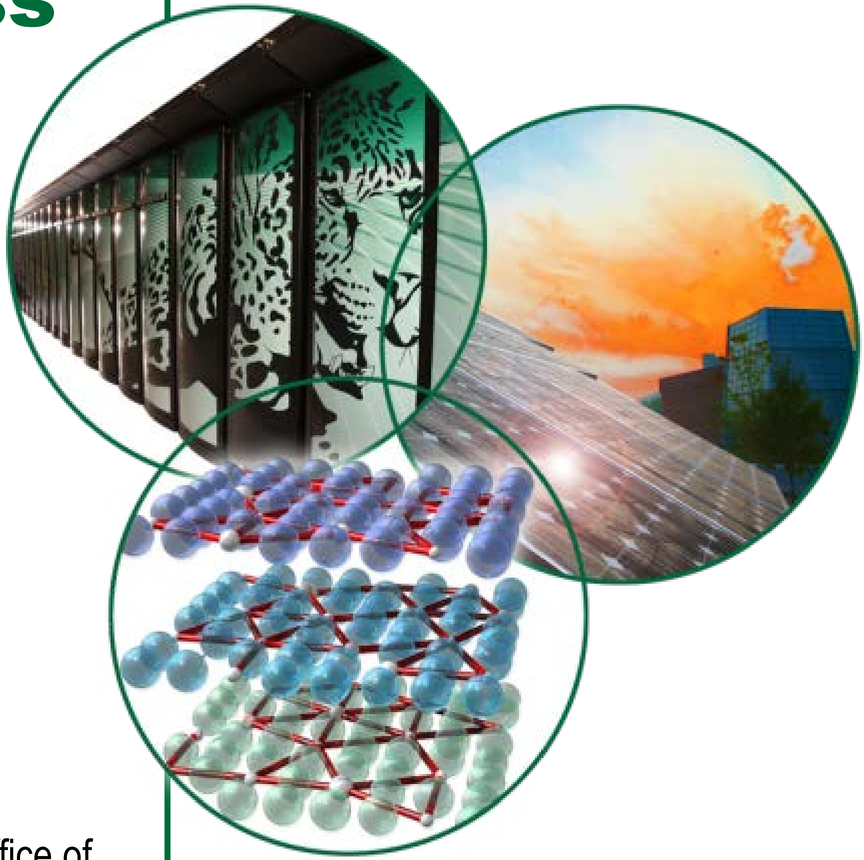
Ionic Liquids as Multifunctional Ashless Additives for Engine Lubrication



Jun Qu, Huimin Luo, Sheng Dai, Peter Blau, Bruce Bunting, John Storey, and Samuel Lewis

Oak Ridge National Laboratory

Michael Viola, Donald Smolenski, and Gregory Mordukhovich,

General Motors Corp.

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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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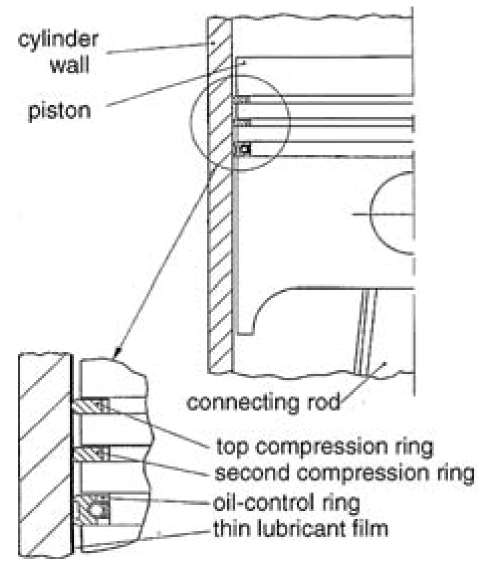
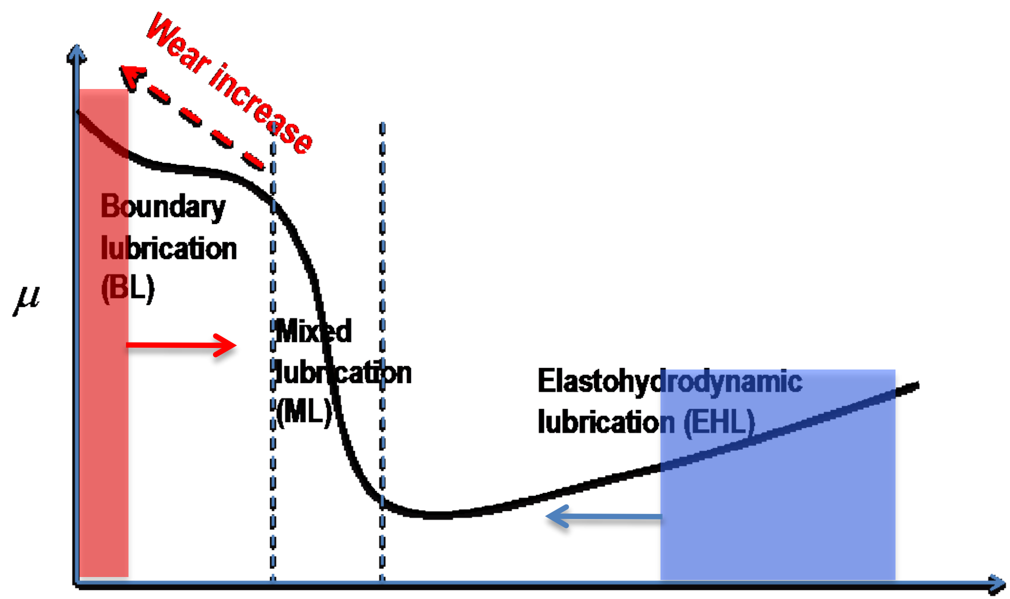
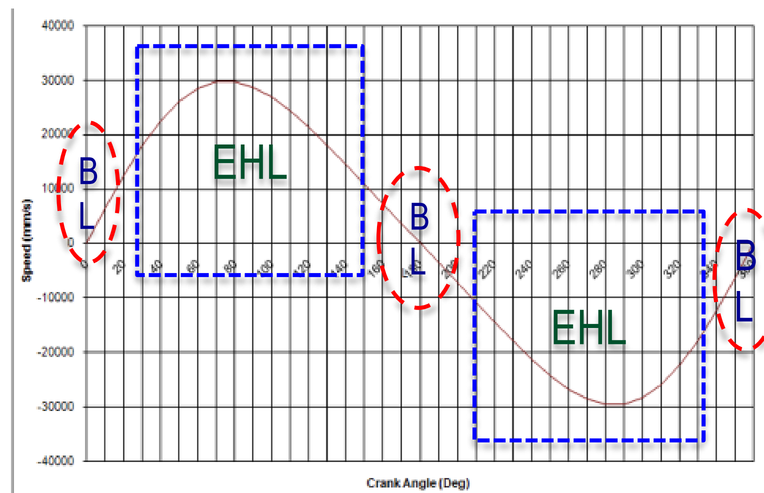
Piston ring–cylinder liner contact

- Majority of the stroke is under EHL, and the traction is from shearing the lubricant film – a low-viscosity lubricant produces lower friction thus better fuel economy.
- Top ring reversal region is under BL, and has wear issue – a high-viscosity lubricant provides better wear protection
- **Approach: anti-wear additives or wear-resistant surface engineering technologies to allow the usage of lower viscosity oils**





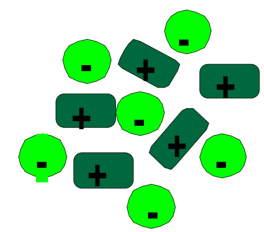
$$\lambda \propto \frac{v \cdot \eta}{P \cdot \sigma}$$



Introduction to ionic liquids

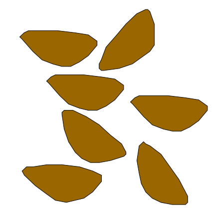
- Ionic liquids are ‘room temperature molten salts’, composed of cations and anions, instead of neutral molecules.
- Properties
  - Inherent polarity
  - High thermal stability and non-flammability
  - Low volatility
  - High flexibility of IL molecular design
  - Economical and environmentally friendly synthesis

Ionic liquid

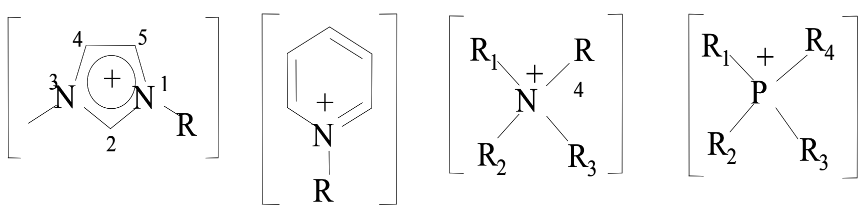


Coulombic forces

Oil



Van der Waals forces



1-alkyl-3-methyl-imidazolium

N-alkyl-pyridinium

Tetraalkyl-ammonium

Tetraalkyl-phosphonium ($R_{1,2,3,4}$ = alkyl)

Common Cations

$[PF_6]^-$

$[(CF_3SO_2)_2N]^-$ (Tf_2N)

$[(C_2F_5SO_2)_2N]^-$ (BETI)

$[BR_1R_2R_3R_4]^-$

$[P(O)_2(OR)_2]^-$ (phosphate)

$[P(O)_2(R)_2]^-$ (phosphinate)

$[BF_4]^-$

$[CF_3SO_3]^-$

$[CH_3CO_2]^-$

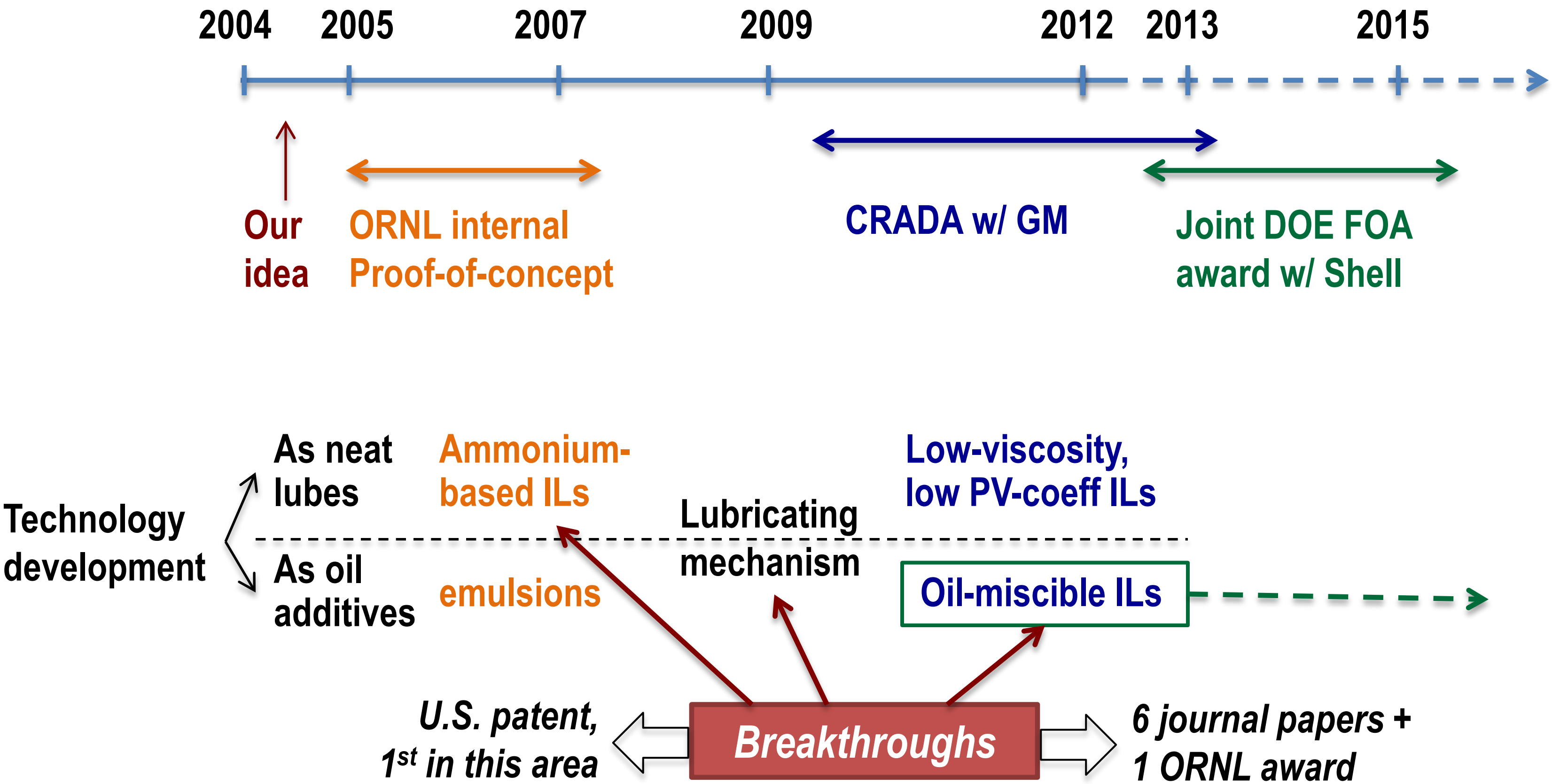
$[CF_3CO_2]^-$, $[NO_3]^-$

Br^-, Cl^-, I^-

$[Al_2Cl_7]^-$, $[AlCl_4]^-$

Common Anions

Program and technology development on Ionic Liquid Lubrication



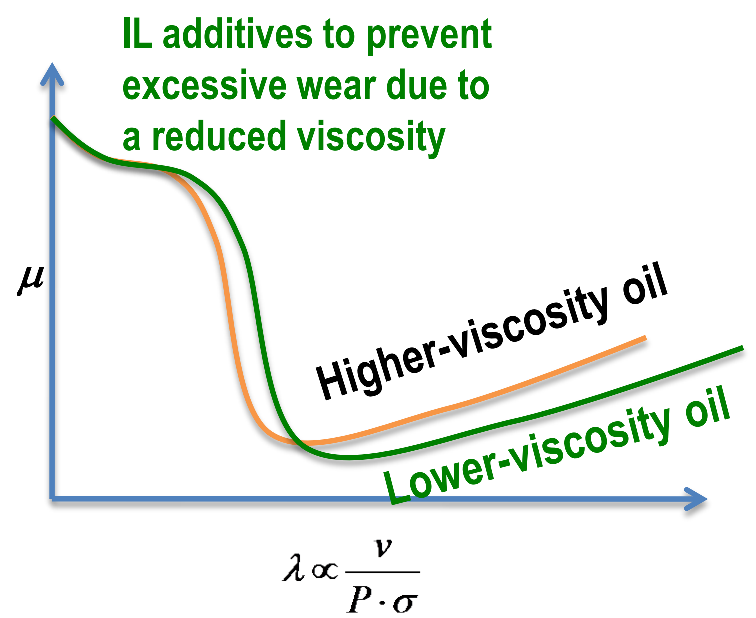
Ionic liquids for lubrication

- **ILs as neat lubricants or base stocks**
  - **High thermal stability (up to 500 ^{o}C)**
  - **High viscosity index (120-370)**
  - **Low elastohydrodynamic (EHL) and mixed friction due to low pressure-viscosity coefficient**
  - **Wear protection at boundary lubrication (BL) by forming a tribo-film**
  - **Suitable for specialty bearing components**
- **ILs as oil additives**
  - **Potential multi-functions: AW/EP,** *FM, corrosion inhibitor, detergent*
  - **Ashless/low sludge**
  - **Allow the use of lower viscosity oils for higher efficiency**
  - **Cost effective and easier to penetrate into the lubricant market**

ORNL-developed phosphonium-based ILs as lubricant additives

Promising properties:

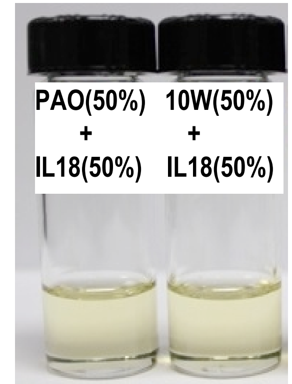
- Mutual miscibility with hydrocarbon oils
- Free of zinc, sulfur, and fluorine
- Non-corrosive
- High thermal stability
- Excellent wettability
- AW, FM, and other potential functions

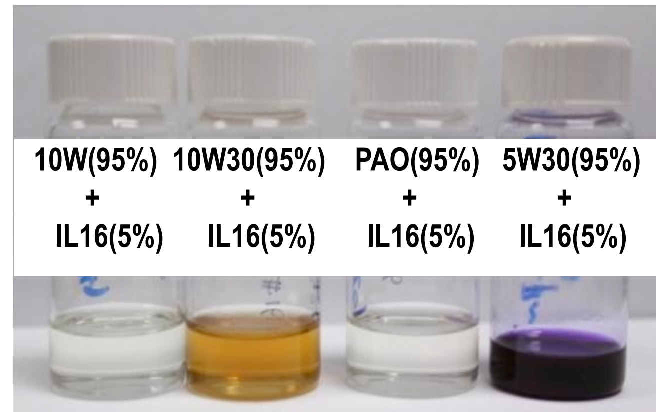


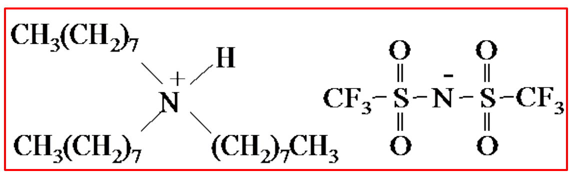
- **Potential benefits**
  - Improves durability and extended service intervals,
  - prevents the wear-induced efficiency loss and emission increase, and
  - more importantly, allows using less viscous oils for better engine efficiency.

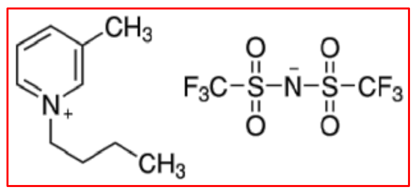
Oil-miscibility

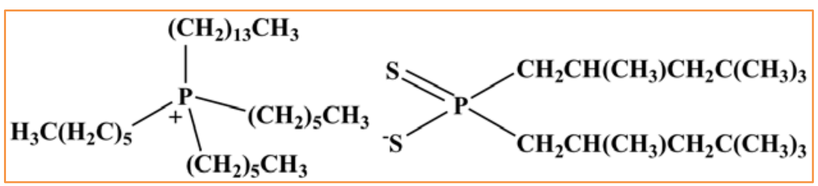
- Most ILs have very limited oil-solubility (<<1%).
- [P_{66614}][DTMPP] (IL16) & [P_{66614}][DEHP] (IL18) are fully miscible with all hydrocarbon oils tested, including both mineral oil- and PAO-based.
  - Hypothesis: 3D quaternary structures for both cation and anion w/ long hydrocarbon chains (high steric hindrance) to dilute the charge
  - But why oxygen donors necessary?



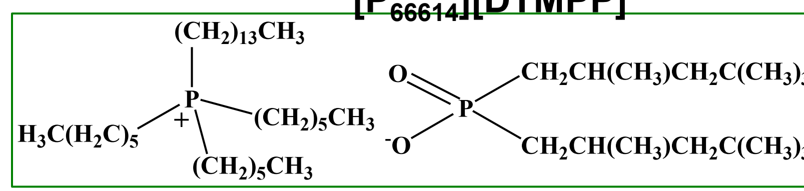


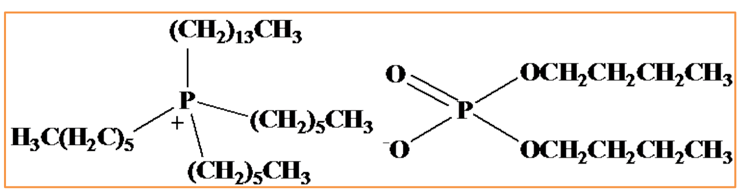




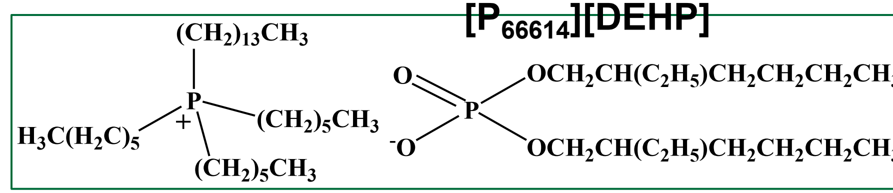


[P_{66614}][DTMPP]





[P_{66614}][DEHP]



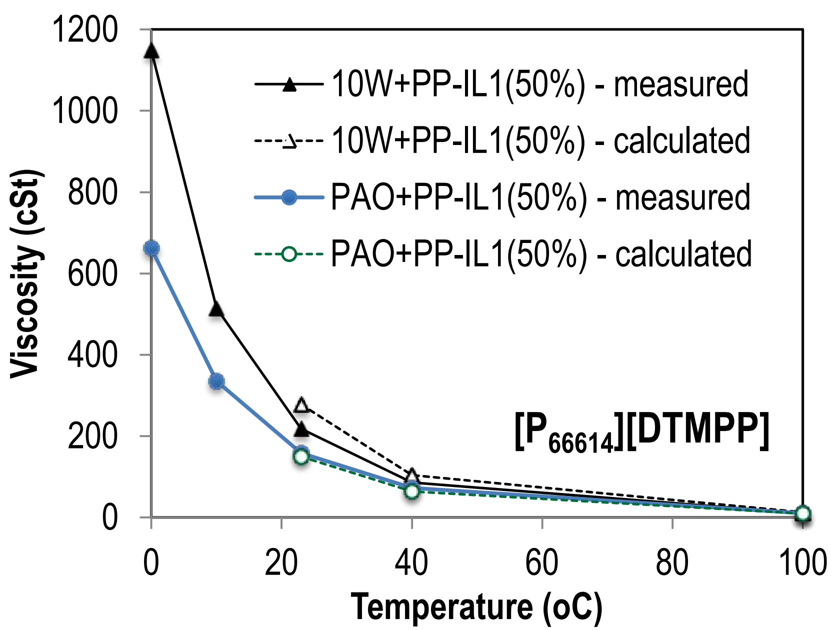
B. Yu, D.G. Bansal, J. Qu*, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, *Wear* (2012) 289 (2012) 58–64.

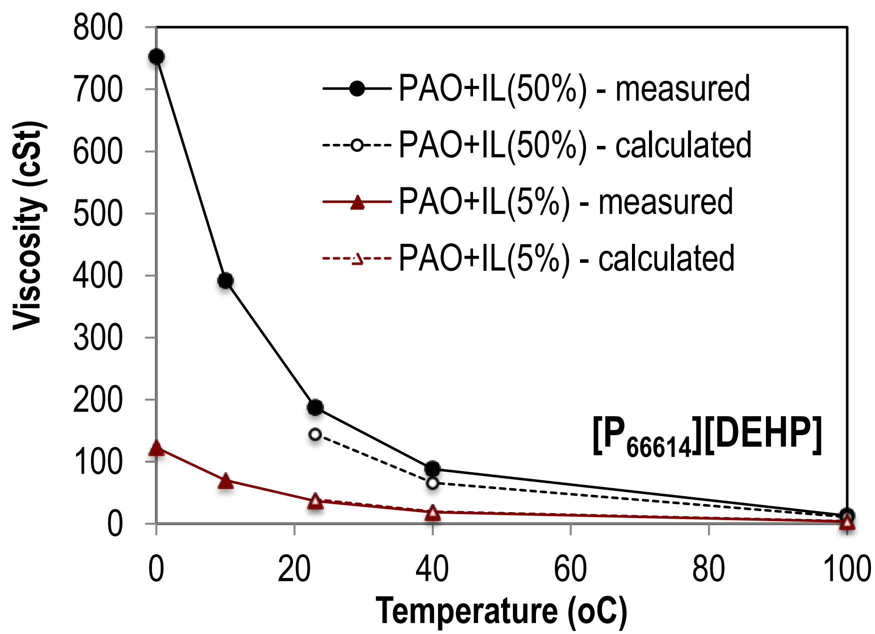
Viscosities of oil-IL blends

- **If a blend of multiple components is a single-phase solution (non-emulsion), the viscosity of the blend can be expressed by the Refutas equation [1].**

$$\upsilon_{blend} = \exp\left(\exp\left(\chi_{oil} \cdot ln\left(ln(\upsilon_{oil} + 0.8)\right) + \chi_{IL} \cdot ln\left(ln(\upsilon_{IL} + 0.8)\right)\right)\right) - 0.8$$

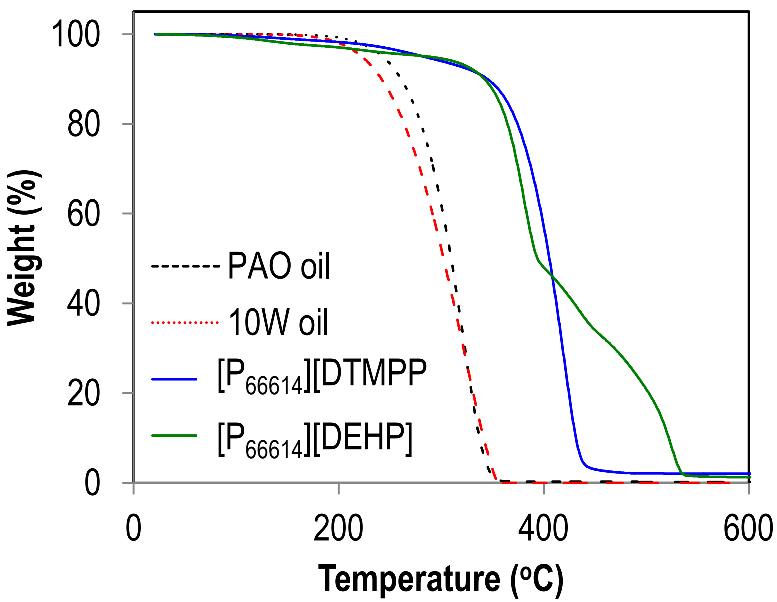
- **Good match between measured and calculated viscosities of the blends confirmed the ILs' oil-miscibility [2].**





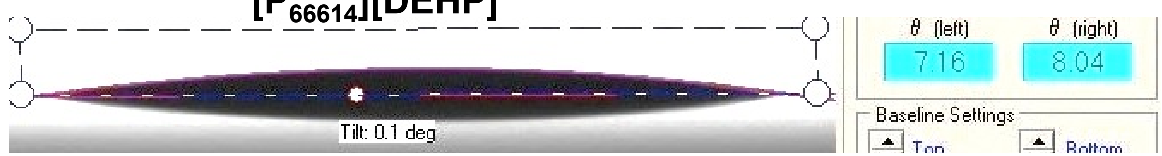
[1] Maples R.E. Petroleum Refinery Process Economics (2nd ed.). Pennwell Books (2000).
[2] B. Yu, D.G. Bansal, J. Qu*, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, *Wear* (2012) 289 (2012) 58–64.

High thermal stability and excellent wettability of oil-miscible PP-ILs



Fluid	Contact angle on cast iron
PAO 4 cSt base oil	13.0
Mobil 1™ 5W-30 engine oil	9.0
$[P_{66614}][DTMPP]$ (oil-miscible)	**6.3**
$[P_{66614}][DEHP]$ (oil-miscible)	**7.6**
$[N_{888H}][NTf_2]$ (oil-insoluble)	33.9
$[BMIM][NTf_2]$ (oil-insoluble)	41.7

$[P_{66614}][DEHP]$



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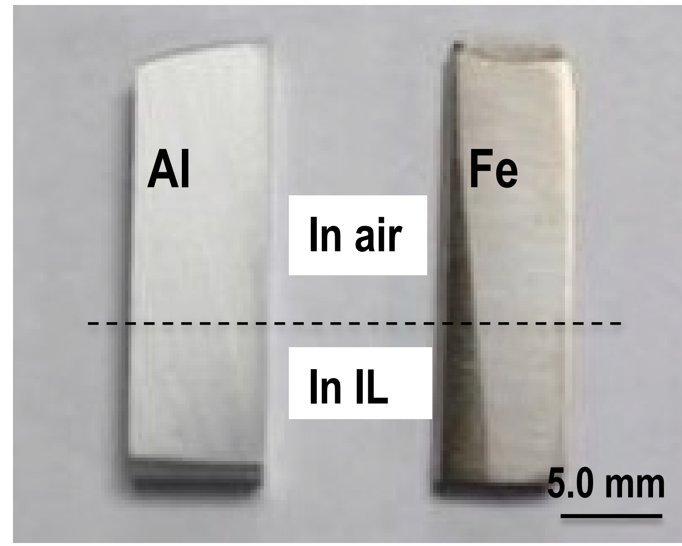
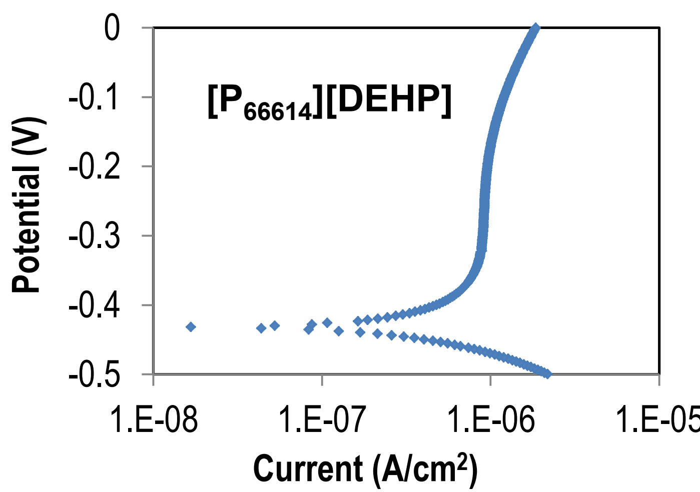
No corrosion to iron or aluminum

- **Non-corrosive to cast iron or aluminum at either room or elevated temperatures**

[P_{66614}][DTMPP] on grey cast iron surface after 60 days



Al and cast iron in [P_{66614}][DTMPP] at 135 ^{o}C for 7 days

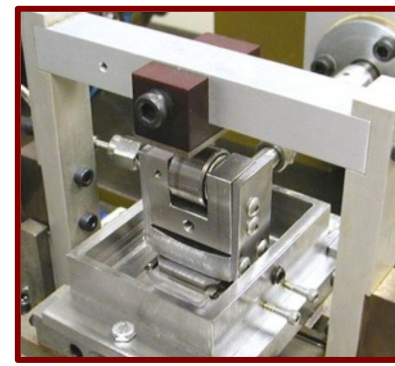


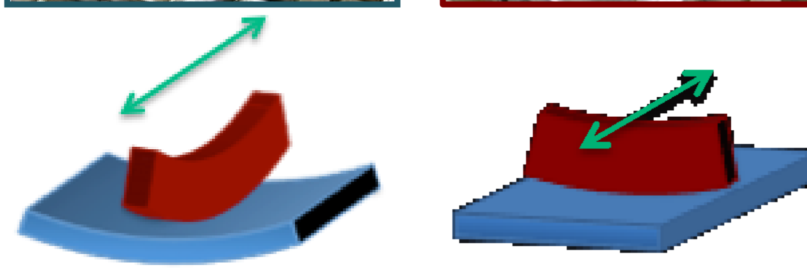
Potentiodynamic polarization curve of [P_{66614}][DEHP] showing active-passive behavior

J. Qu*, D.G. Bansal, B. Yu, J. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, "*ACS Applied Materials & Interfaces 4* (2) (2012) 997–1002.

Development of simulated rig tests

- **Lubricants: commercial and candidate engine oils**
- **Materials:**
  - **Ring: cut from an actual piston top ring**
  - **Liner: either cut from an actual a cylinder liner or a cast iron coupon with simulated liner surface finish**

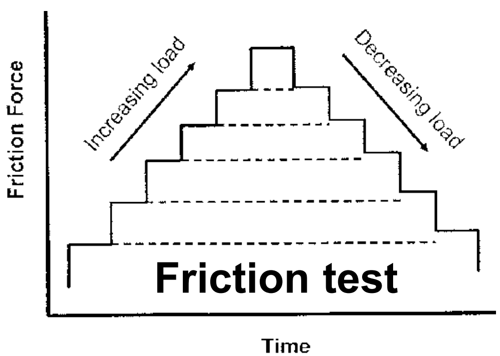


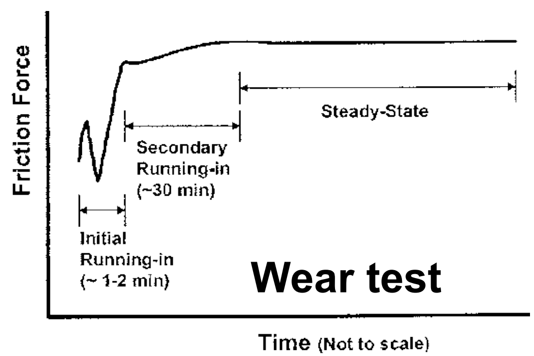


cross ring-on-liner **ring-on-flat**

Two ASTM standard tests G 181 & 206 developed at ORNL

- **Test parameters:**
  - Temperature: 100 °C
  - Sliding speed: 0.2 m/s (10 Hz, 10 mm stroke)
  - Friction test: Stepping load from 20 to 240 N w/ 20 N increment for 1 min each
  - Wear test: 240 N load for 6 hours

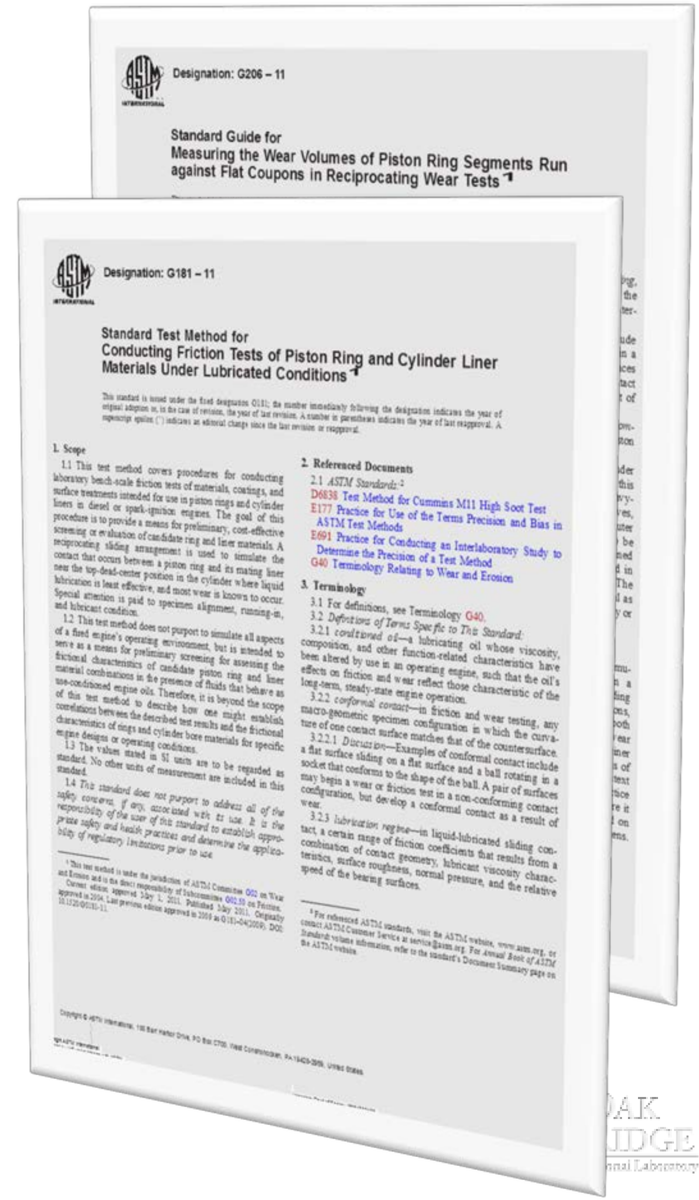




Wear quantification:

$$V_{flat} = L_s \left[r_f^2 \arcsin\left(\frac{W}{2r_f}\right) - \frac{W}{2}\sqrt{r_f^2 - \frac{W^2}{4}} \right] + \pi \frac{(L - L_s)}{3W} \left[2r_f^3 - \left(2r_f^2 + \frac{W^2}{4}\right)\sqrt{r_f^2 - \frac{W^2}{4}} \right]$$

$$V_{ring} = \pi \frac{a}{3b} \left[2r_o^3 - 2r_w^3 - (2r_o^2 + b^2)\sqrt{r_o^2 - b^2} + (2r_w^2 + b^2)\sqrt{r_w^2 - b^2} \right]$$



Designation: G206 – 11

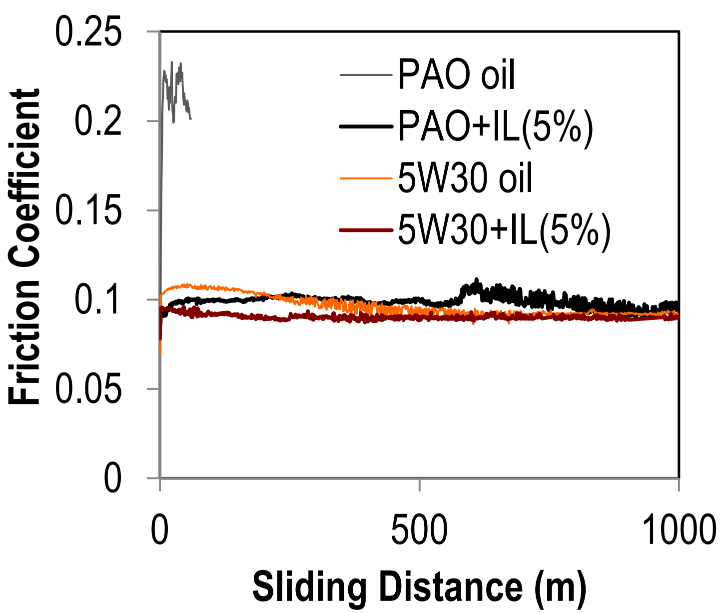
Standard Guide for
Measuring the Wear Volumes of Piston Ring Segments Run against Flat Coupons in Reciprocating Wear Tests

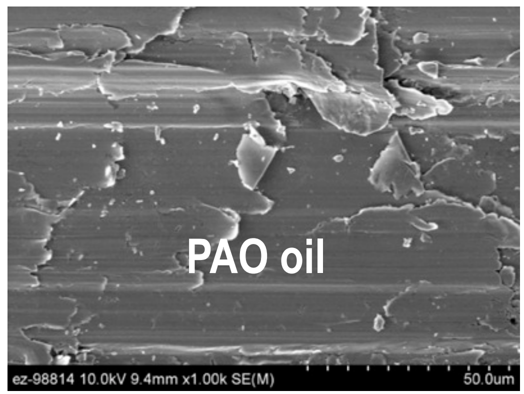
Designation: G181 – 11

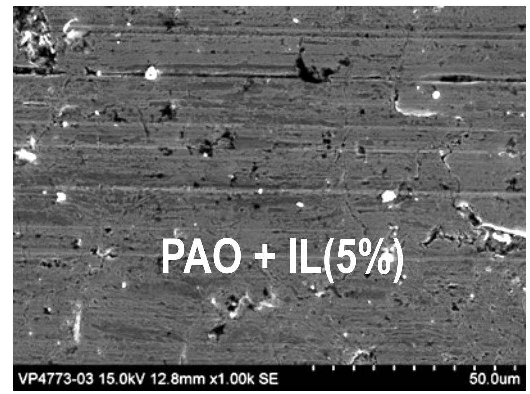
Standard Test Method for
Conducting Friction Tests of Piston Ring and Cylinder Liner Materials Under Lubricated Conditions

Anti-scuffing/anti-wear of $[P_{66614}][DEHP]$

- When added into PAO base oil, $[P_{66614}][DEHP]$ eliminates scuffing and significantly reduces wear – this low-viscosity blend performing as well as the more viscous 5W30 oil.
- When added into 5W30 engine oil, $[P_{66614}][DEHP]$ further reduces wear – suggesting a synergistic anti-wear effect with ZDDP.







Lubricant	Viscosity (cSt, 23 °C)	Wear rate (mm^3/N-m)	
		Liner	Ring
PAO 4 cSt base oil	34.5	$5.9 \pm 4.7 \times 10^{-4}$	$>1.0 \times 10^{-6}$
PAO+IL(5%)	36.6	$5.6 \pm 3.5 \times 10^{-7}$	$1.4 \pm 0.5 \times 10^{-8}$
5W30 engine oil	140.9	$4.7 \pm 0.3 \times 10^{-7}$	$6.6 \pm 4.9 \times 10^{-9}$
5W30+IL(5%)	149.9	$1.3 \pm 0.2 \times 10^{-7}$	$2.0 \pm 1.6 \times 10^{-9}$

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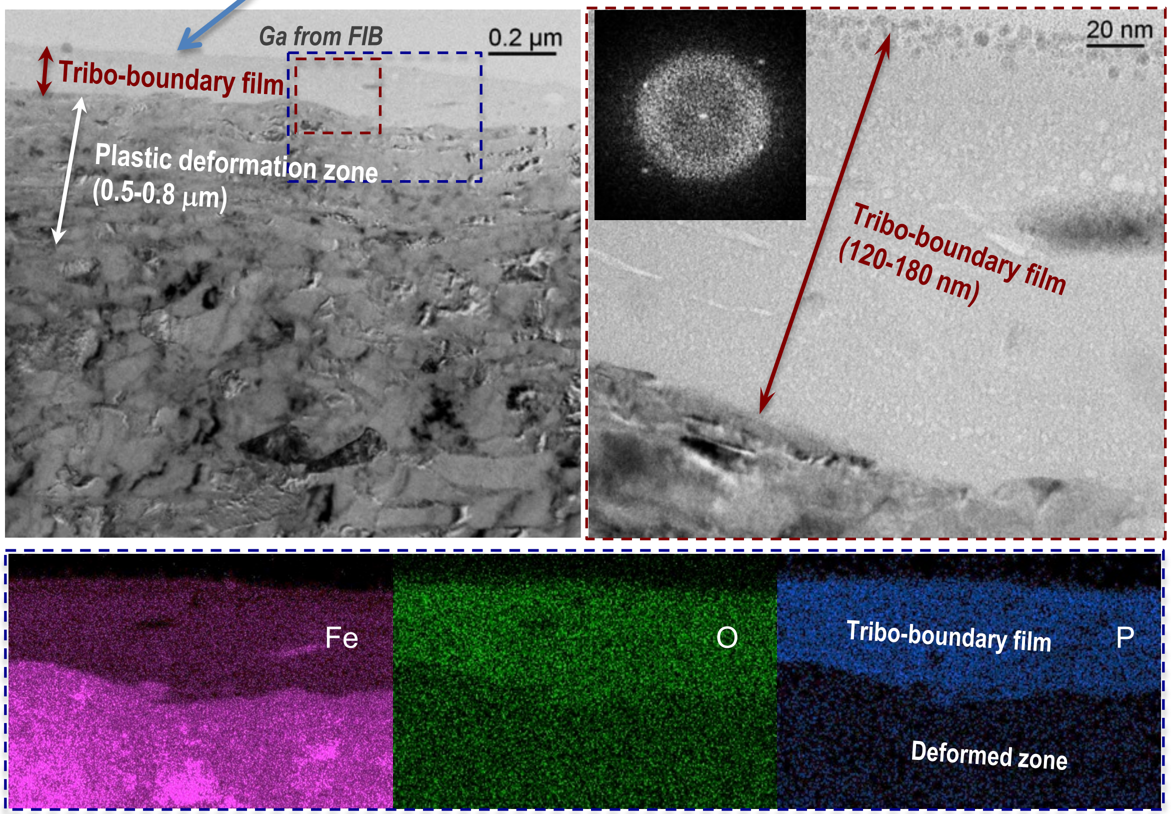
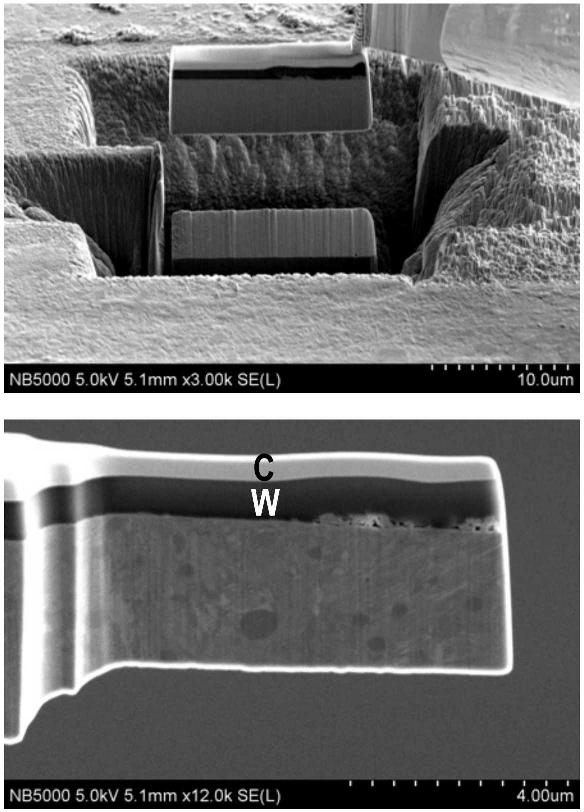
Tribo-film on cast iron liner lubricated by PAO+5% [P_{66614}][DEHP]

TEM

Smoother than original surface due to chemical-mechanical polishing effect?



Focused ion beam (FIB)



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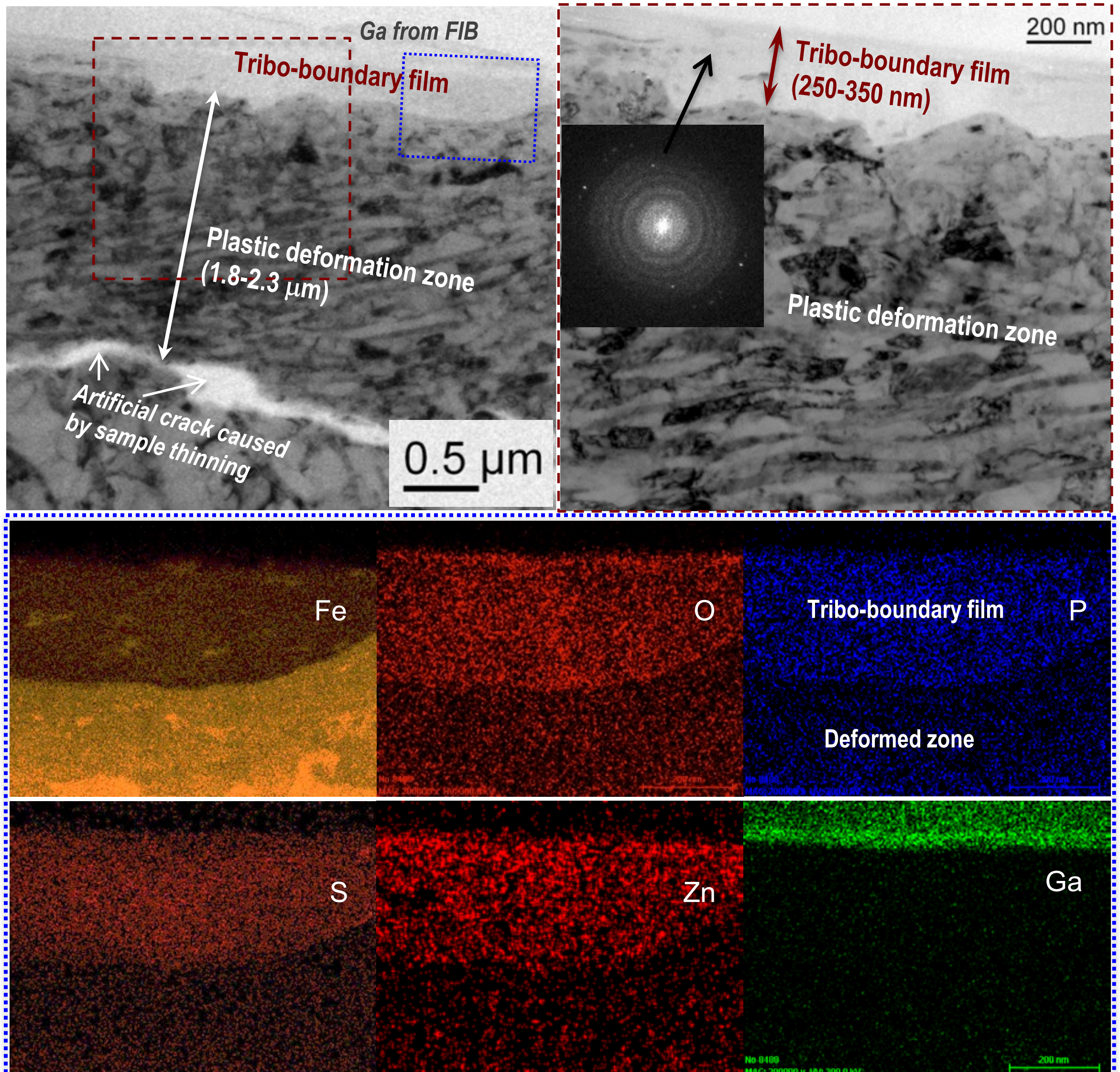
Tribo-film by 5W-30 oil+5% [P_{66614}][DEHP]



A thicker tribo-film with

- **O, P, S, and Zn rich**

Suggesting a synergistic effect between IL and ZDDP in wear protection.

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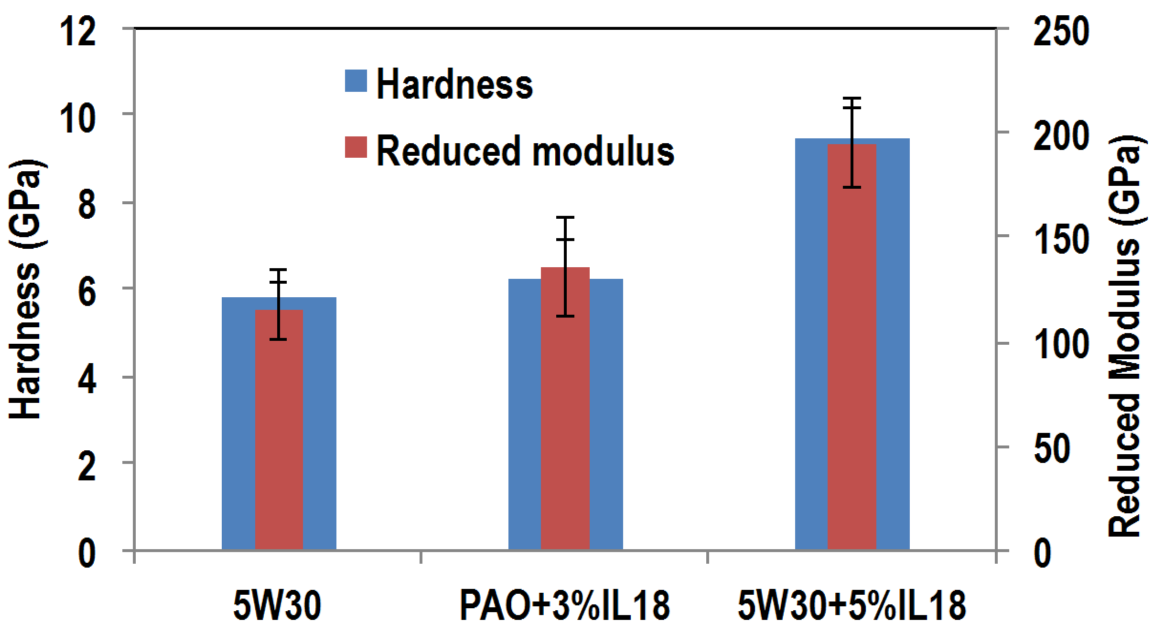
Hardness and modulus of tribo-films

- **Nanoindentation to characterize the hardness and modulus of tribo-films: 2x25 indents, displacement control: 75 nm.**
- **The tribo-film formed by ZDDP+[P_{66614}][DEHP] is harder and stronger than the tribo-film formed by either alone – a synergy?**



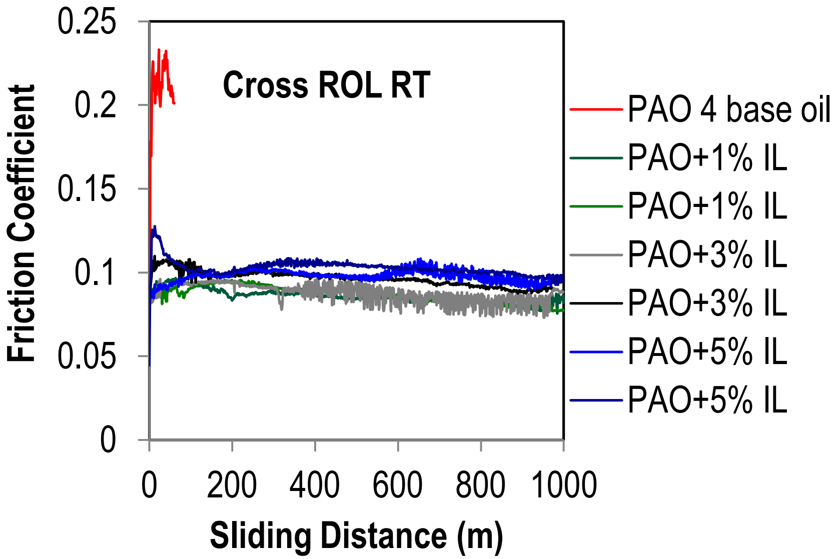
API/ILSAC limits IL's concentration

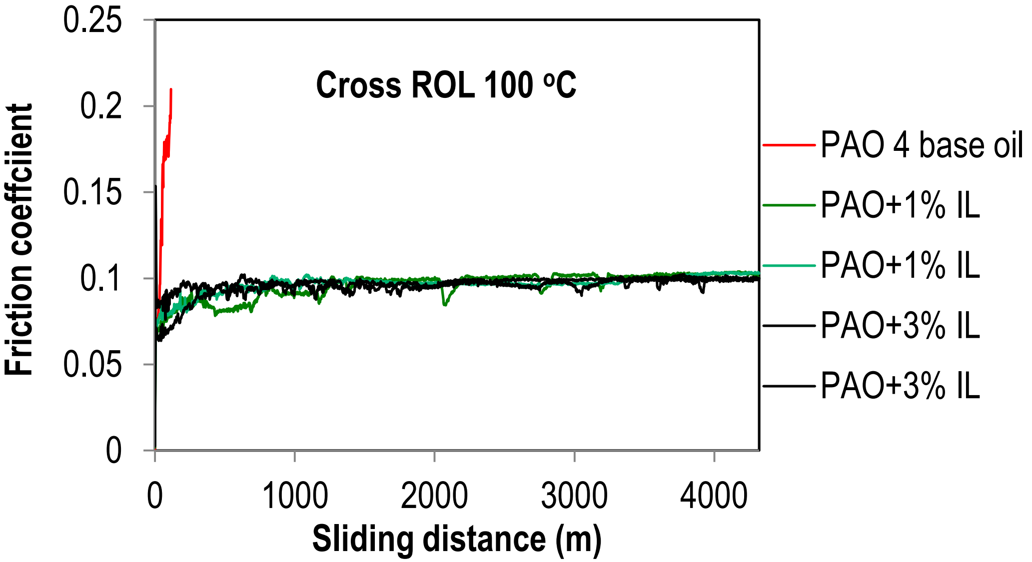
ILSAC GF-5

$[P_{66614}][DEHP]$: 0.78-1.03 wt%

	Molecular weight	P (wt%)	S (wt%)	Zn (wt%)
ZDDP (Octyl)	771	8.04	16.6	8.43
IL16	772	8.03	0	0
IL18	804	7.71	0	0
IL20	689	4.49	0	0

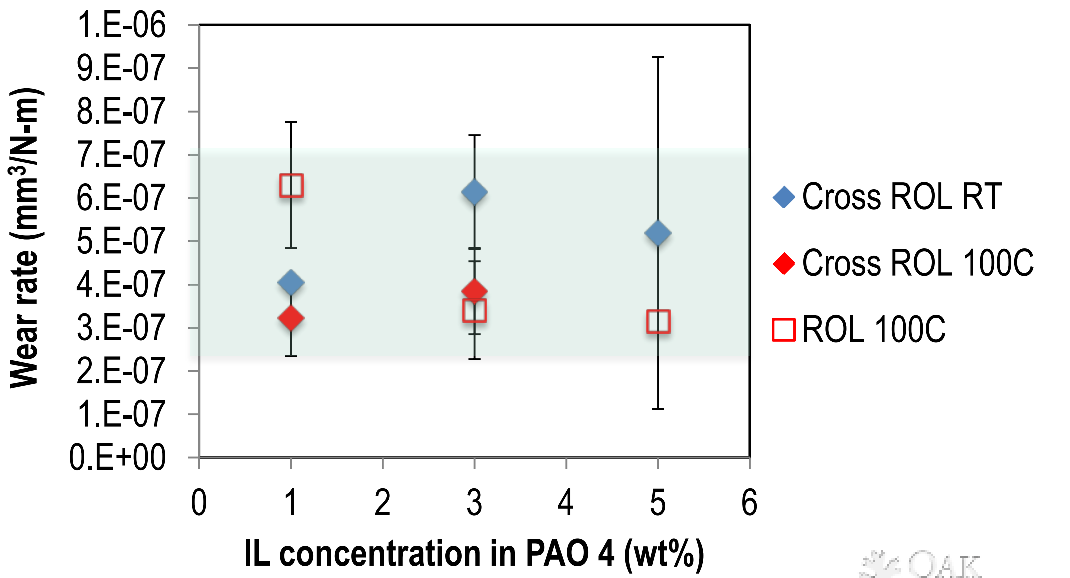
Effects of IL concentration





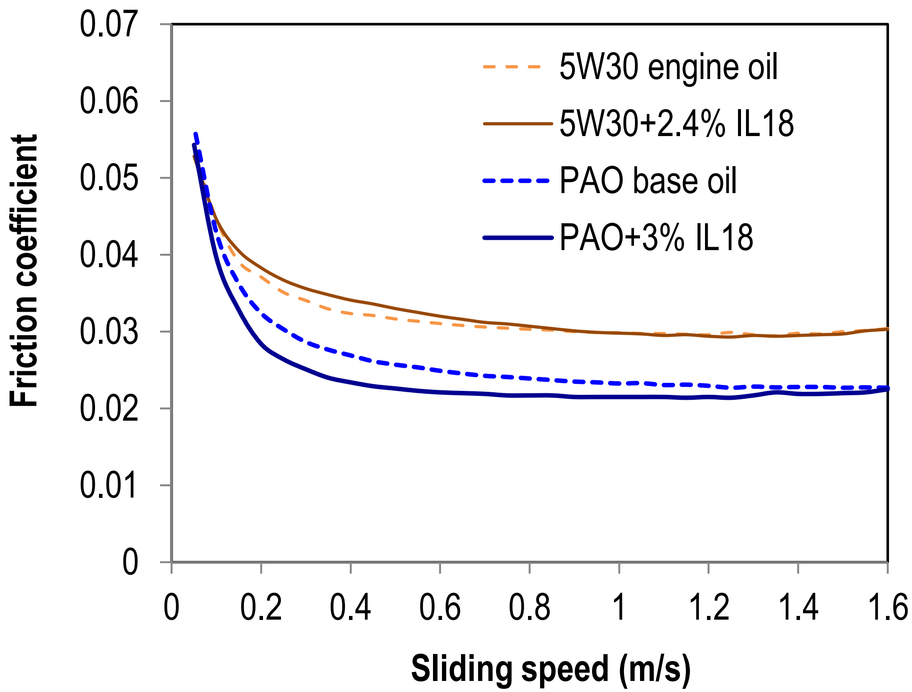
- **PAO 4 base oil + 1-5 wt% [P_{66614}][DEHP]**
- Test type-1: cross ring-on-liner (Cross ROL), RT, 160 N, 10 Hz, 10 mm stroke, 1000 m
- Test type-2: cross ring-on-liner (Cross ROL), 100 °C, 240 N, 10 Hz, 10 mm stroke, 4320 m
- Test type-: ring-on-flat liner (ROL), 100 °C, 240 N, 10 Hz, 10 mm stroke, 4320 m

Observation: 1 wt% of IL worked as well as 3 or 5 wt% in short-term bench testing.



Friction modifier functionality

- **When added into PAO base oil, [P_{66614}][DEHP] reduces the friction at mixed lubrication – suggesting the potential functionality as a friction modifier.**
  - **No friction reduction for Mobil 1™ 5W30 or RP 0W10 engine oils, suggesting competition against existing friction modifiers.**

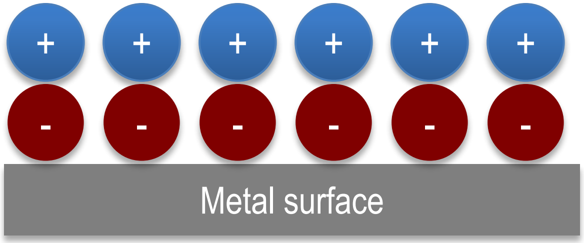


PCS MTM2 Mini-Traction Machine
– steel-on-steel pin-on-disc rolling/sliding

- Temperature: 100 °C
- Load: 75 N
- Rolling speed: 0.1–3.2 m/s
- Sliding/rolling ratio: 50%

Lubricating mechanisms of ionic liquids as multi-functional additives

- Under mixed or EHL regime, function as friction modifier
  - First layer of anions absorbed onto the metal surface
  - Second layer of large-molecule cations attracted by the anions
  - *Additional layers possible…*
  - The layer-structured boundary lubricant film easier to shear → improving engine efficiency

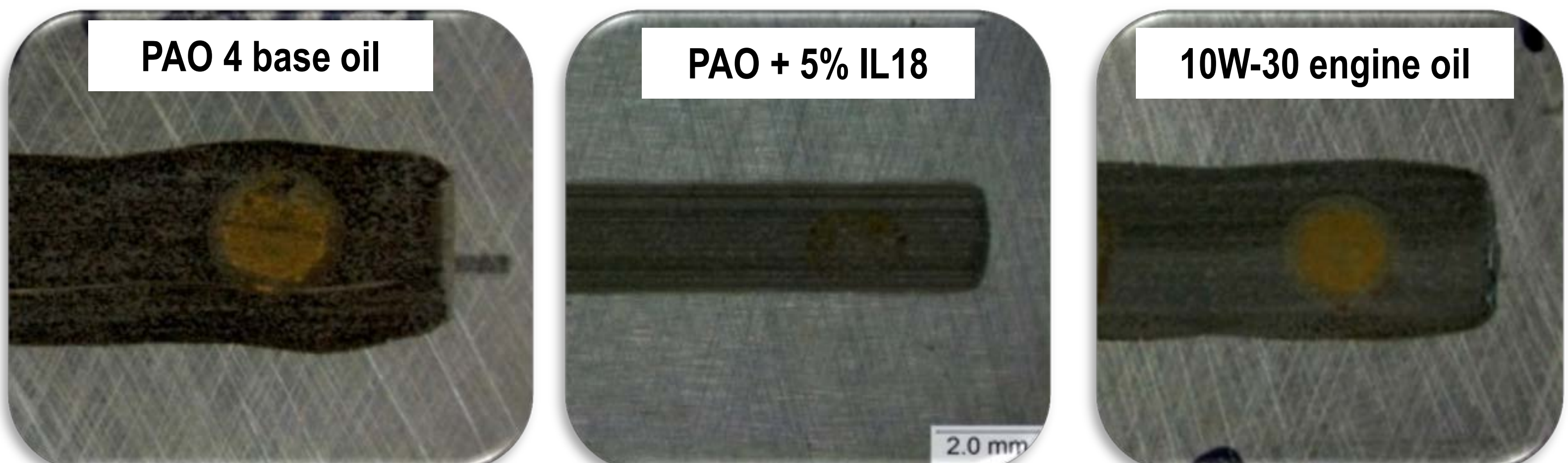


- Under boundary lubrication, function as anti-wear additive
  - Tribo-chemical reactions to form a protective tribo-film → improving engine durability
  - Allowing to use lower viscosity oils → improving engine efficiency

IL tribo-film shows signs of corrosion-resistance

- Water droplets placed on the wear scars on cast iron liner surfaces in ambient.
- Less rust on the surface lubricated by PAO+5% [P_{66614}][DEHP] compared to those lubricated by PAO base or fully-formulated 10W-30 engine oil.

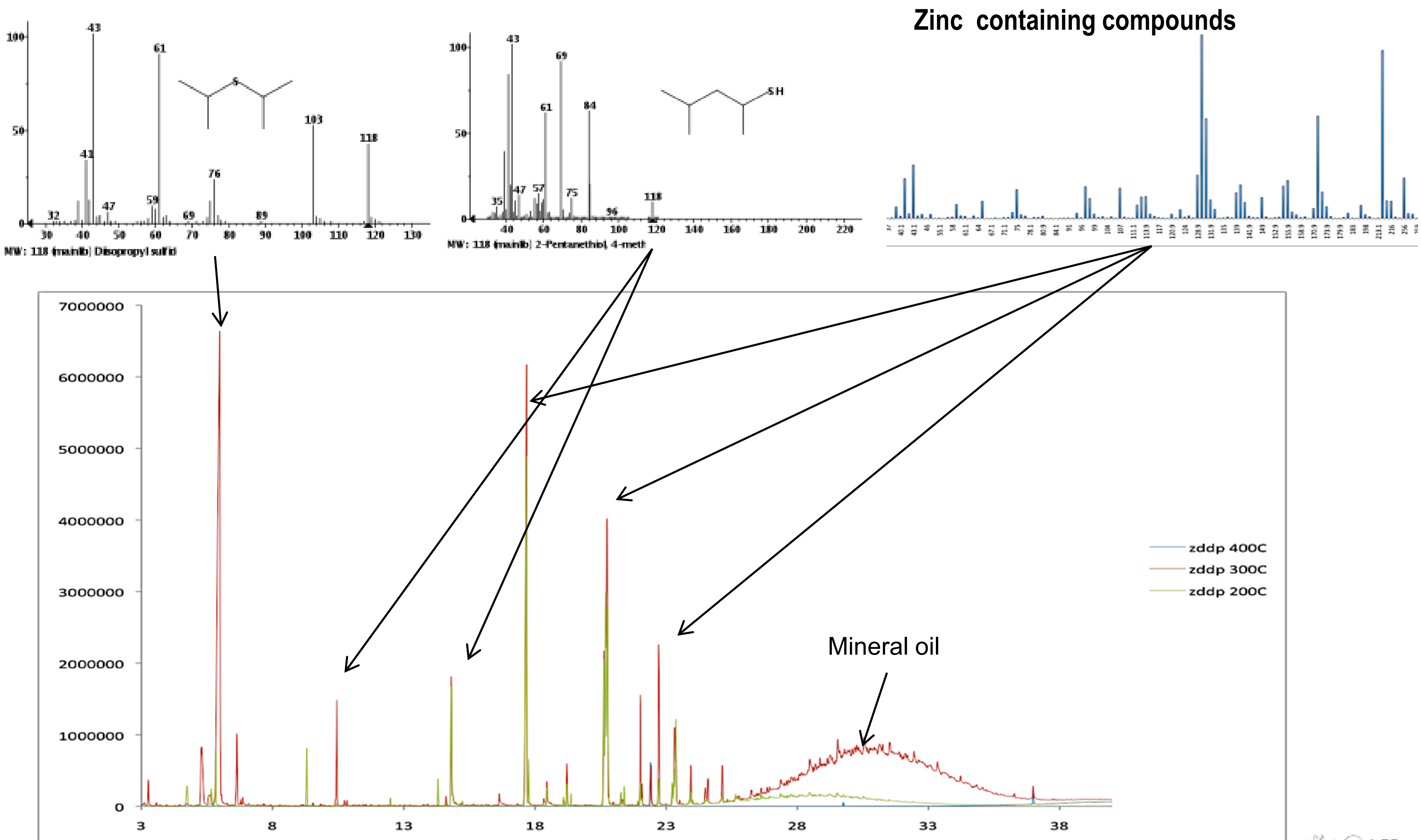
- Hint-1: [P_{66614}][DEHP] tribo-film has higher corrosion resistance than ZDDP tribo-film
- Hint-2: [P_{66614}][DEHP] may perform as corrosion-inhibitor…



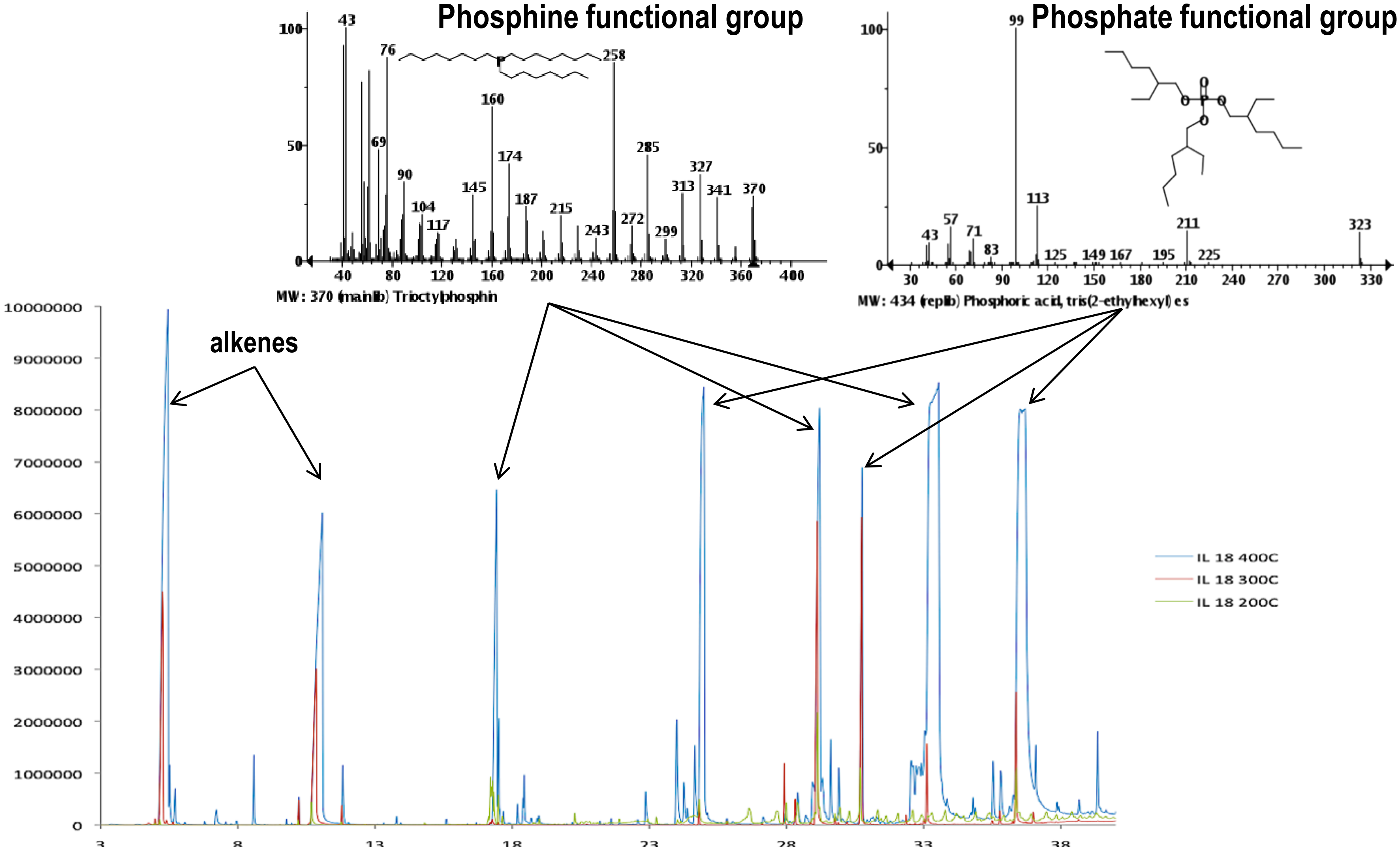
Thermo/pyrolysis analyses

- Method: 1 mg of hexane extracted residue from impingers was analyzed. These are gas phase compounds. Anions in solution analyzed by capillary electrophoresis.
- In helium
  - $[P_{66614}]$[DEHP] had very little decomposition at 200 ^{o}C. When decomposed at 400 ^{o}C, electropherogram of residue pyrolysis showed no detectable anions, indicating all volatile phosphorous – ashless.
  - ZDDP largely decomposed at 200 ^{o}C with trace amounts when heated to 400 ^{o}C. Electropherogram of residue pyrolysis showed the presence of non-volatile phosphoric acid anion and unknown anion.
- In oxygen
  - $[P_{66614}]$[DEHP] was stable below 200 ^{o}C but completely decomposed at 300 ^{o}C.
  - Decomposition products different than those in helium, but again are volatile phosphorous – ashless.
  - Olefin and paraffin compounds no longer exist but large number of carbonyl compounds suggest that the alkyl legs of IL were oxidized.

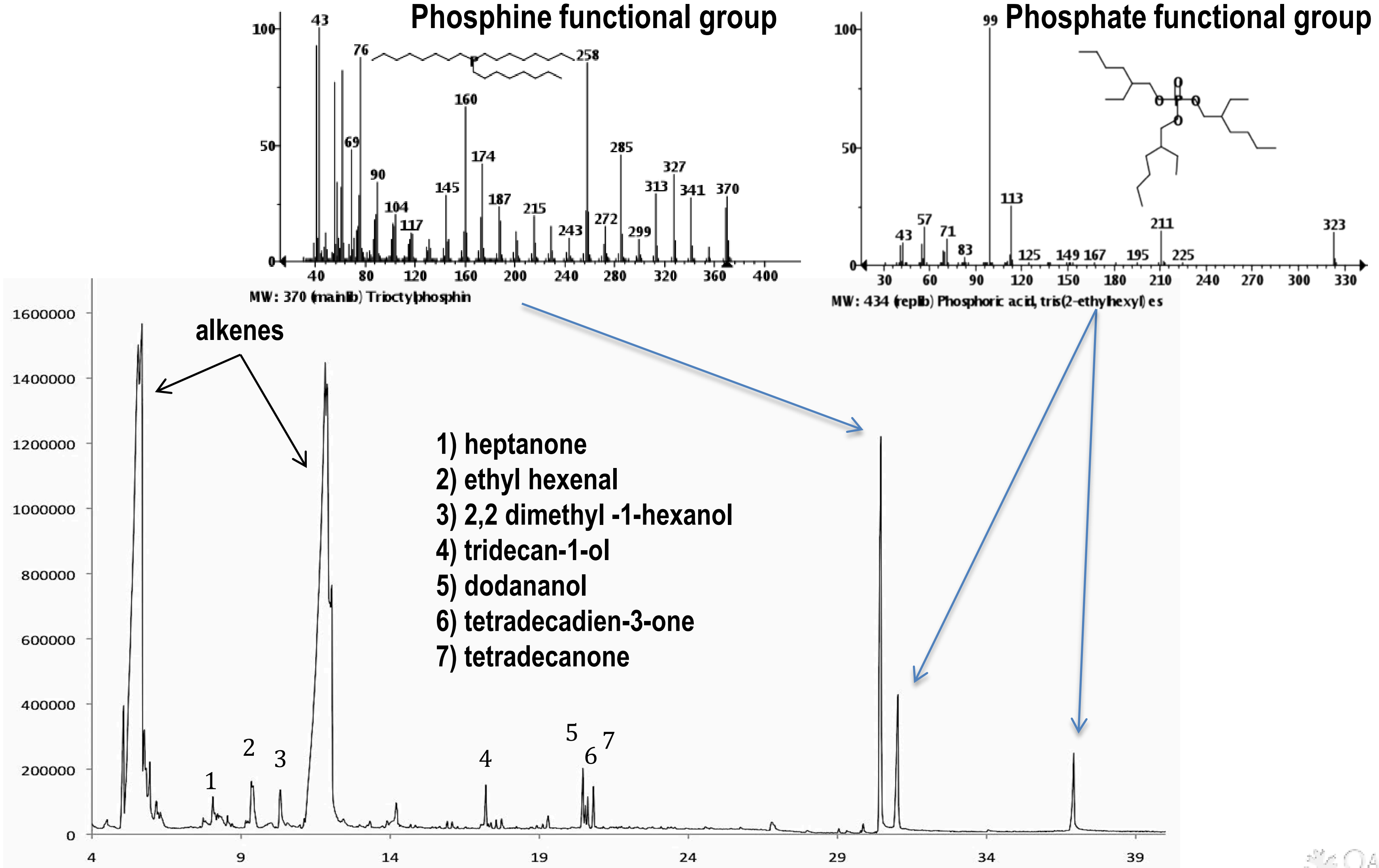
Chromatographs of ZDDP thermo/pyrolysis in helium



Chromatographs of [P_{66614}][DEHP] thermo/pyrolysis in helium

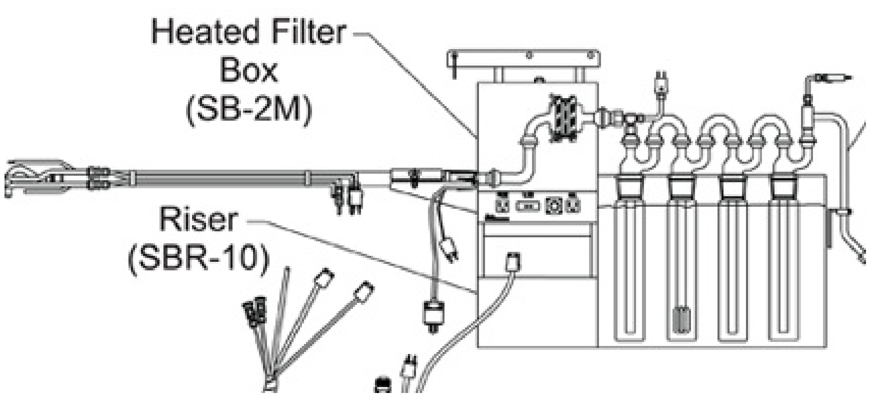


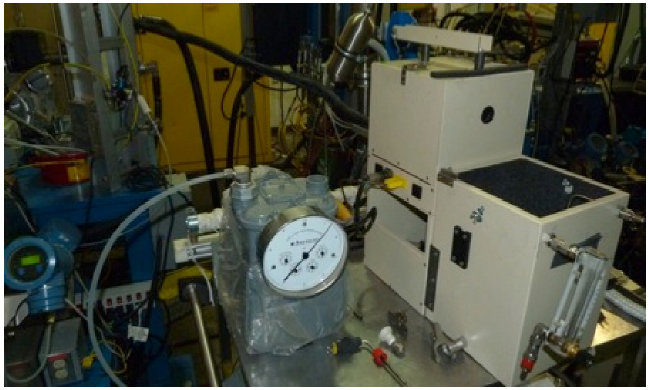
Chromatographs of [P_{66614}][DEHP] thermal decomposition in oxygen at 300 °C



Exhaust analysis

- Three fuels, base diesel, base diesel+ZDDP, and base diesel+[P_{66614}][DEHP], evaluated in an single-cylinder research engine.
- 81 mm quartz fiber filters for particulate collection, pre-fired at 650 ° C in a furnace.
- Sample gas exited the oven and flowed through impingers kept at ice water temperatures for water removal from the exhaust, and then to a dry gas meter.

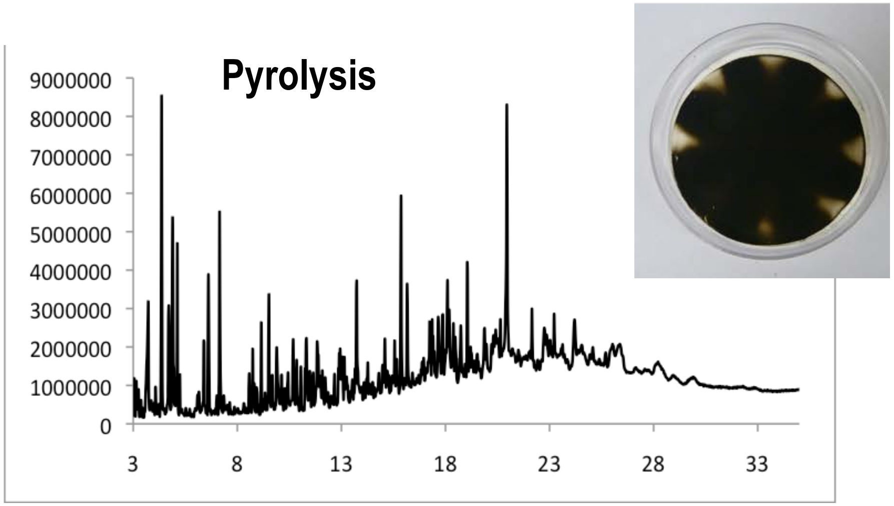




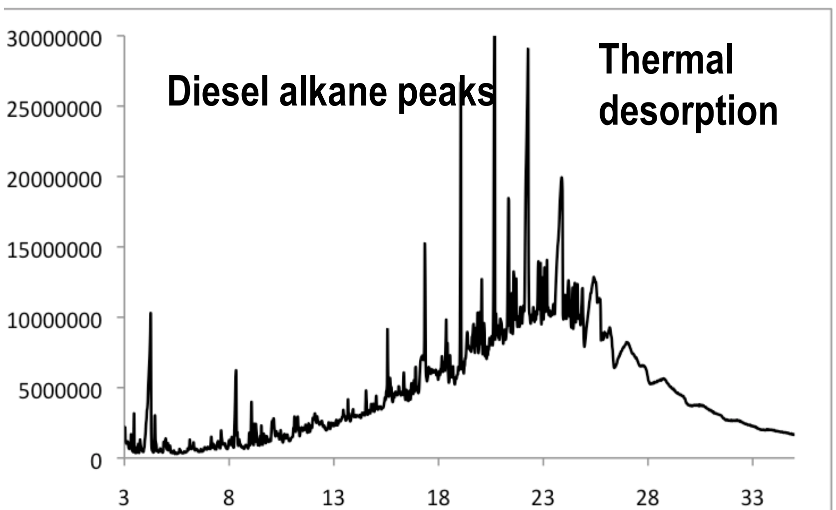
PM filters

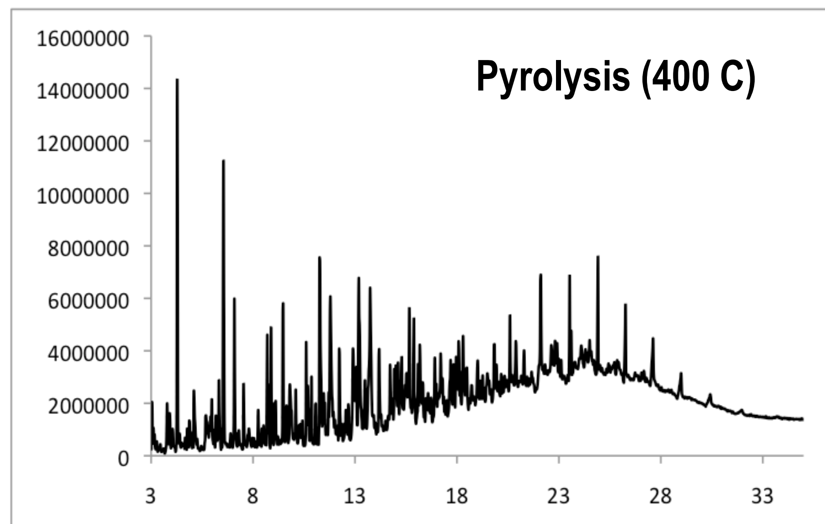
High load | Medium load | Low load

Chromatograph of thermo/pyrolysis of diesel+IL low load PM filter and hexane extracted residue from impinger



No $[P_{66614}]$[DEHP] decomposition products were detected.





Summary

- A group of oil-miscible ionic liquids has been developed by an ORNL-GM team as candidate lubricant additives with
  - Promising physical/chemical properties
    - Fully miscible/soluble with hydrocarbon base oils (mineral and synthetic)
    - Non-corrosive to ferrous or aluminum alloys
    - High-thermal stability
    - Excellent wettability
  - Potential multiple functionalities
    - Anti-scuffing/anti-wear,
    - Friction modifier,
    - and possibly corrosion inhibitor
  - Thermal decomposition products of IL all volatile phosphorous (ashless) and very different from those of ZDDP
  - Exhaust analysis showing no IL decomposition products in PM filter or residue
- An oil-miscible IL is being formulated into an engine oil…
- Emission catalyst poisoning and HLHT engine test are to be conducted…

Comments and Questions?

Acknowledgements

- **Sponsored by the Fuels and Lubes Program of the Vehicle Technologies Program, Office of Energy Efficiency & Renewable Energy, DOE**
- **Partner: General Motors (CRADA)**
- **Part of characterization was supported by SHaRE User Facility, Office of Basic Energy Sciences, DOE**

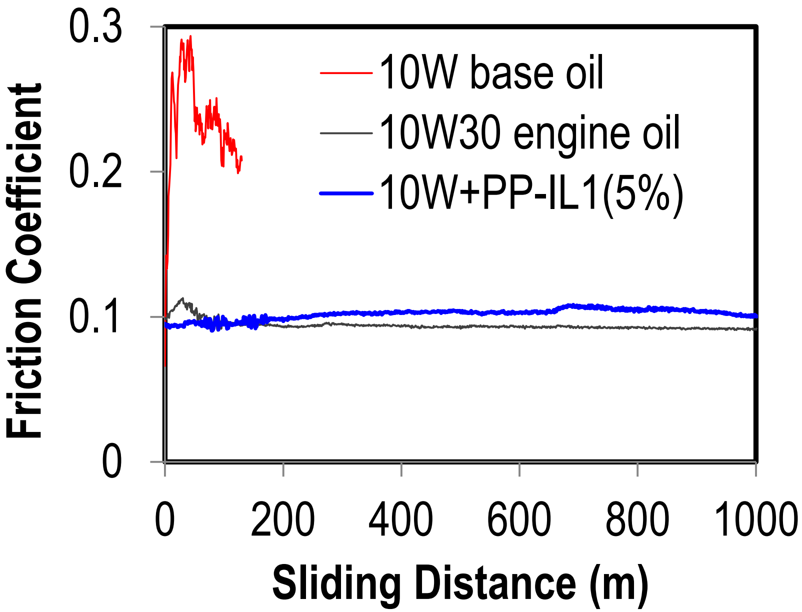
References

1. J. Qu*, D.G. Bansal, B. Yu, J. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Anti-Wear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive,” ***ACS Applied Materials & Interfaces*** *4* (2) (2012) 997–1002.
2. B. Yu, D.G. Bansal, J. Qu*, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Oil-Miscible and Non-Corrosive Phosphonium-Based Ionic Liquids as Candidate Lubricant Additives,” ***Wear*** (2012) 289 (2012) 58–64.

Backup slides

Anti-scuffing/anti-wear of [P$_{66614}$][DTMPP]

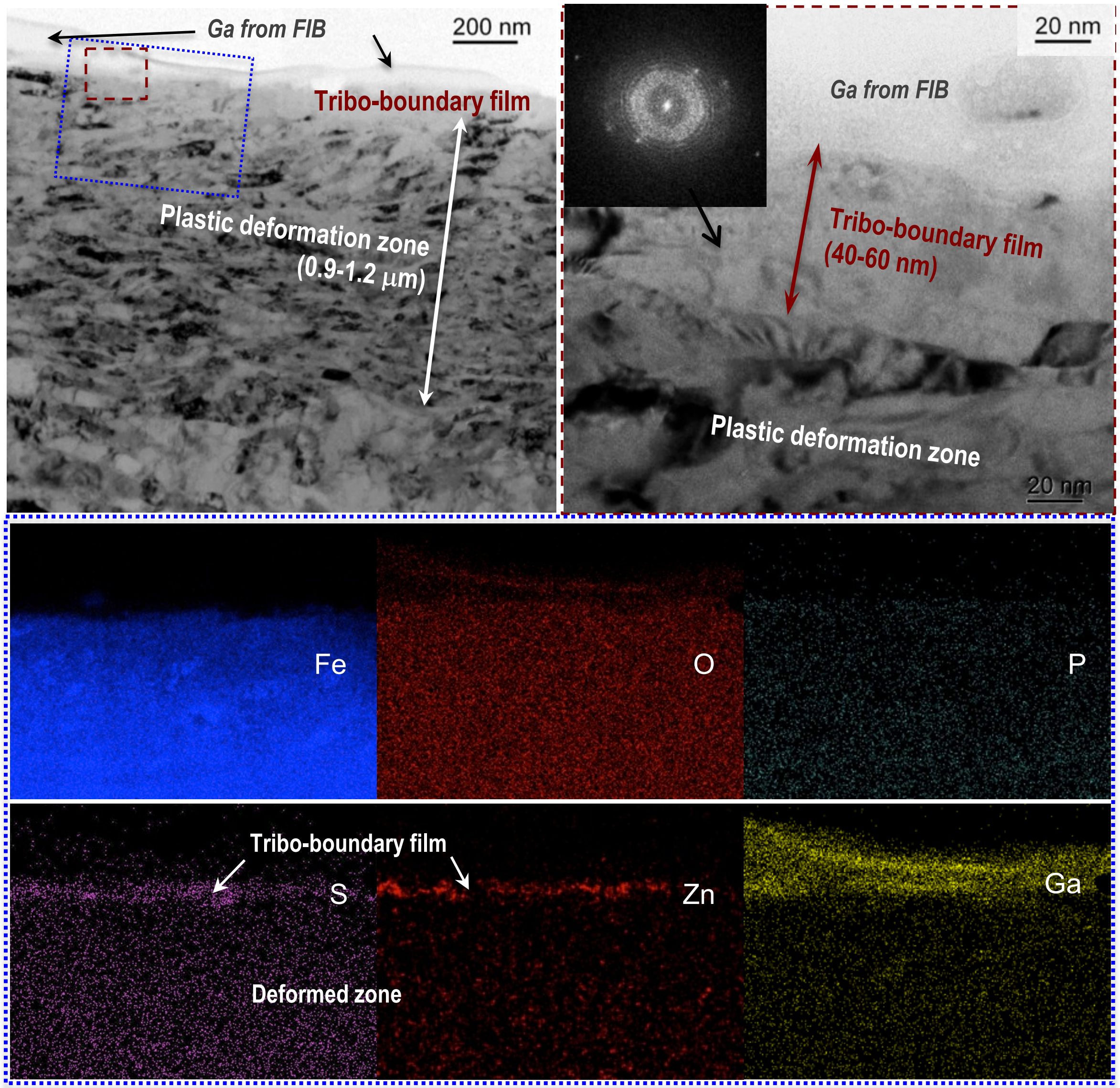
- When added into the 10W base oil, [P$_{66614}$][DTMPP] eliminates scuffing and significantly reduces wear.
- This low-viscosity blend performing as well as the more viscous 10W30 engine oil.



Lubricant	Viscosity (cSt, 23 °C)	Liner wear rate (10^{-7} mm^3/N-m)
10W base oil	89.0	1660
10W+PP-IL1(5%)	90.0	7.5
10W30 engine oil	178.6	9.9

B. Yu, D.G. Bansal, J. Qu*, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, *Wear* (2012) 289 (2012) 58–64.

Tribo-film lubricated by 5W-30 engine oil



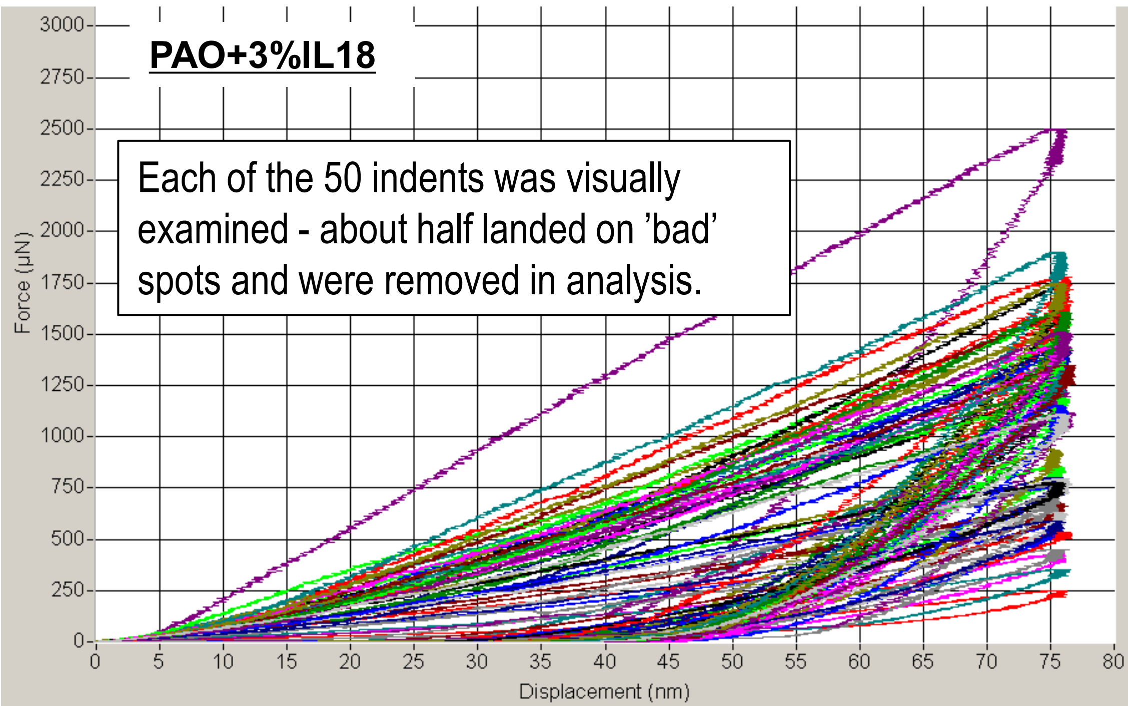
A ZDDP-based tribo-film

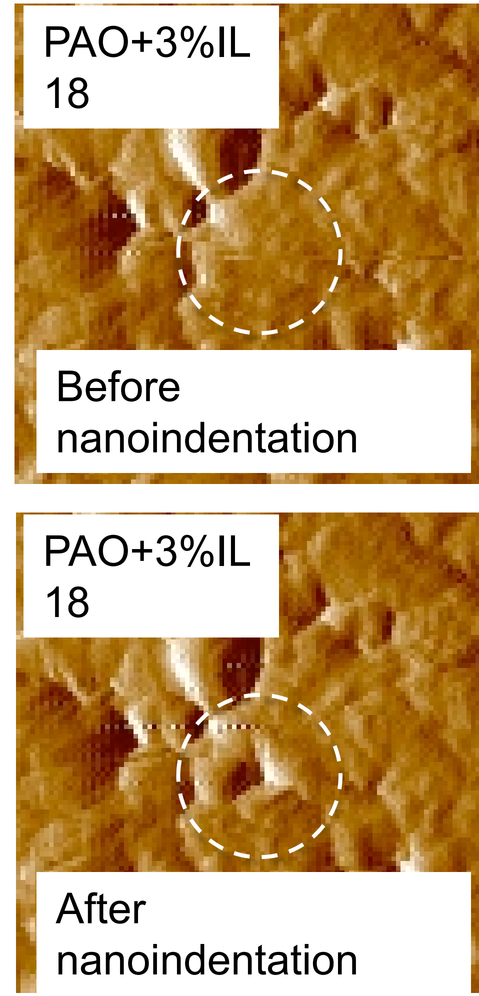
- **S and Zn rich**
- **P and O in lower-concentrations**

J. Qu*, D.G. Bansal, B. Yu, J. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, "*ACS Applied Materials & Interfaces 4* (2) (2012) 997–1002.

Nanoindentation to characterize the hardness and modulus of tribo-films

- **Nanoindentation:** **2x25 indents, displacement control: 75 nm.**
- **Wear scars generated at 100C in Mobil 1™ 5W30, PAO+3%IL18, and 5W30+5%IL18**





10x10 μm scan

Chromatographs of the base low load hexane extracted residue thermo/pyrolysis (gas phase compounds)