ExxonMobil Phosphorus Volatility Studies

ESCIT

September 28, 2006

Need for Bench Phosphorus Volatility Test

- **Phosphorus in believed to be detrimental to three-way-catalysts used in gasoline engines**
- **No tests are available to quantify this effect**
- **Engine oil specifications today use elemental limits to control the phosphorus impact on TWCs**
- **There is significant interest in developing a laboratory test to measure phosphorus volatilization**
  - To provide better protection for emission catalysts
  - To provide greater formulating flexibility

Phosphorus Volatility Study Overview

- **Comparison of 1° & 2° ZDDP impact on phosphorus volatilization in several tests**
  - PEI
  - Literature
  - TGA
  - IIIG
  - VIB
  - Bulk oxidation test
  - ROBO

ZDDPs Studied & Expected Results

- **Low molecular weight 2° ZDDP & high molecular weight 1° ZDDP were evaluated for phosphorus volatilization**
- **Expected results**
  - 1° ZDDP should volatilize less phosphorus
    - High molecular weight molecules are less volatile
    - 1° ZDDP are more stable than 2° ZDDP

ZDDPs Studied

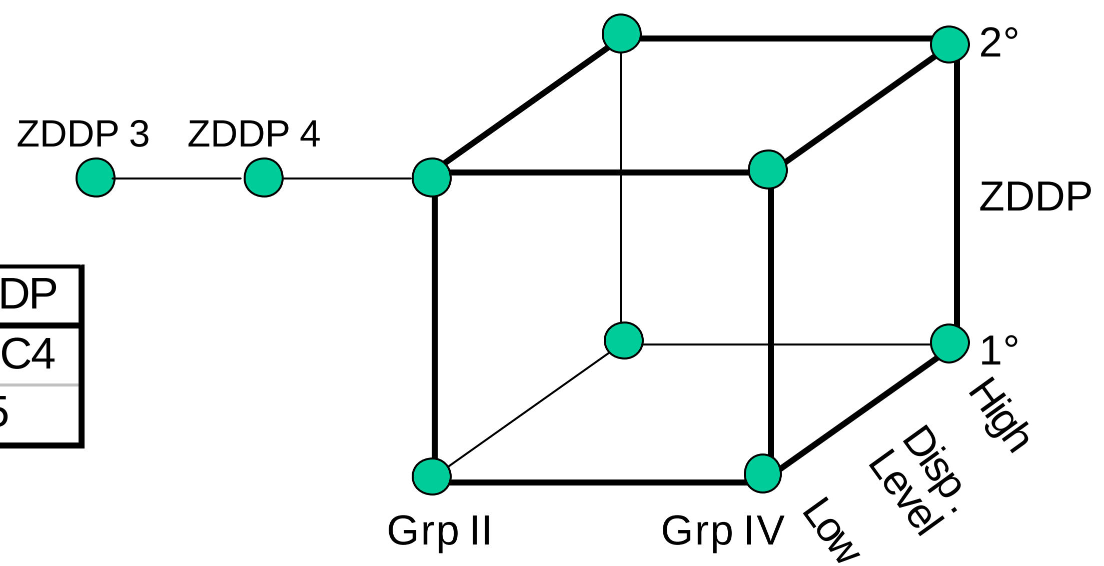
	1° ZDDP	2° ZDDP
R Group	octyl	C3 & C4
MW	771	575

Phosphorus Emission Index Study

Variables Studied

- **Volatility affects (Group II vs Group IV)**
- **Dispersant level (ZDDP complexing agent)**
- **1° vs 2° ZDDP**
- **Alternate 2° ZDDP (ZDDP 3 & 4)**
- **0.075% P**

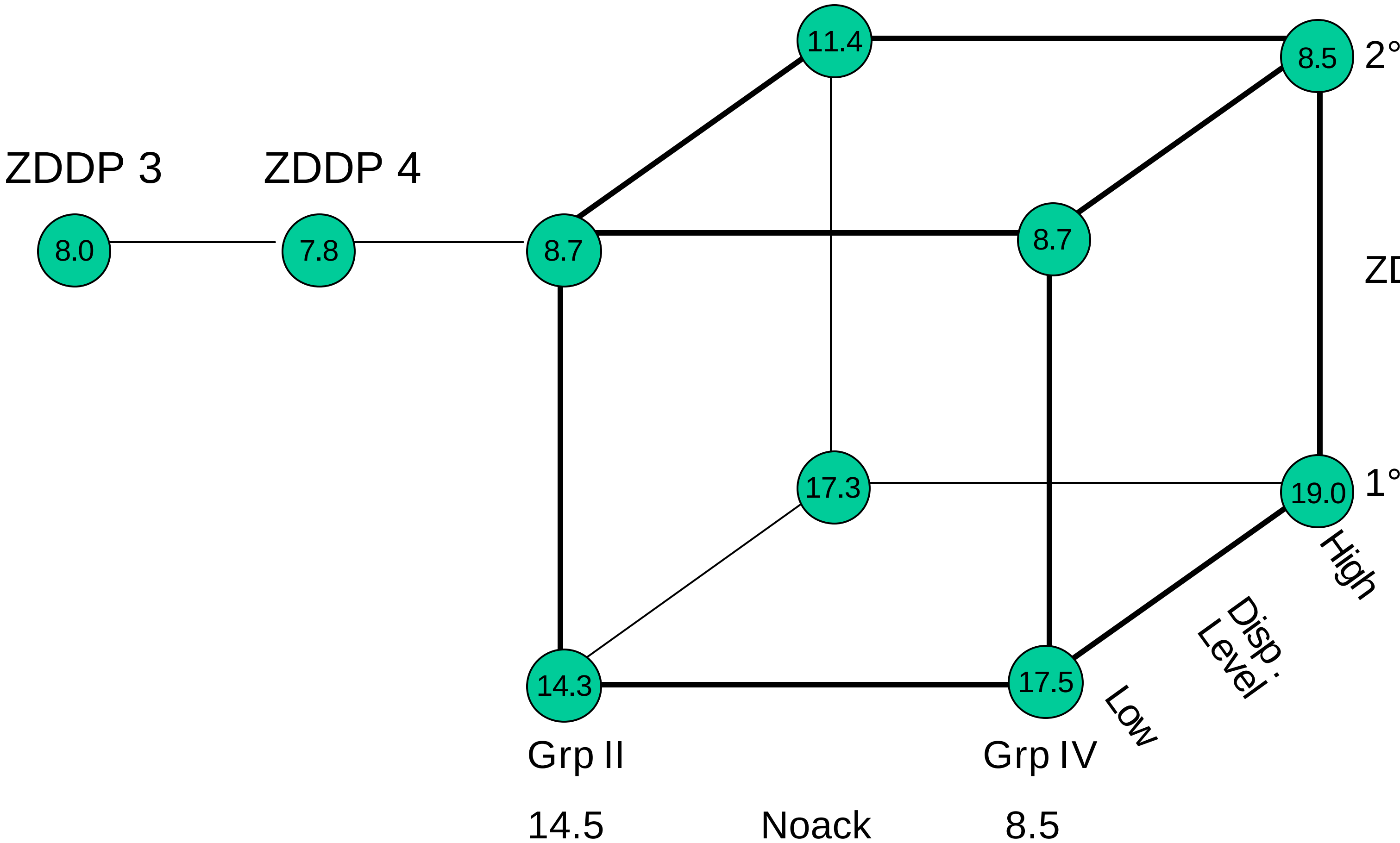
	1° ZDDP	2° ZDDP
R Group	octyl	C3 & C4
MW	771	575



Phosphorus Emission Index Data

PEI of 10 = 1.6% P loss

(bigger number indicates more P volatilization)



Phosphorus Emission Index Conclusions

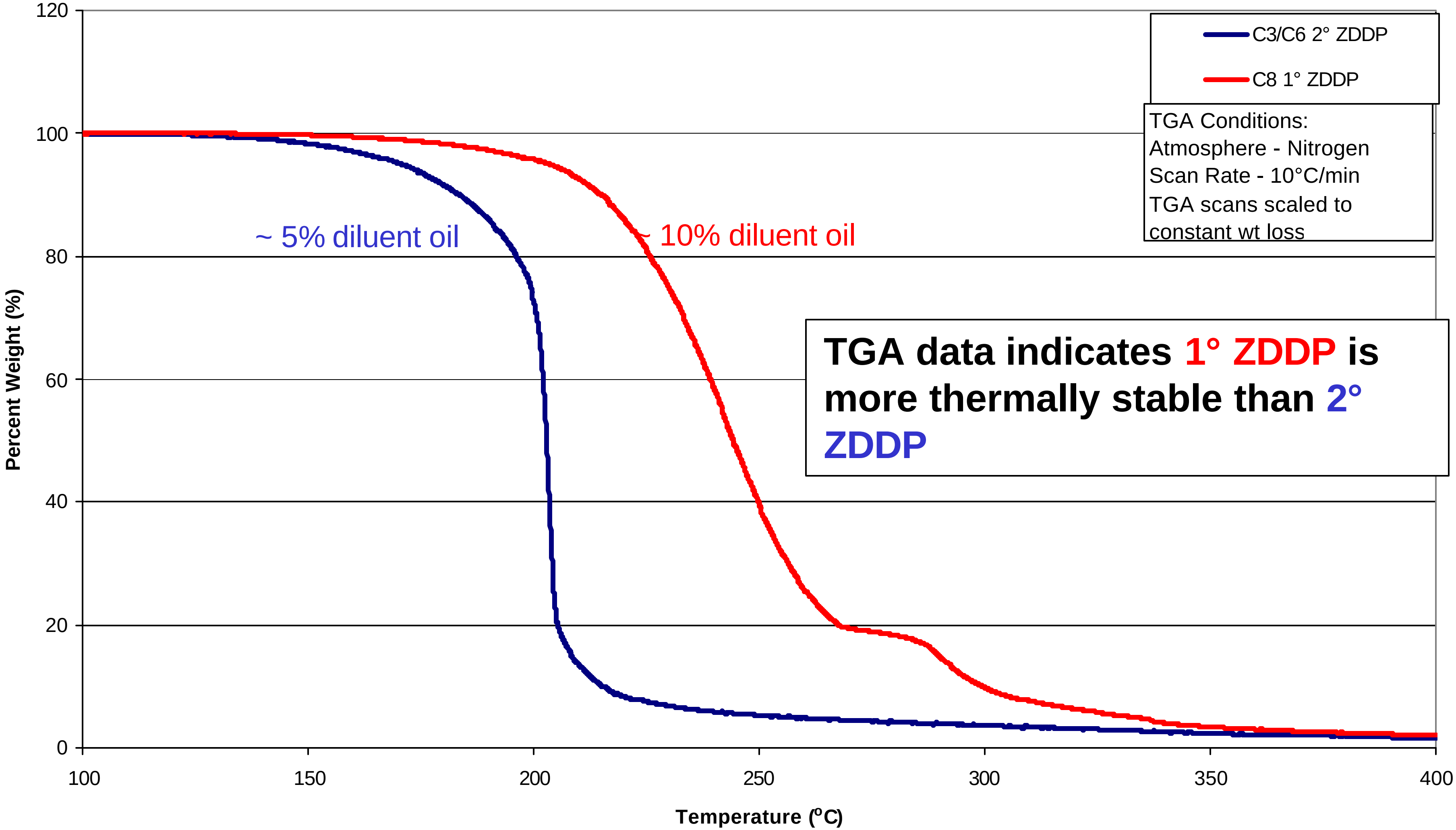
- Main effect is ZDDP type; 2° lower PEI than 1° ZDDP
- Noack volatility has no effect (8-15%range)
- Dispersant effect not statistically significant

- Results agree with PEI literature
  - Phosphorus Additive Chemistry & its Effects on the Phosphorus Volatility of Engine Oil - TSelby
- Results agree with other Selby Noack studies at EM

ZDDP Literature

- **1° ZDDP is more stable than 2° ZDDP**
  - Spikes, Tribology Letters V17, 3, 469-489 (2004)
  - Coy & Jones, ASLE Trans V24, 1, 17-90 (1980)
  - Coy & Jones, ASLE Trans V24, 1, 91-97 (1980)
  - Larson, Scientific Lubrication 12-19 (1958)
  - Born, Hipeaux, Marchand, & Parc, Engine Oils & Automotive Lubrication, 335-358 (1992)
  - Rowe & Dickert, ASLE Trans V10, 85-90 (1967)
  - Bennett, ASLE Trans V2, 78-90 (1959)

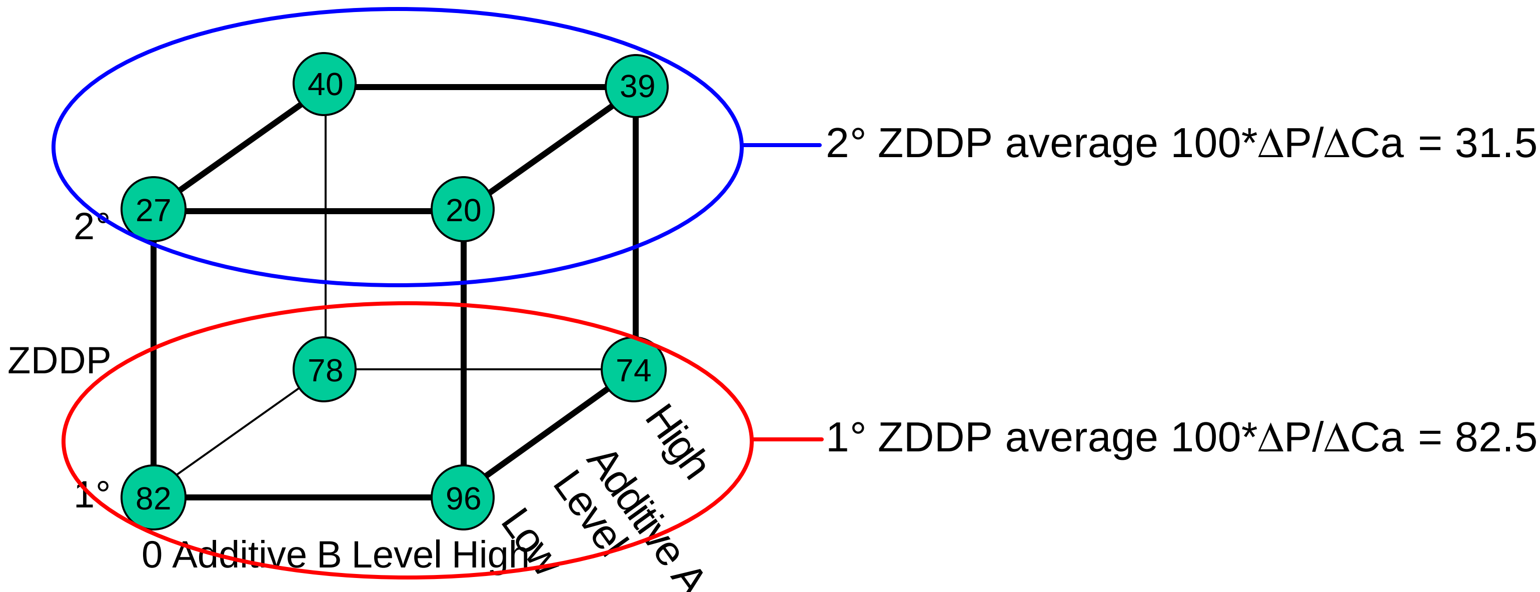
TGA Weight vs Temperature for 1° & 2° ZDDP Samples



TGA data indicates 1° ZDDP is more thermally stable than 2° ZDDP

Phosphorus Volatility - IIIG Data

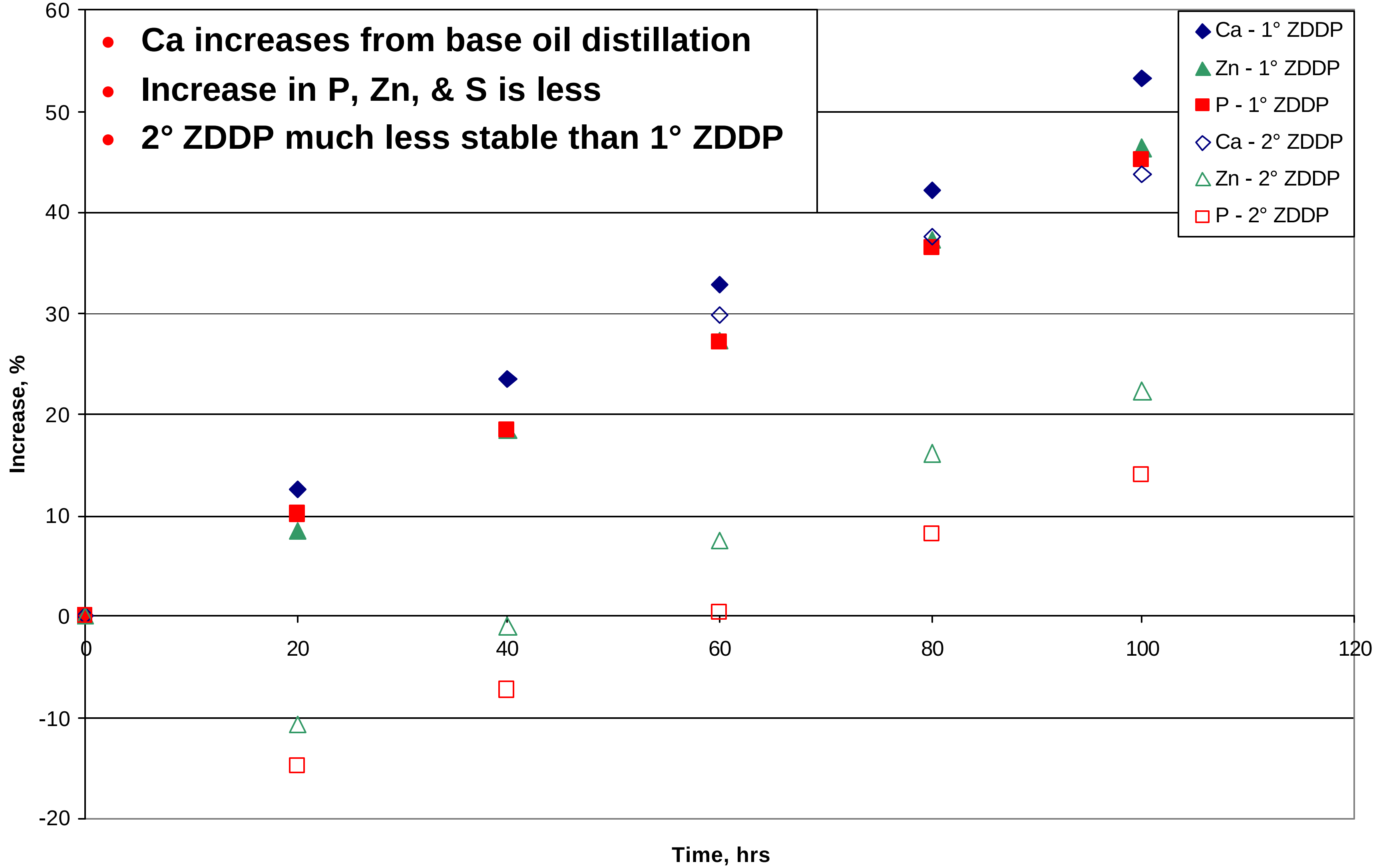
- **Significant amounts of base stock are distilled in IIIG engine test**
- **EOT sump oil analyzed**
- **Ca increase used as a marker**
- **Measure [DP/DCa]*100**
  - +100 = no phosphorus emissions (higher number is better)
- **1° ZDDP has significant P emission benefit over 2° ZDDP in the IIIG**
- **1° ZDDP has significant S emission benefit over 2° ZDDP in the IIIG**



IIIG Phosphorus Emission, 100 = no emission

IIIG Sump Sample Concentration Change

(Data from Slide 7 Presented in a Different Manner)



Sequence VIB Data

- **Consecutive VIB tests run (same stand) on 0W-30 oils blended with 0.075% 1° ZDDP and 2° ZDDP**
- **122 hr sump sample analyzed**
  - 1° ZDDP volatilizes less phosphorus than 2° ZDDP
  - 1° ZDDP volatilizes less sulfur than 2° ZDDP
  - Bias between ICP & XRF

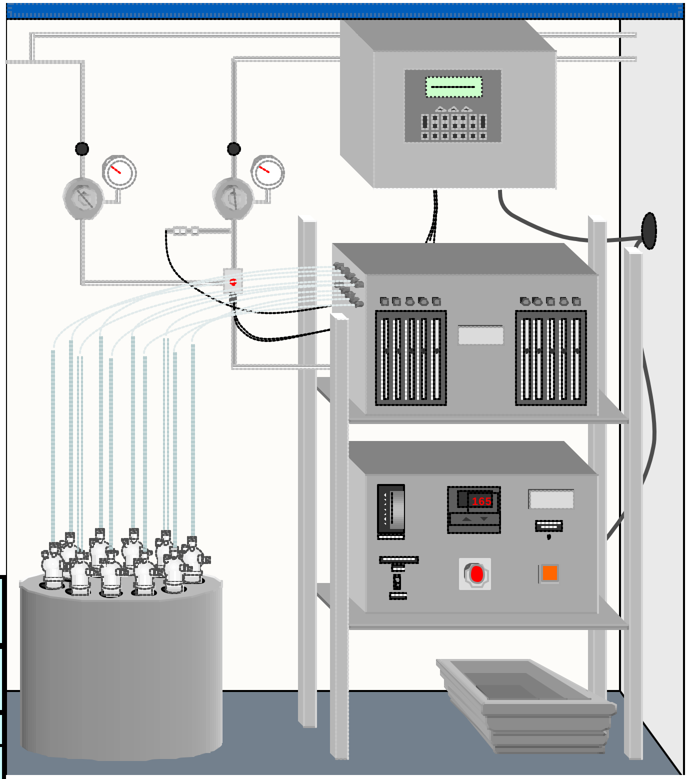
		0W-30 w/1° ZDDP New Oil	0W-30 w/1° ZDDP after VIB	0W-30 w/2° ZDDP New Oil	0W-30 w/2° ZDDP after VIB
D 4951 ICP	Ca, wt%	0.264	0.273	0.263	0.272
D 6443 XRF	Ca, wt%	0.2605	0.2725	0.2592	0.2774
D 4951 ICP	P, wt%	0.077	0.084	0.076	0.071
D 6443 XRF	P, wt%	0.0756	0.0792	0.0753	0.0687

Retained Phosphorus

	1° ZDDP	**2° ZDDP**
ΔP (ICP), %	109.1	93.4
ΔCa (ICP), %	103.4	103.4
DP/DCa (ICP)	**105.5**	**90.3**
ΔP (XRF), %	104.8	91.2
ΔCa (XRF), %	104.6	107.0
DP/DCa (XRF)	**100.1**	**85.2**

Bulk Oxidation Comparison

- **Conditions**
  - soluble iron added to accelerate degradation
  - air bubbled through samples
  - 309 hour test duration
  - 0W-30 oils tested (0.10% P)
- **Results**
  - 1° ZDDP volatilizes less P than 2° ZDDP
  - 1° ZDDP volatilizes less S than 2° ZDDP
  - Bias between ICP & XRF



		0W-30 w/1° ZDDP New Oil	0W-30 w/1° ZDDP after Bench Test	0W-30 w/2° ZDDP New Oil	ZDDP after Bench Test
D 4951 ICP	Ca, wt%	0.2621	0.311	0.254	0.342
D 6443 XRF	Ca, wt%	0.2621	0.3053	0.2621	0.3205
D 4951 ICP	P, wt%	0.1035	0.135	0.1032	0.128
D 6443 XRF	P, wt%	0.1035	0.1177	0.105	0.1103

Retained Phosphorus

	1° ZDDP	**2° ZDDP**
ΔP (ICP), %	130.4	124.0
ΔCa (ICP), %	118.7	134.6
DP/DCa (ICP)	**109.9**	**92.1**
ΔP (XRF), %	113.7	105.0
ΔCa (XRF), %	116.5	122.3
DP/DCa (XRF)	**97.6**	**85.9**

ROBO Comparison

- **Conditions**
  - soluble iron added to accelerate degradation
  - Atmosphere contains air & NO_2
  - 40 hour test duration
  - 0W-30 oils tested (0.10% P)
- **Results**
  - 1° ZDDP volatilizes less P than 2° ZDDP

		0W-30 w/1° ZDDP New Oil	0W-30 w/1° ZDDP after ROBO	0W-30 w/2° ZDDP New Oil	0W-30 w/2° ZDDP after ROBO
D 4951 ICP	Ca, wt%	0.2512	0.4098	0.2512	0.3545
D 4951 ICP	P, wt%	0.0993	0.1542	0.0967	0.1200

Retained Phosphorus

	1° ZDDP	**2° ZDDP**
ΔP (ICP), %	155.3	124.1
ΔCa (ICP), %	163.1	141.1
ΔP/ΔCa (ICP)	**95.2**	**87.9**

Phosphorus Volatilization Conclusions

- **Impact of HMW 1° & LMW 2° ZDDP on phosphorus volatilization in several tests was studied**
- **PEI ranking did not agree with other tests**
  - PEI results suggest more P volatilized from the HMW 1° ZDDP than LMW 2° ZDDP
  - Literature, TGA, IIIG, VIB, Bulk oxidation test, & ROBO indicate that the LMW 2° ZDDP volatilizes more P than the HMW 1° ZDDP
    - Magnitude of Phosphorus loss varies for each test
      - IIIG>VIB
- **Discrimination of phosphorus volatiles is possible with either a bench or engine test**