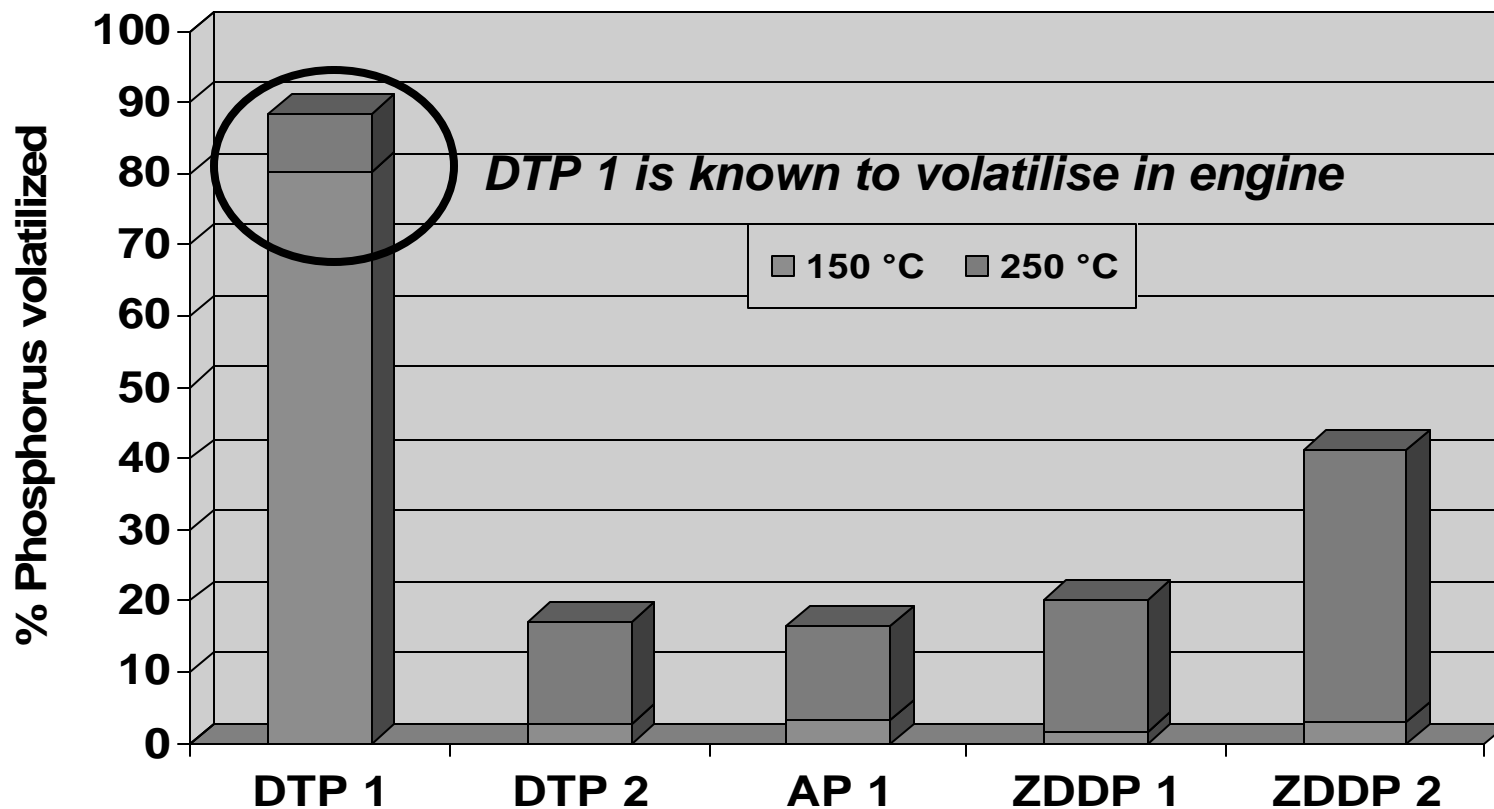
* Gas Chromatograph with, in parallel, a phosphorus detector and a FID (C, H)

Thin film N₂ stripping addresses piston ring/liner model



Phosphorus losses from *thin oil layers*

Losses are measured as volatilisation of phosphorus from formulated oils (0.03 % P in Euro IV oil) over a thin film at 150 and 250 °C for 10 minutes

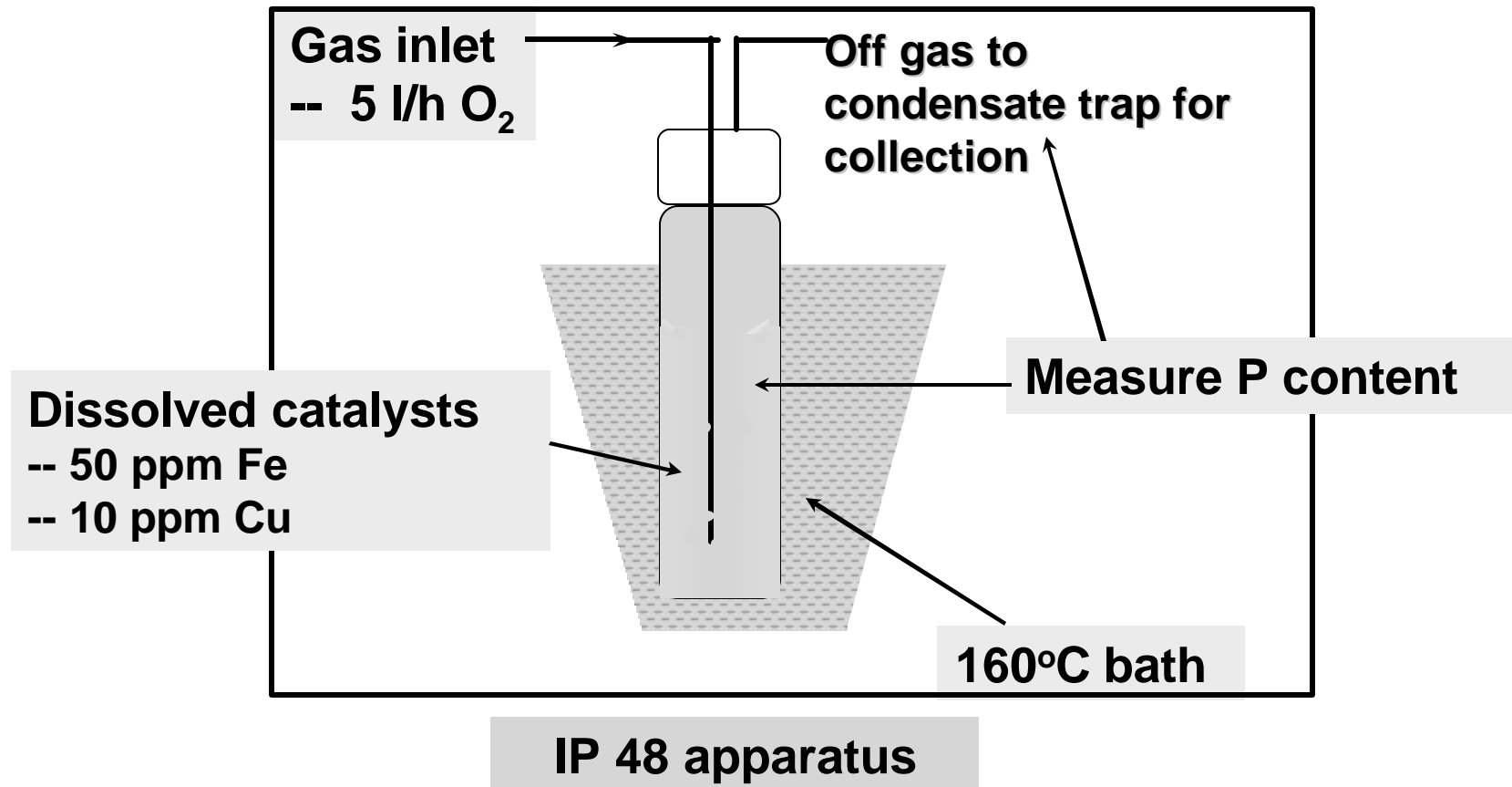


Noack PEI ₂₅₀ :	108	90	6	8	20
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Phosphorus losses from *bulk oil*

Realistic Exposure and Ageing conditions

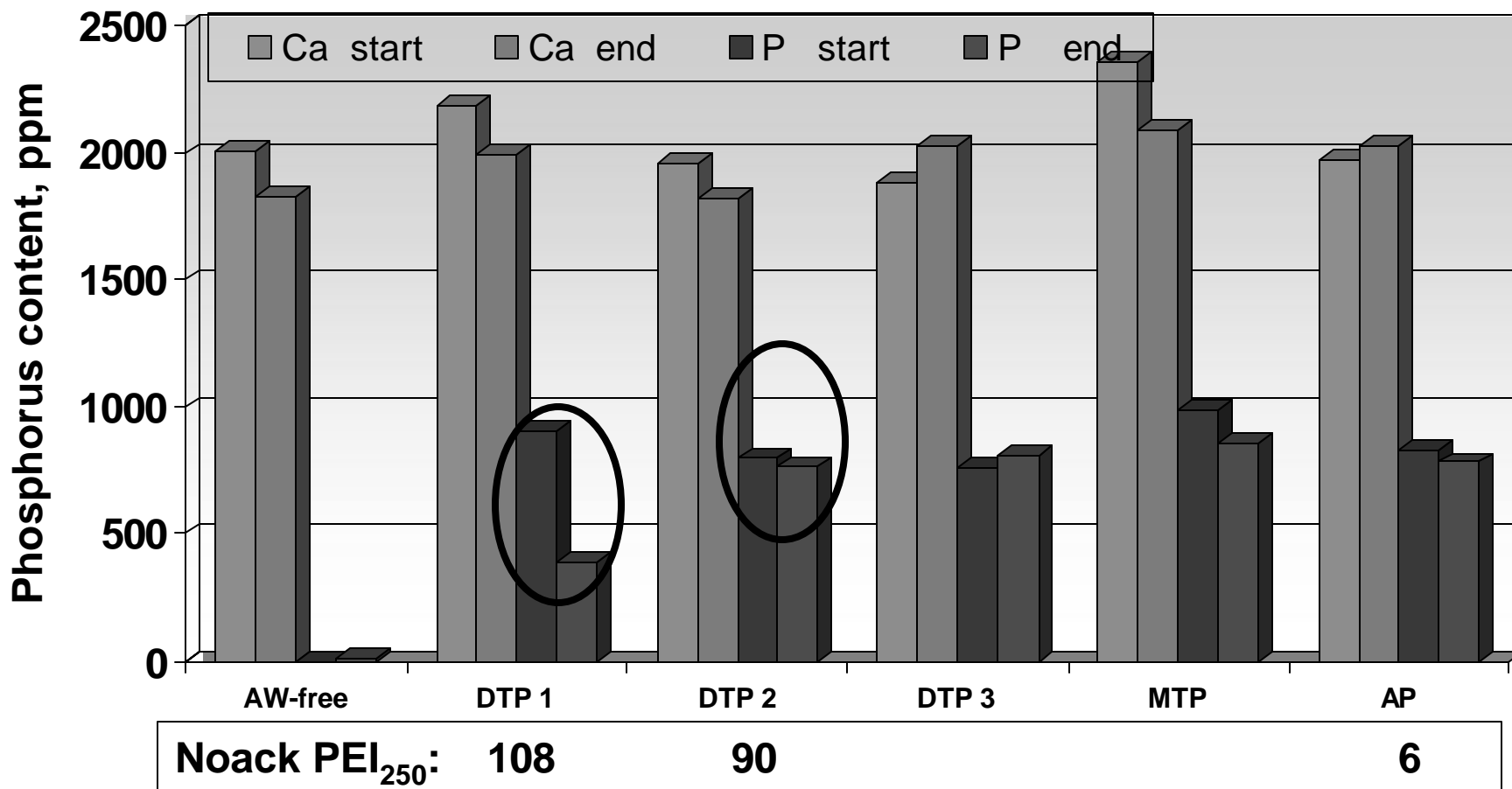


Bulk oil aging addresses the crankcase model



Phosphorus losses from *bulk oil*

EURO IV prototype oil



DTP 1 is known to volatilize in engine

Whereas DPT2 does not.

AW Performance in the OM 611

Two 5W-40 DB 228 candidate oils were tested in the OM611 from two different ashless AW systems :

- Candidate 1 containing 650 ppm phosphorus
- Candidate 2 containing 650 ppm phosphorus

OM611 Test Results	Ashless AW Candidate 1	Ashless AW Candidate 2	DB 228.5 Limit
kV100, mm ² /sec	14.3	13.2	
P content, ppm	647	701	
Camshaft intake wear, μm	155	91	120 max.
Camshaft exhaust wear, μm	208	134	140 max.
Cylinder liner wear, μm	2.3	2.1	5.2 max.
Piston rating	30	29	27 min.
CRBWL, mg	1.0	0.5	2.1 max
Main BWL, mg	0.2	1.3	2.1 max.
Timing chain, % elongation	0.38	0.32	0.4 max.
Sludge rating	9.10	9.18	9.0 min.
EOT P, ppm	680	770	--
EOT Fe, ppm	740	701	--
EOT Cu, ppm	23	30	--



Catalyst Compatibility

- Engine bench aging of three-way catalyst (TWC) was used by operating an engine with fuel doped with engine oil.
- The **ash accumulation profile** & the **total amount of phosphorus** of this catalyst **corresponded quite well** to the profiles and amounts which were measured from over-the-road aged catalysts after 100,000 km.
- Thereby validating the engine bench catalyst compatibility test method.

Candidate oils for Catalyst Compatibility Tests

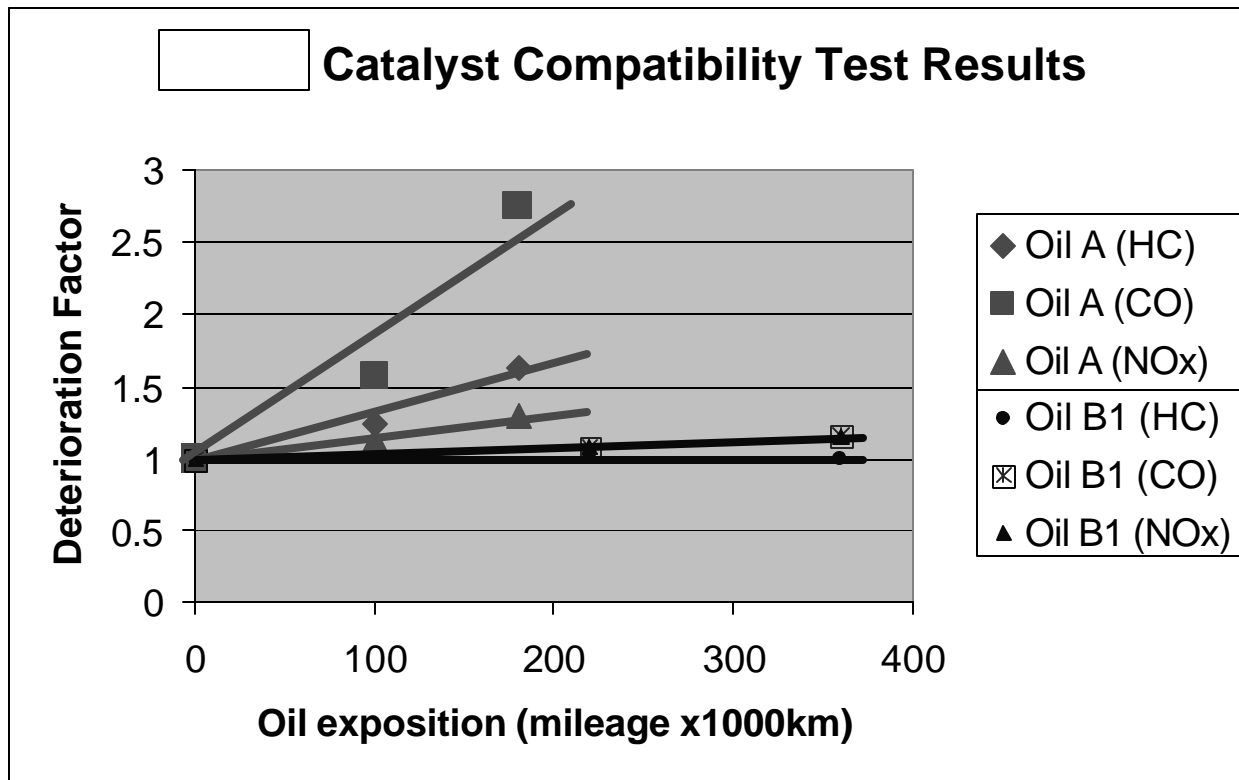
	Type A	Type B1
P, ppm	1080	530
Ca, ppm	1590	2200
Mg, ppm	1000	0
Zn, ppm	1200	0
S, ppm	4080	2000

Ref: Jens Franz et al, SAE 2005-01-1097 Deactivation of TWC as a Function of Oil Ash Accumulation A Parameter Study



Catalyst Compatibility

- Deterioration factors for HC, CO, and NO_x over a FTP-75 for six exhaust systems, three aged with different amounts of oil type A [ZDDP-based] and three aged with oil type B1 [ashless AW-based]. The HC, CO and NO_x emissions increase with increasing exposition of the catalysts to oil type A.



It is clear from the pictures that oil type B1 causes a much lower increase in emission compared to oil type A, even though the total amount of exposed oil is higher.



Conclusions

- For the determination of P losses from engine oils, a test method which relates to actual engine conditions has been identified
 - ✓ The measurement of P losses during a standard bulk oil ageing test (similar to the known industry standard mod. IP 48, ERCOT, Ford ageing test) provide a reliable assessment of the persistency of additives
 - TGA on pure additives cannot reliably predict the emission
 - Stripping from formulated oils for 10 minutes at 250°C is too severe

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