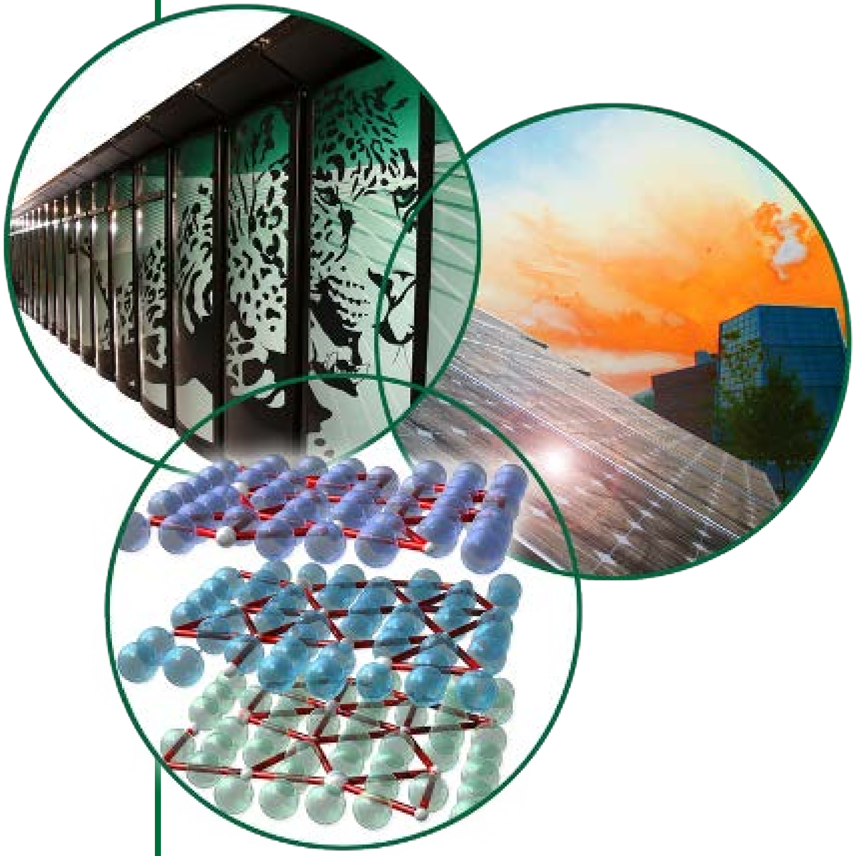
Ionic Liquids as Novel Engine Lubricants or Lubricant Additives



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U.S. DEPARTMENT OF ENERGY

OAK RIDGE NATIONAL LABORATORY
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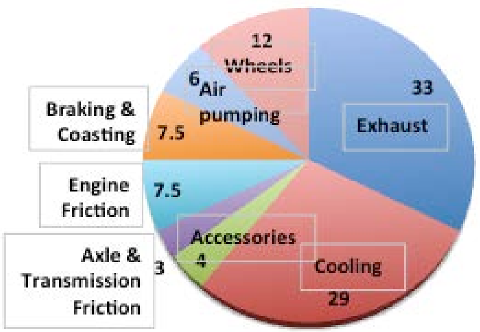
Ionic Liquids as Lubricants and/or Lubricant Additives

STATUS QUO

In an automotive, 10~15% of the energy is lost to friction.



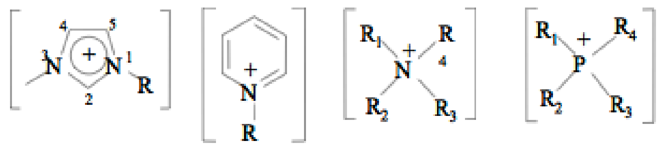
Distribution of energy consumption in car

NEW INSIGHTS

DOE's Goal: 2% improvement on fuel economy through advanced lubricants.

Ionic Liquids – A new class of candidate lubricants or lubricant additives with potential benefits in both engine efficiency and emission control.

Ionic Liquids



(R$_{1,2,3,4}$ = alkyl)

(a) Common cations

$[PF_6]^-$ $[(CF_3SO_2)_2N]^-$ $[BR_1R_2R_3R_4]^-$

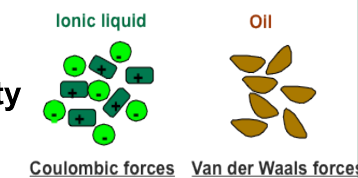
$[BF_4]^-$ $[CF_3SO_3]^-$

$[CH_3CO_2]^-$ $[CF_3CO_2]^-$, $[NO_3]^-$ Br^-, Cl^-, I^- $[Al_2Cl_7]^-$, $[AlCl_4]^-$ (decomp.)

(b) Common anions

Unique properties

- Inherent polarity
- High thermal stability
- Negligible volatility
- Non-flammability
- High flexibility of IL molecular design



Superior lubricating characteristics compared to fully-formulated engine oils

Projected cost <\$5/L if scaled-up, comparable to synthetic oils

Output

ILs as base stocks

- Significant friction and wear reductions
- Tolerating the operation temperature up to 500 °C
- Suitable for specialty bearing components

ILs as oil additives

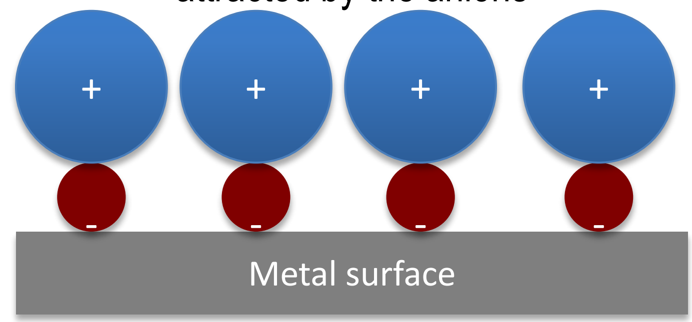
- Multi-function: AW, FM, anti-oxidant, detergent
- Allow the use of lower viscosity oils for better fuel economy
- Potentially replace or reduce the usage of the emission catalyst-poisoning ZDDP
- Cost effective and easier to penetrate into current lubricant market

Patent: *J. Qu, J.J. Truhan, S. Dai, H. Luo, P.J. Blau, "Lubricants or Lubricant Additives Composed of Ionic Liquids Containing Ammonium Cations," U.S. Patent #7,754,664, July 13, 2010.*

Hypotheses for lubricating mechanism of ionic liquids (ILs)

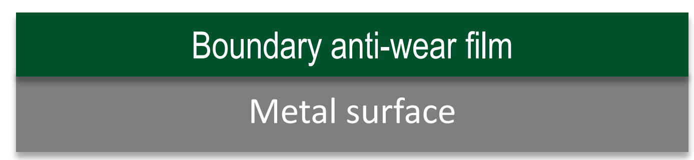
- **At non-EP condition, function as FM additive by a two-layer structure to reduce friction and wear**
  - **A bottom layer of anions absorbed onto metal surface**
  - **A top layer of large-molecule cations attracted by the anions**
- **At EP condition, function as AW additive by tribo-chemical reactions between the ions and the metal surface to form a protective boundary film**

A top layer of large-molecule cations attracted by the anions

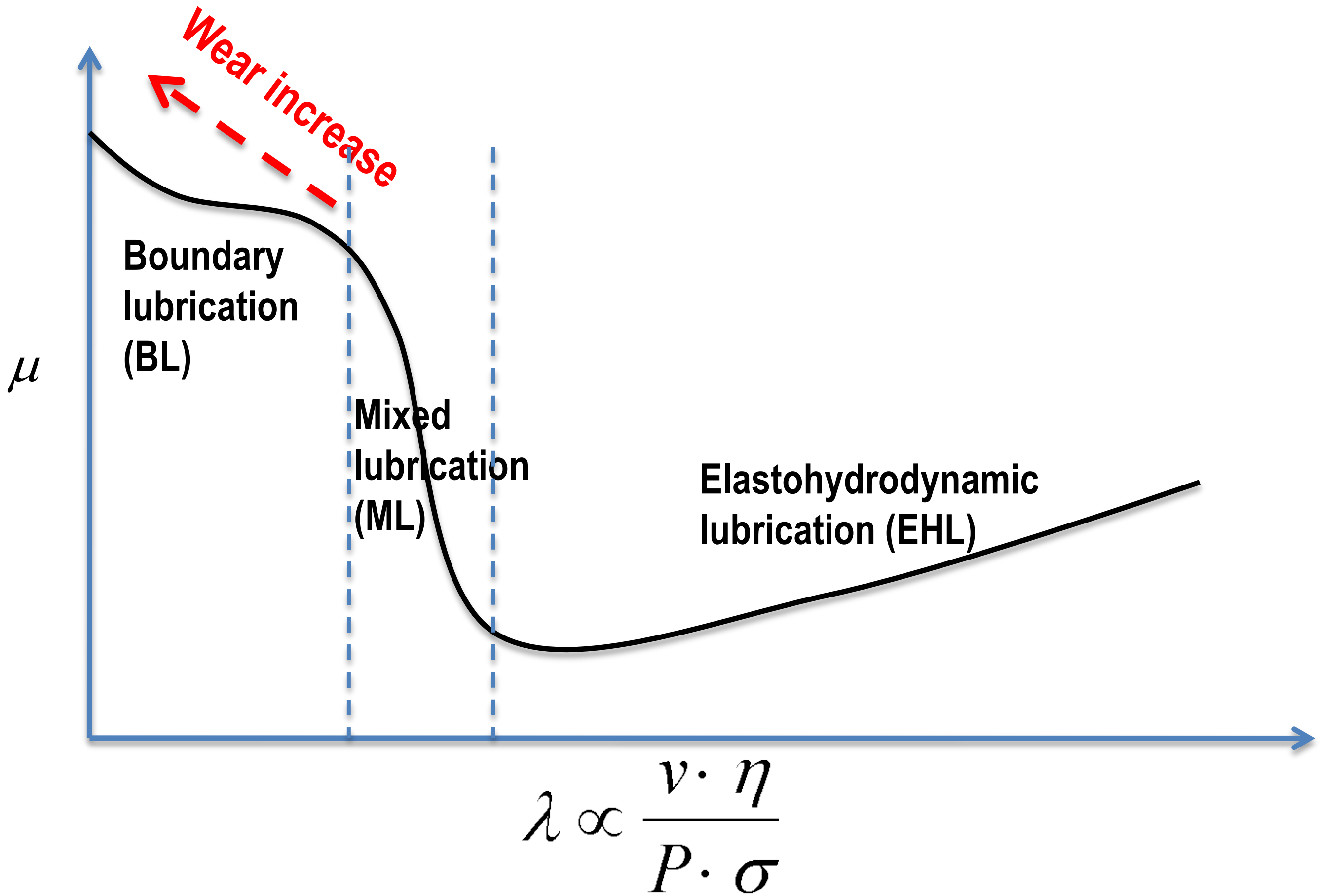


A layer of anions absorbed onto metal surface

A thin anti-wear film formed by ILs reacting with metal surface

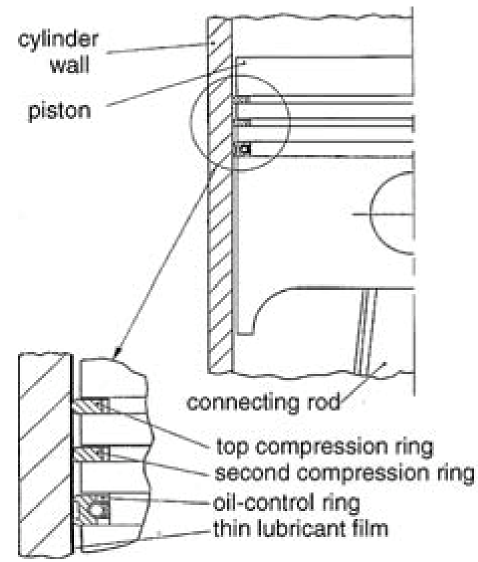


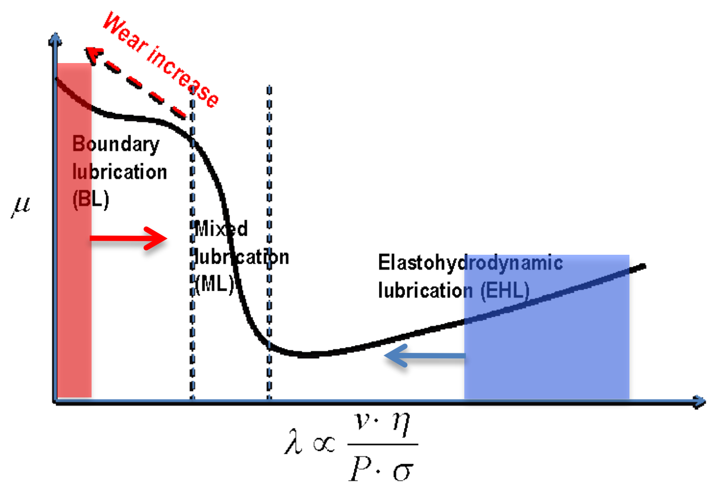
Background: lubrication Regimes (Stribeck curve)

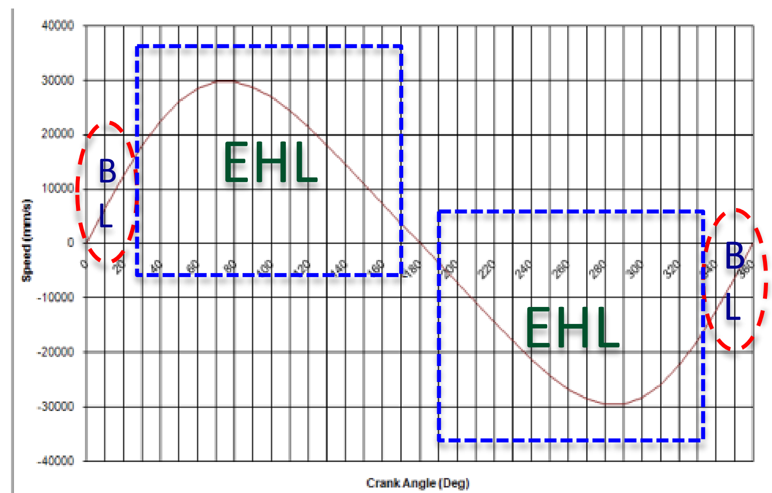


Piston ring–cylinder liner contact in Engine

- **Top ring reversal zone (5-10 mm) determines the durability due to wear**
  - **BL: high-viscosity lubricants provide better wear protection**
- **Majority of the stroke (~80 mm) dominates the energy loss by friction**
  - **EHL: low-viscosity lubricants produce lower friction thus better fuel economy.**
- **Trend: using lower viscosity oils enabled by <u>improved base stock</u> and/or <u>anti-wear additives</u>.**
  - ***Mobil 1 Advanced Fuel Economy oils (0W20 and 0W30) claim to improve fuel economy by up to 2%.***

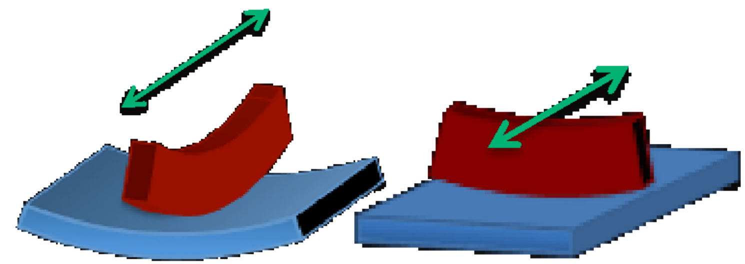


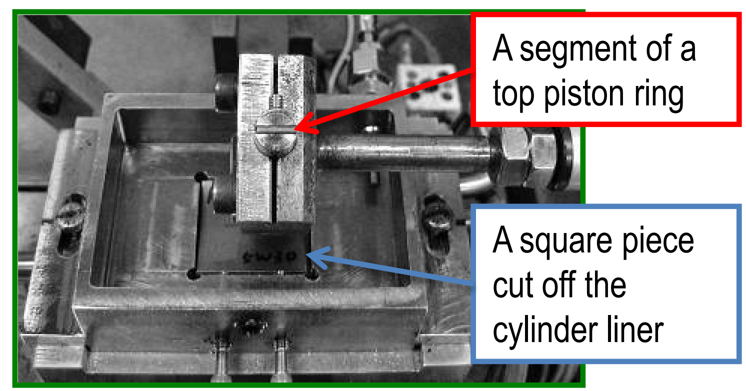




Screening bench test: ring-on-liner reciprocating sliding

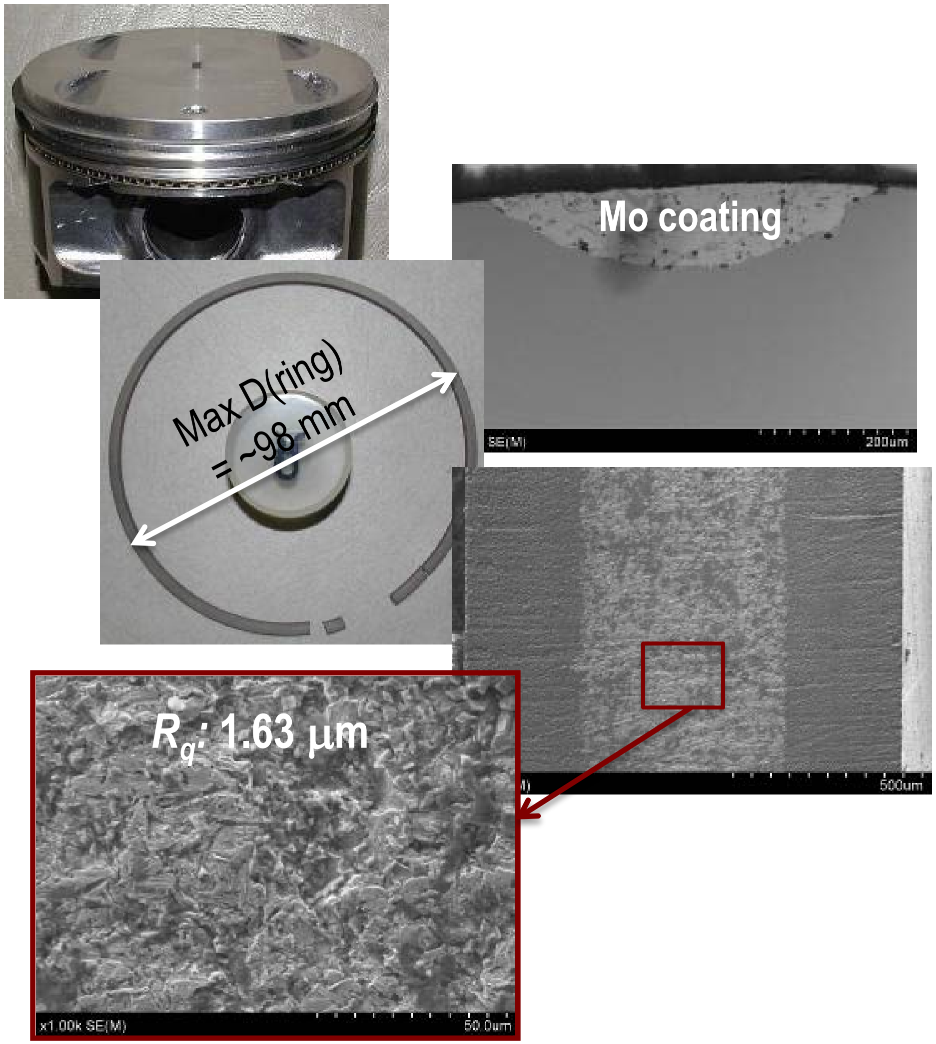
- **Test materials: actual piston top ring (Mo-coated) against cylinder liner (cast iron)**
- **Screening test (cross ring-on-liner reciprocating sliding)** at RT (23 ^{o}C) and 100 ^{o}C
  - Normal load: 160 N → Hertzian contact stress (point-contact): 781 MPa (max) and 521 MPa (mean).
  - 10 Hz, 10 mm stroke (Mean sliding speed: 0.2 m/s)
  - **λ-ratio at 100 ^{o}C: 0.015 << 1 → boundary lubrication**
  - **λ-ratio at 23 ^{o}C: 0.09 << 1 → boundary lubrication**

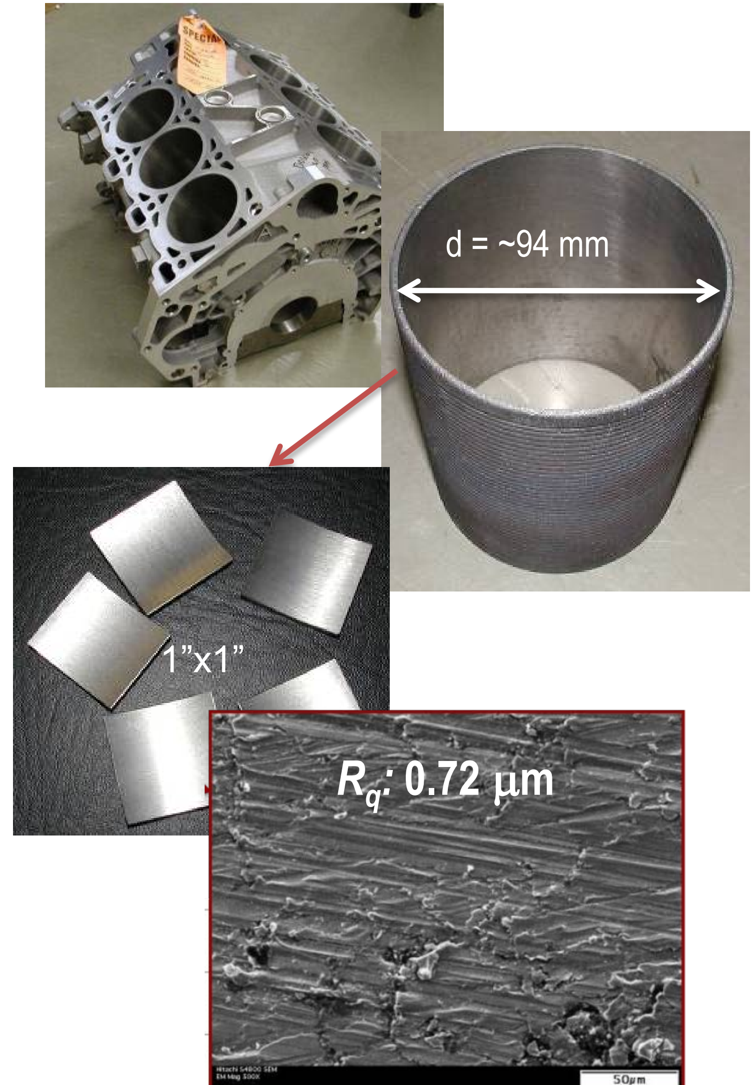




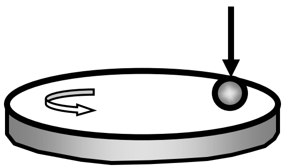
Same lubrication regime as in an actual engine, but a lower λ-ratio indicating worse lubrication condition → accelerated wear process.

Test coupons from actual piston rings and cylinder liners

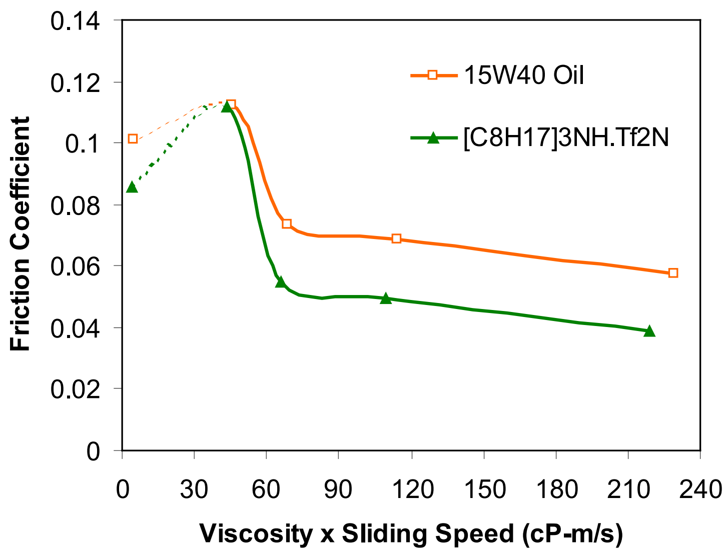




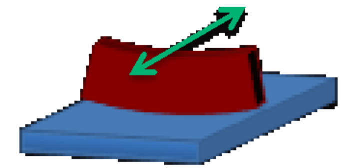
Ionic liquids as neat lubricants – substantially friction/wear reductions

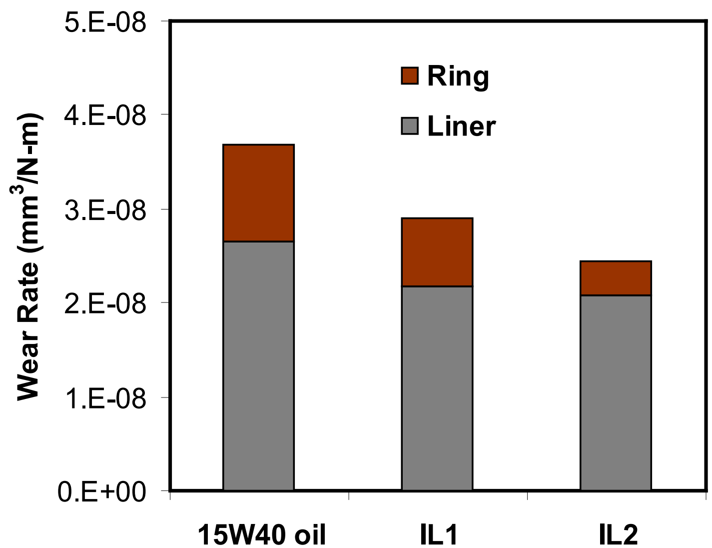


Steel-Al contact



Ring-liner contact

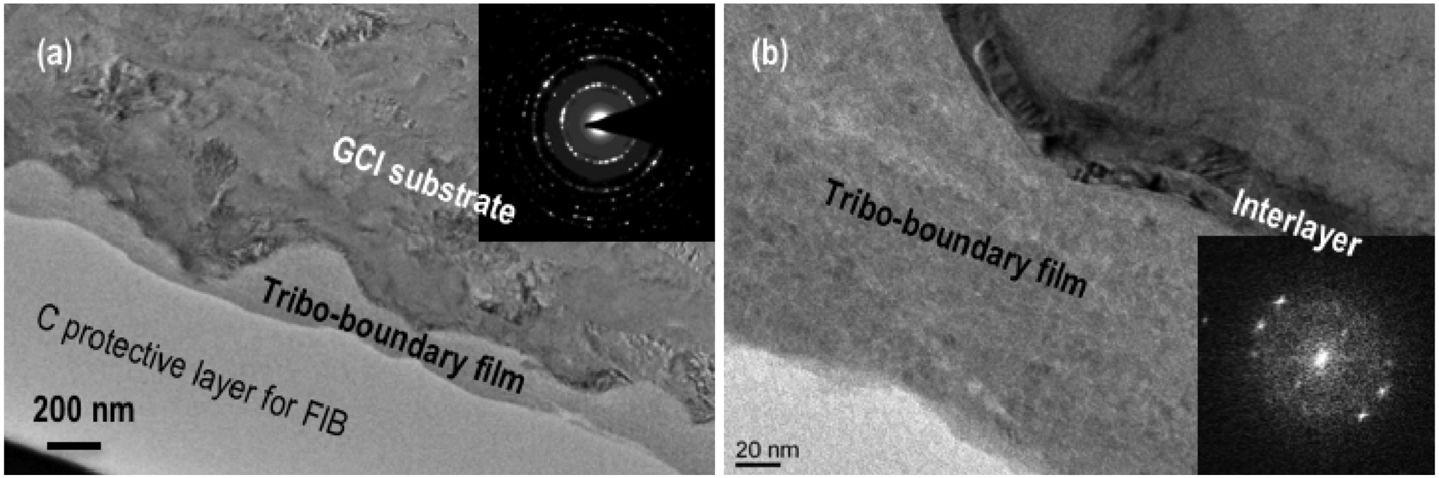


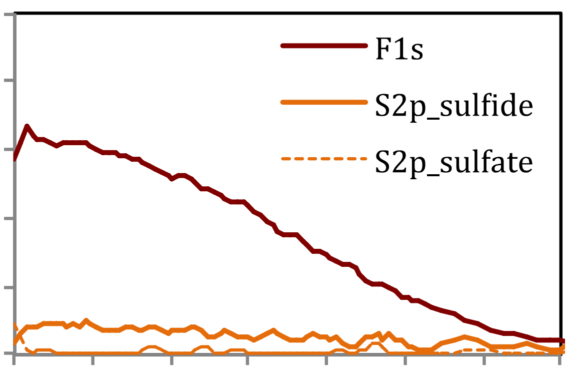


[1] Qu, J., Truhan J.J., Dai S., Luo, H., Blau, P.J., Tribology Letters, 22(3) 2006, pp. 207-214.
[2] J. Qu, P.J. Blau, S. Dai, H. Luo, H.M. Meyer III, J.J. Truhan, Wear 267(5-8) (2009) 1226-1231.

[3] J. Qu, P.J. Blau, S. Dai, H. Luo, H.M. Meyer III, Tribology Letters 35(3) (2009) 181-189..

Lubricative, anti-wear boundary film formed on the metal surface in IL-lubrication





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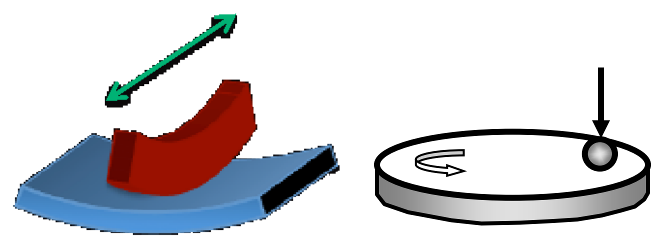
[4] *J. Qu*, M. Chi, H.M. Meyer III, P.J. Blau, S. Dai, H. Luo, Tribology Letters 43(2) (2011) 205-211.*

Recently developed low-viscosity ILs

- 200 °C higher thermal stability than hydrocarbon oils
- 20% lower viscosity than 0W-10 engine oil
- Significantly better wear protection than 0W-10 engine oil
- Lower pressure-viscosity coefficient than oils – potential lower friction under EHL

Lubricant	Decomp. temp (°C)	Density (g/ml, 23°C)	Kinematic viscosity (cSt)				
			0 °C	10 °C	23 °C	40 °C	100 °C
Mobil 1™ 5W30 engine oil	263	0.80	593.0	299.8	140.9	63.3	10.5
Royal Purple™ 0W-10 engine oil	236	0.87	182.4	99.2	50.5	24.6	4.8
IL17	472	1.42	130.6	70.8	35.7	17.8	4.1

Lubricant	23 °C	150 °C
	Wear rate (mm^3/N-m)	Wear rate (mm^3/min)
IL17	1.8×10^{-7}	0.6×10^{-4}
Royal Purple™ 0W-10	3.5×10^{-7}	7.9×10^{-4}
Mobil 1™ 5W-30 engine oil		0.5×10^{-4}

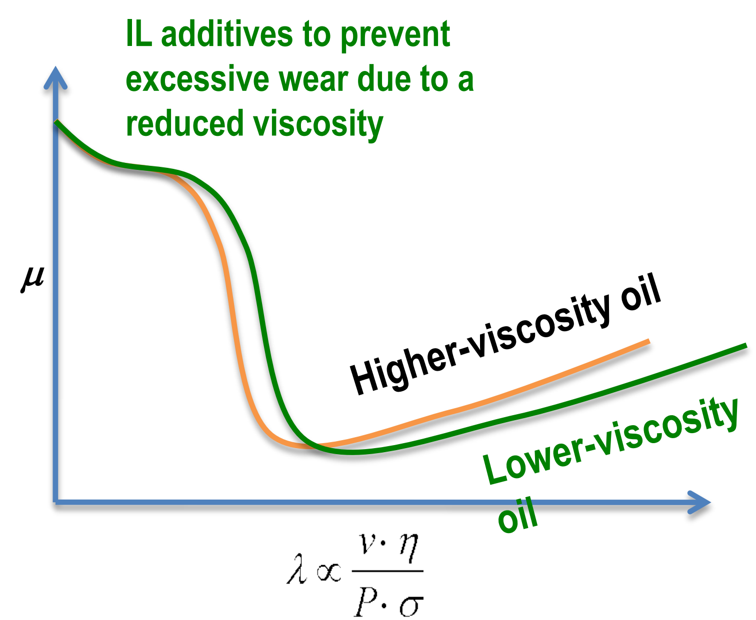


Ionic liquids as oil additives

- Enhanced wear protection by ionic liquid additives
  - improves engine durability and extended service intervals,
  - prevents the wear-induced engine efficiency loss and emission increase, and
  - more importantly, allows using less viscous oils, leading to better fuel economy.

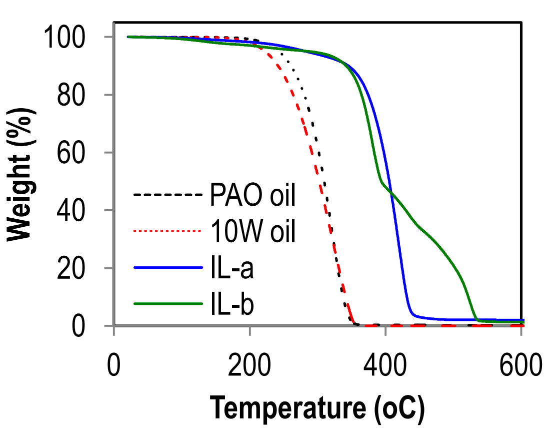
ORNL discovered a unique group of ILs:

- Mutual miscibility with hydrocarbon oils (first in the literature)
- Fluorine-free
- Non-corrosive
- High thermal stability
- Excellent wettability
- Friction reduction and anti-wear functions when added to oils

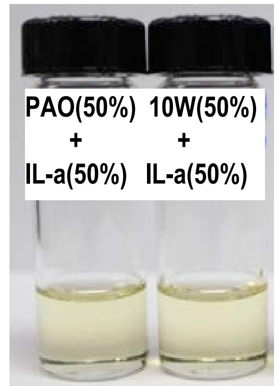


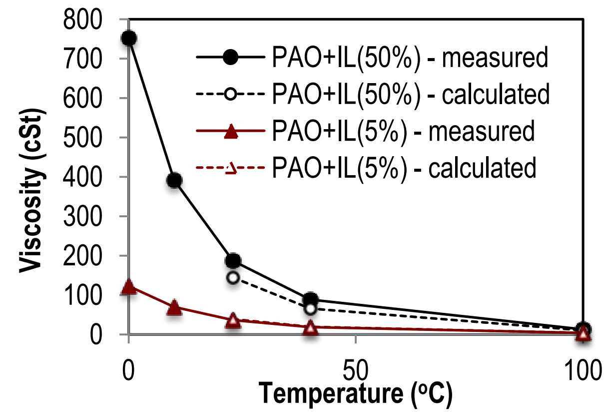
Recent breakthrough: oil-miscible ILs

- High thermal stability

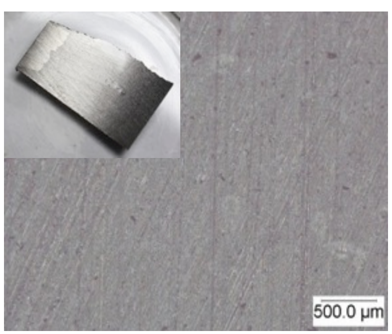


- Fully miscible with lubricating oils

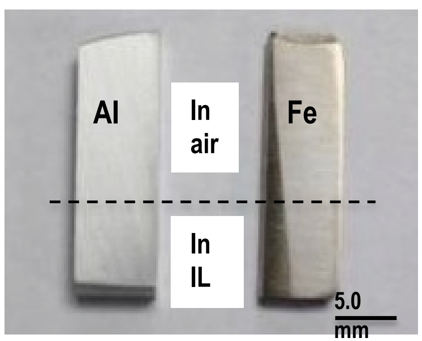




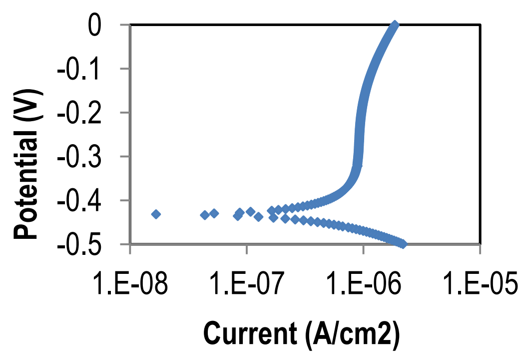
- Non-corrosive to Al or Fe



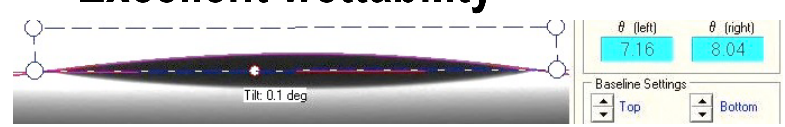
IL on cast iron surface for 60 days



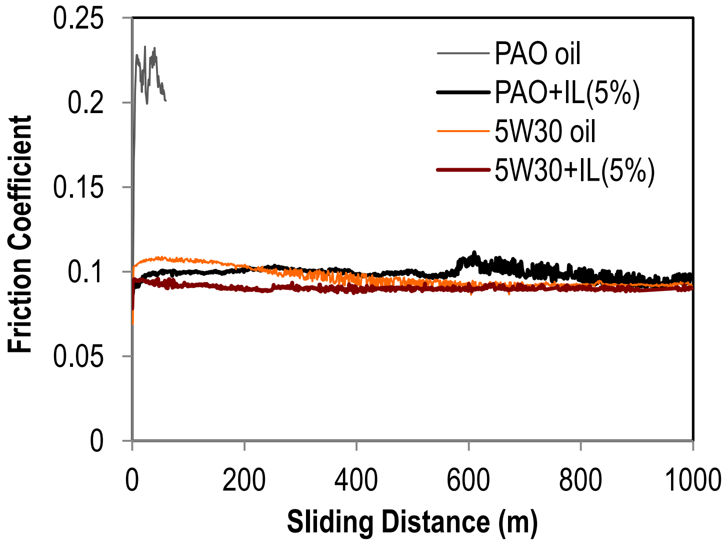
Al and cast iron in IL at 135 °C for 7 days

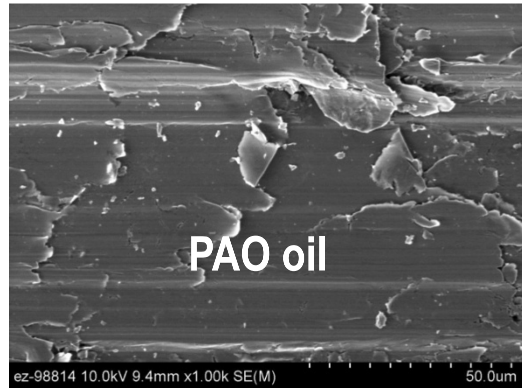


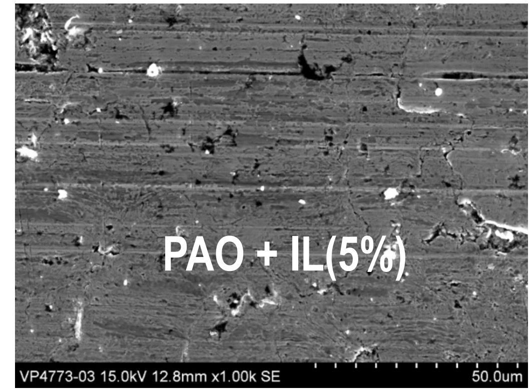
- Excellent wettability



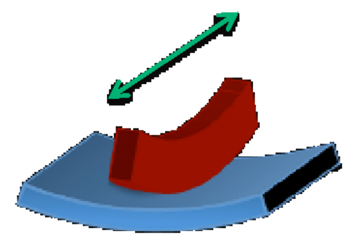
Oil-miscible ILs as oil additives are effective in anti-scuffing and anti-wear





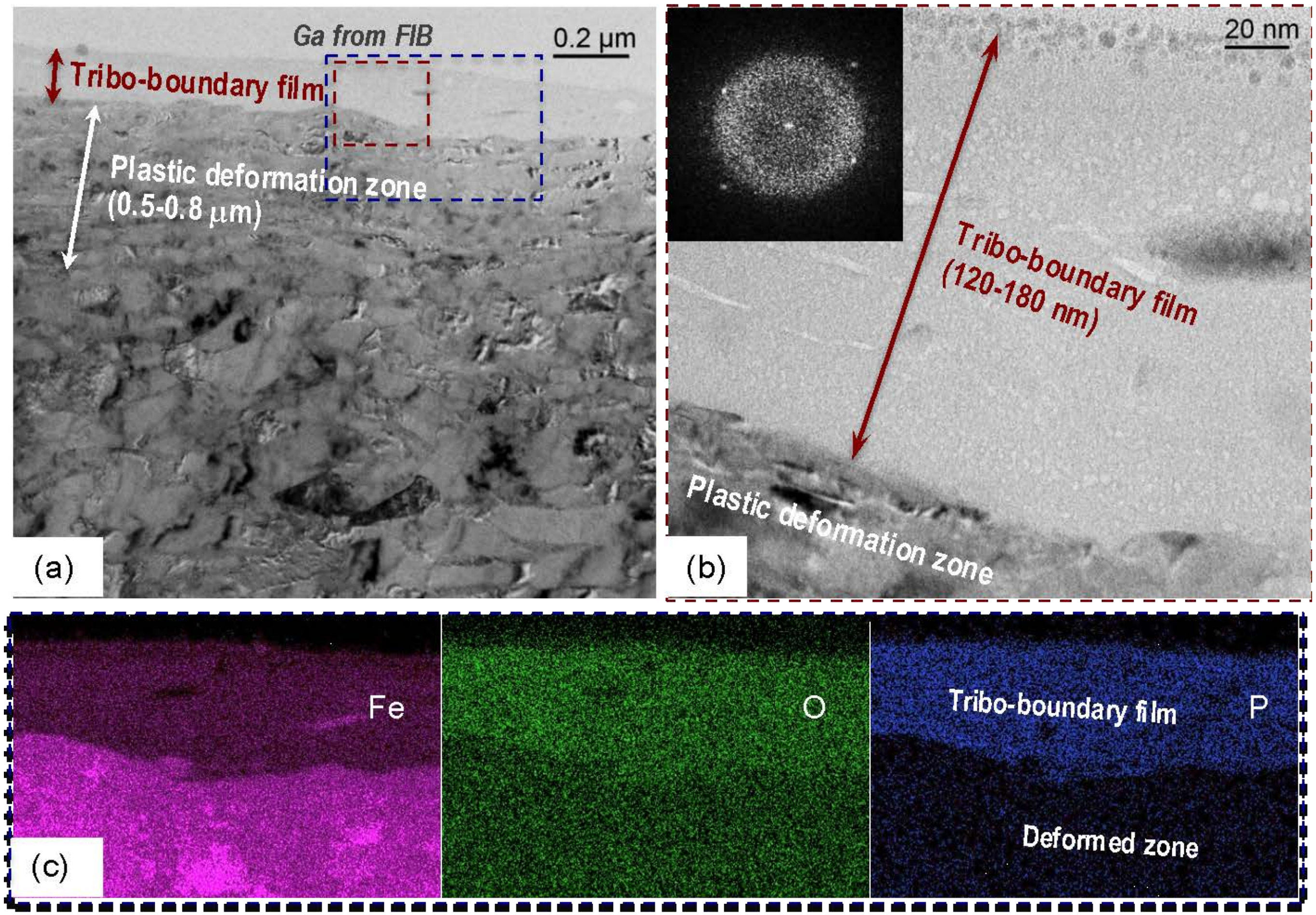


Lubricant	Viscosity (cSt, 23 °C)	Wear rate (mm^3/N-m)	
		Liner	Ring
PAO 4 cSt base oil	34.5	$5.9\pm4.7\times10^{-4}$	$>1.0\times10^{-6}$
PAO+IL(5%)	36.6	$5.6\pm3.5\times10^{-7}$	$1.4\pm0.5\times10^{-8}$
5W30 engine oil	140.9	$4.7\pm0.3\times10^{-7}$	$6.6\pm4.9\times10^{-9}$
5W30+IL(5%)	149.9	$1.3\pm0.2\times10^{-7}$	$2.0\pm1.6\times10^{-9}$

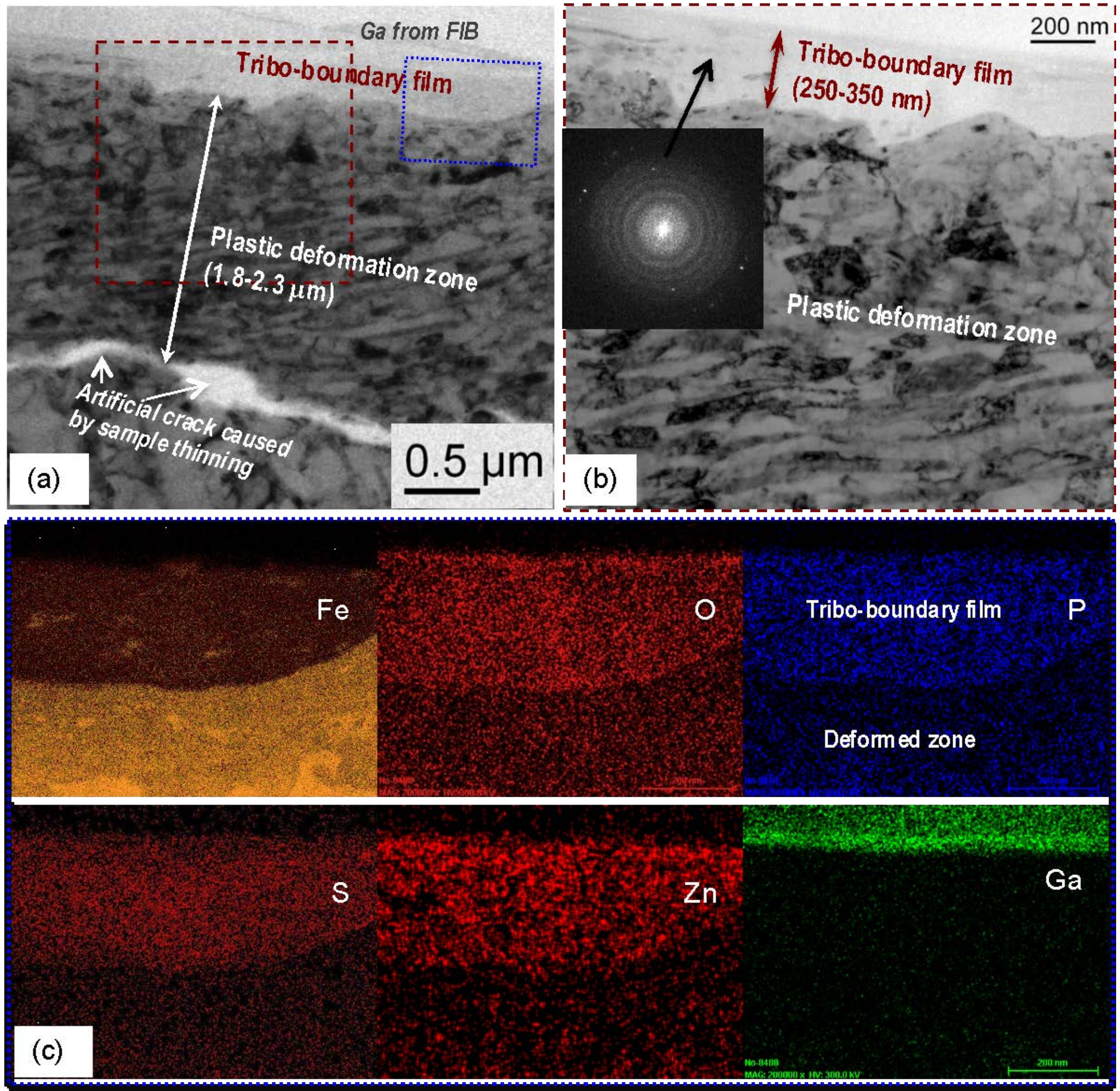


The addition of ILs make the low-viscosity base oils perform as well as the more viscous, fully formulated engine oils in both friction and wear perspectives.

Boundary film on cast iron liner lubricated by PAO+IL(5%)



Boundary film on cast iron liner lubricated by 5W-30 engine oil+IL(5%)



A thicker boundary film containing elements from both IL and ZDDP confirms the synergistic effect in wear protection.

Summary

- Great progress achieved in developing ILs for lubrication
  - Low-viscosity ILs as neat lubricants
    - ➢ Lower viscosity, higher thermal stability, and superior wear protection than fully-formulated 0W-10 engine oil.
  - Oil-miscible ILs as oil additives
    - ➢ High thermal stability, non-corrosive, excellent wettability, and effective in anti-scuffing and anti-wear.
- Future work
  - Motored and fired engine tests for demonstrating improvement on engine efficiency and durability.
  - Accelerated fired engine tests for investigating effects of ILs on emission catalyst aging and poisoning.
  - Full formulation of IL-containing lubricants.