Ionic Liquids as Multi-Functional Lubricant Additives to Enhance Engine Efficiency

– An award of FOA0000239

Project ID: FT014

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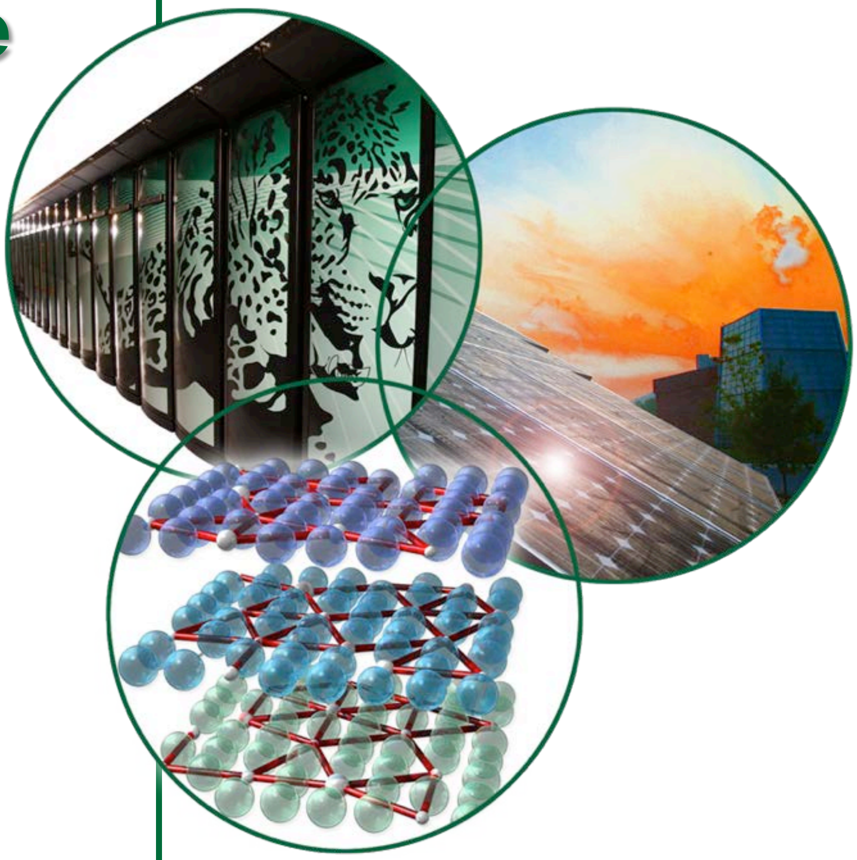
Sheng Dai, Brian West

Shell: Brian Papke, Cheng Chen, Hong Gao

DOE Management Team:

Kevin Stork and Steve Przesmitzki

2013 DOE Vehicle Technologies Program Annual Merit Review, May 16th 2013



U.S. DEPARTMENT OF ENERGY

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OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

- Project (CRADA) start date: July 23, 2012
- Project (CRADA) end date: July 22, 2015
- Percent complete: 20%

Budget

- Total project funding $1.6M
  - DOE share: $1.2M
  - Shell in-kind cost share: $400K
- FY12 funding
  - DOE share: $400K
  - Shell in-kind cost share: $100K
- FY13 funding
  - DOE share: $400K (expected)
  - Shell in-kind cost share: $150K

Barriers

- 10-15% energy generated in an IC engine is lost to parasitic friction, which is governed by the engine lubricant.
- Emission catalysts 'poisoned' by conventional anti-wear additives in the engine lubricant.
- Low-viscosity engine oils increase fuel economy but post challenges on wear protection.

Partners

- Project lead: ORNL
- CRADA partner: Shell Global Solutions (U.S.)

Relevance – Objectives

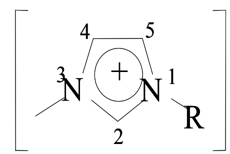
- **Objective: Develop and demonstrate oil-soluble ionic liquids as engine oil additives to substantially improve the mechanical efficiency of internal combustion engines.**
  - **Potential advantages and disadvantages of this new category of additives will be explored with a combination of systematic laboratory experiments, modeling, engine dynamometer tests, and field tests.**
- **Potential benefits:**
  - **The goal of this project is 2% increase on the engine fuel efficiency that would save ~80 million barrels of oil for U.S. each year.**
  - **Potentially produce no or less emission catalyst-poisoning compounds compared with ZDDP that would improve the catalyst life and performance to reduce emissions.**

Background – Ionic liquids

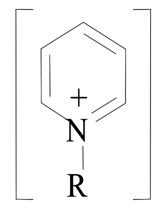
- **ILs as neat lubricants or base stocks**
  - High thermal stability (up to 500 ºC)
  - High viscosity index (120-370)
  - Low EHL/ML friction due to low pressure-viscosity coefficient
  - Wear protection by tribo-film formation
  - Suitable for specialty bearing components

- **ILs as oil additives**
  - Potential multi-functions: AW/EP, FM, *corrosion inhibitor, detergent*
  - Ashless/low sludge
  - Allow the use of lower viscosity oils
  - Cost effective and easier to penetrate into the lubricant market

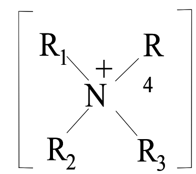
Ionic liquids are 'room temperature molten salts', composed of cations & anions, instead of neutral molecules.



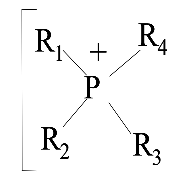
1-alkyl-3-methyl-imidazolium



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

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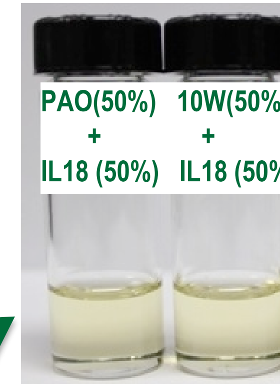
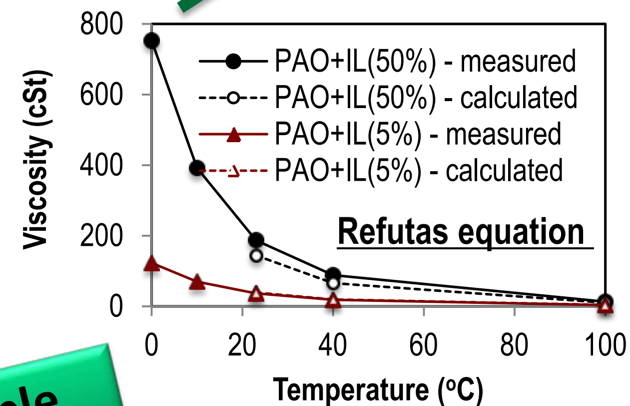
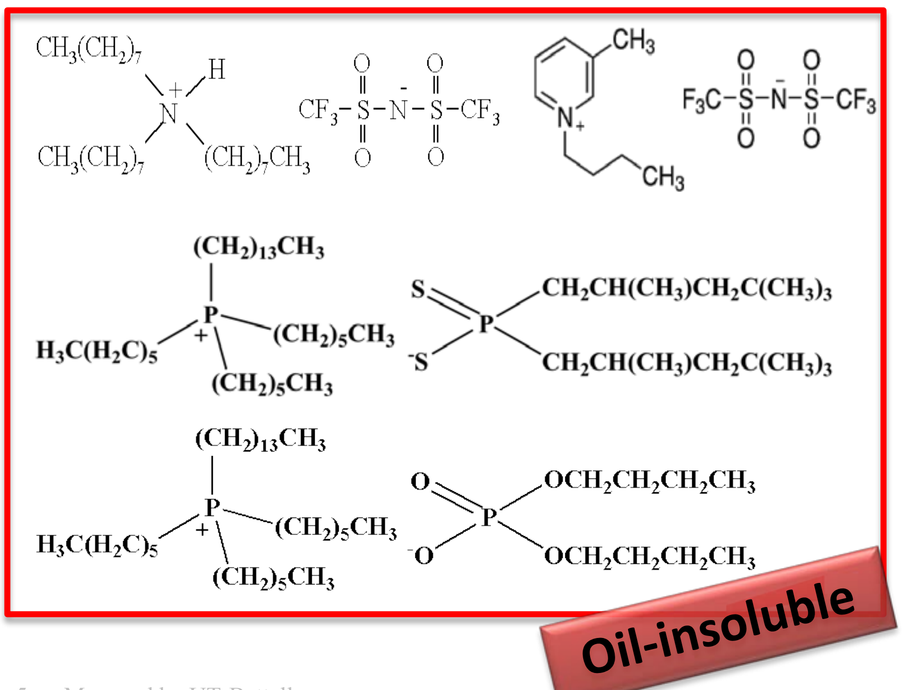
Background – Breakthrough in developing oil-miscible ionic liquids

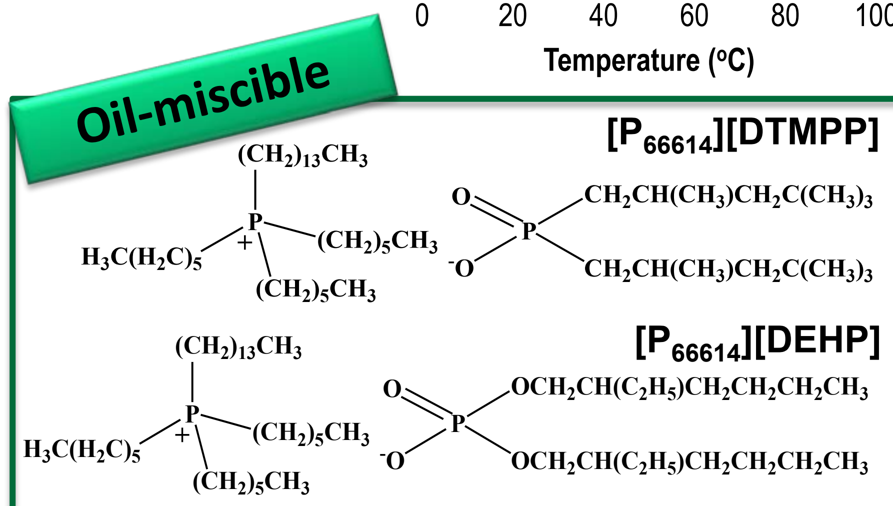
- **Most ILs have very limited oil-solubility (<<1%).**
- **[P_{66614}][DTMPP] (IL16) & [P_{66614}][DEHP] (IL18) are fully miscible with hydrocarbon oils.**
  - Hypothesis: 3D quaternary ion structures w/ long hydrocarbon chains (high steric hindrance) to dilute the charge, and
  - Containing oxygen (but why?)



Confirming miscibility







B. Yu, and J. Qu, et al., Wear (2012) 289 (2012) 58–64.*

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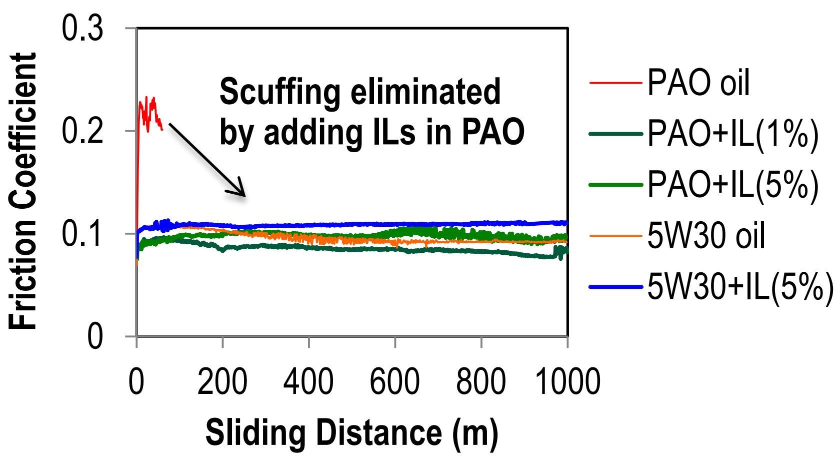
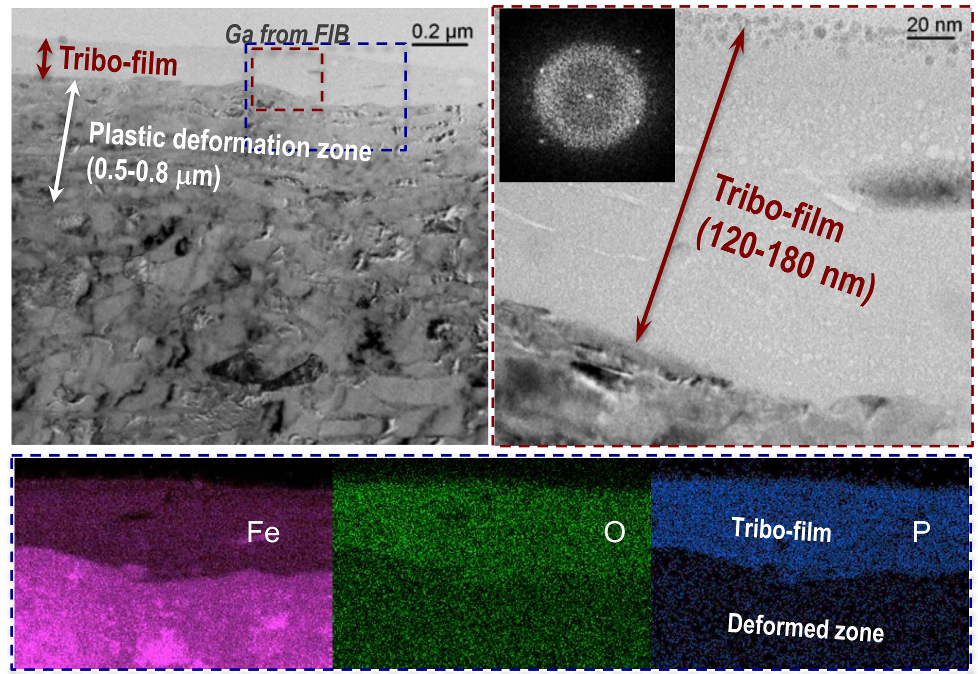
Background – One oil-miscible IL has demonstrated anti-wear in RT bench tests

- **Adding 1-5% of ILs into PAO eliminating scuffing and reducing wear.**
- **Low-viscosity oil-IL single blend performing as well as the Mobil 1™ 5W30 engine oil.**
- **Synergistic anti-wear effect with ZDDP.**



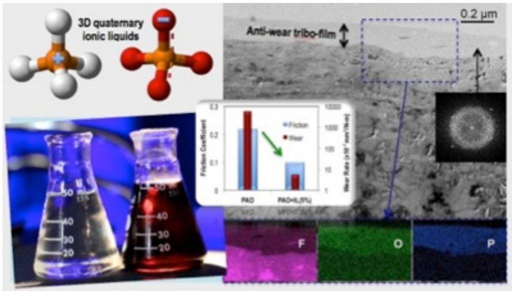
Lubricant	Viscosity (cSt, 23 °C)	Wear rate (x10^{-7} mm^3/N-m)
PAO base oil	34.5	5910 ^{4700}
PAO+IL(1-5%)	34.9-36.6	4.0-5.7 $^{0.1}$
5W30 engine oil	141	4.8 $^{0.3}$
5W30+IL(5%)	150	1.2 $^{0.2}$

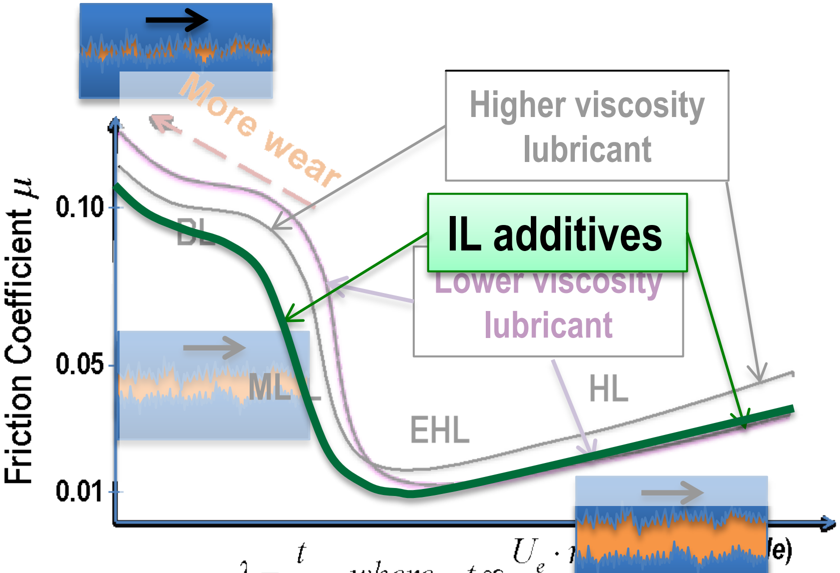


J. Qu, et al., *ACS Applied Materials & Interfaces 4* (2) (2012) 997.

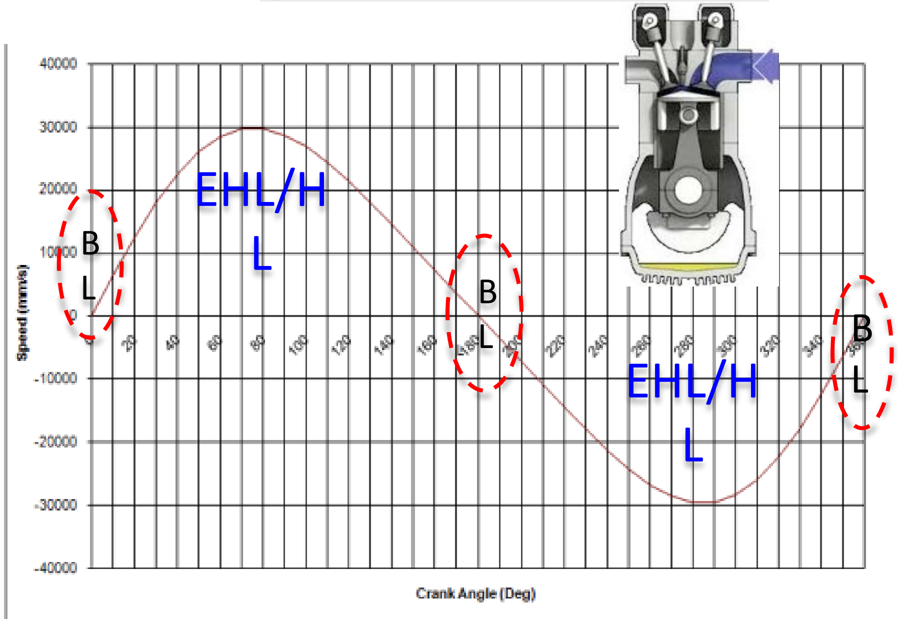
Approach – Developing ionic liquids-based multi-functional additives

- **Majority of the stroke under EHL/HL (lower viscosity oil→lower friction) while top ring reversal region under BL (lower viscosity oil→higher wear).**
- **Ionic liquids (ILs) as multi-functional oil additives**
  - **Anti-wear tribo-film to allow the usage of lower viscosity engine oils to improve fuel economy, and**
  - **Smoother, low-friction tribo-film to reduce BL/ML traction.**





$$\lambda = \frac{t}{\sigma}, \quad where \quad t \propto \frac{U_e \cdot \eta}{P}$$



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Milestones

- **July 2013 – Design and synthesize a series of oil-soluble ILs with various molecular structures and conduct standard lubricant additive evaluations.** ***(in progress)***
- **July 2013 *(Go/No-Go point #1)* – Demonstrate 10% or more friction reduction without sacrificing the wear performance for low-viscosity oils by using the IL additives from the tribological bench tests*.*** ***(in progress)***

Approach – Tasks

- **Overall program timeline: 7/23/2012 – 7/22/2015**

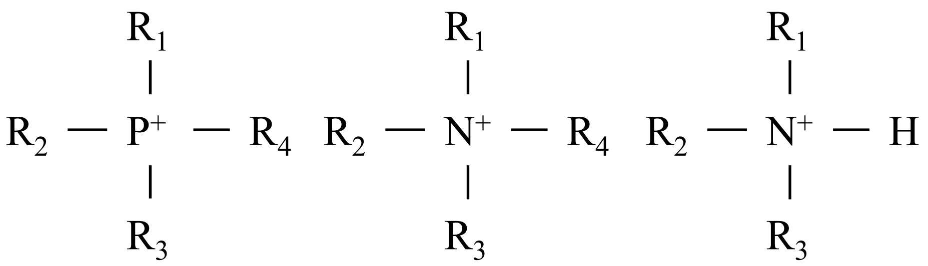
	PY 1				PY 2				PY 3			
Month	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1. Design, synthesis, and optimization of oil-soluble ILs												
Task 2. Characterization of physical/chemical properties of ILs												
Task 3. Standard additive evaluation for ILs and lubricant formulation												
Task 4. Tribological bench tests and analyses												
Task 5. Investigation and modeling of lubrication mechanism of IL additives												
Task 6. Instrumented single-cylinder motored engine tests												
Task 7. Instrumented single-cylinder fired engine tests with emission analysis												
Task 8. Multi-cylinder fired engine fuel efficiency dynamometer tests (ASTM D 7589 Sequence VI)												
Task 9. Initial field tests												

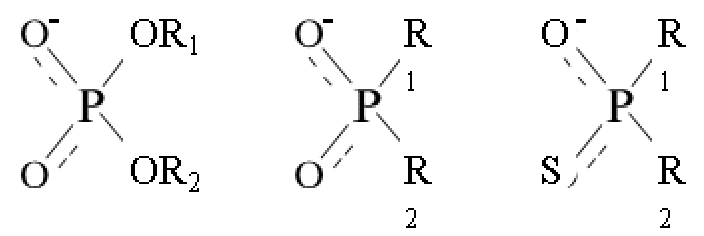
Technical accomplishments – summary

- Task 1. Design, synthesis, and optimization of oil-soluble ionic liquids
  - ✓ Several groups of ILs with 3D quaternary structures designed/synthesized.
- Task 2. Characterization of physical/chemical properties of ILs
  - ✓ Oil-solubility, density, viscosity, thermal stability, and corrosivity conducted on selected ILs.
- Task 3. Standard additive evaluation for ILs and lubricant formulation
  - ✓ 3-month storage stability tests completed on selected ILs
  - – Elastomer compatibility tests planned.
- Task 4. Tribological bench tests and analyses
  - ✓ Base oil and baseline lubricants determined and acquired.
    - Shell GTL 4 cSt base oil and GTL-based formulated engine oils: fully-formulated, w/o AW, and w/o FM
  - ✓ Bench tests selected: ball-on-flat sliding (BL, 100 ^{o}C) and rolling-sliding (Stribeck, 120 ^{o}C)
  - ✓ Test specimens have been designed, machined, and shared between ORNL and Shell.
  - ✓ Test parameters and test matrices defined.
  - \- Friction and wear tests being conducted.
- Task 5. Investigation and modeling lubrication mechanism of IL additives
  - ✓ Contact mechanics and lubrication modeling conducted.
  - \- Wear mode examination and tribo-film characterization in progress.

Design and synthesis of oil-soluble ILs

- Several groups of ILs with 3D quaternary structures designed and synthesized.
  - 12 ILs fully miscible (>10%) and another 3 soluble (>1%) in Shell GTL 4 cSt base oil
  - 5 ILs fully miscible (>10%) and another 2 soluble (>1%) in Shell GTL 4-based formulated engine oil without precipitates or color change (no reaction w/ existing additives)





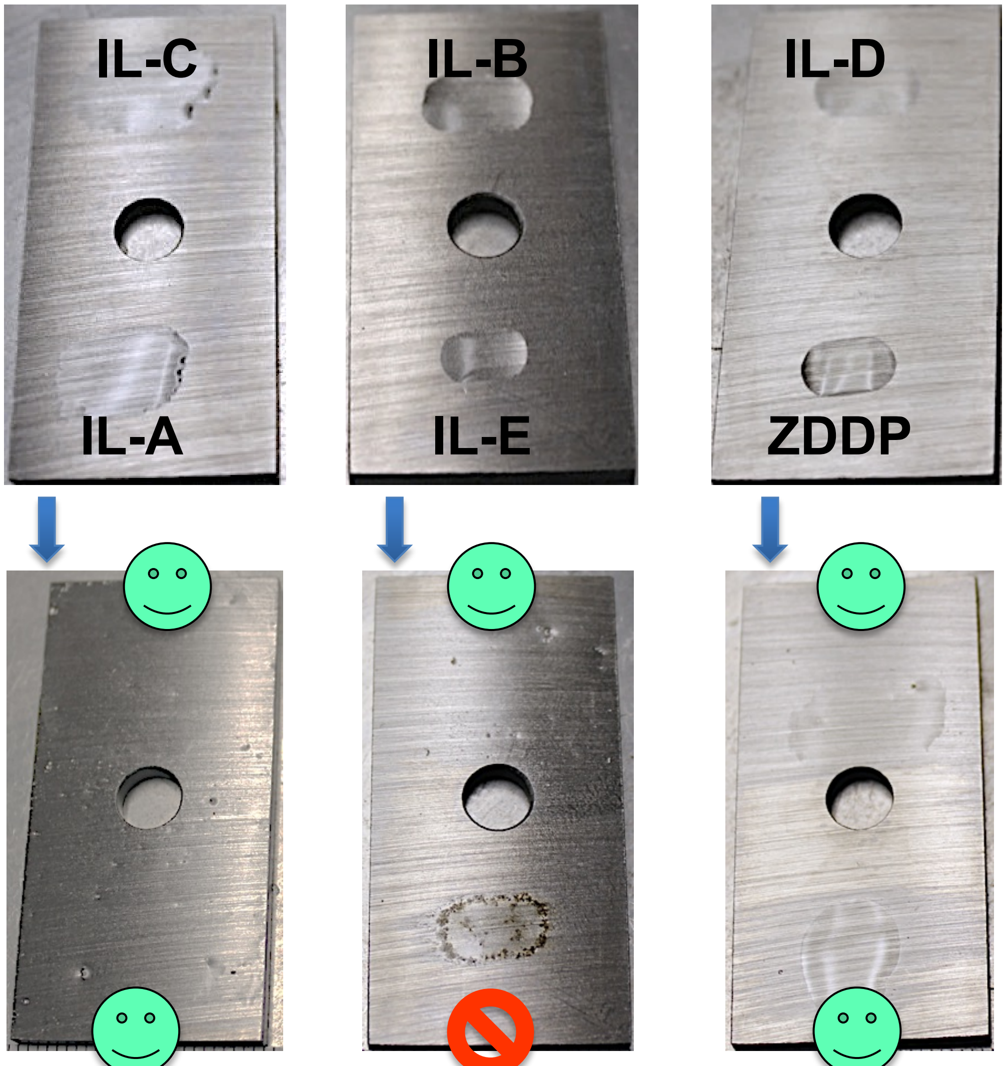
Oil-solubility	Shell GTL 4	Shell GTL 4-based fully formulated engine oil	Shell GTL 4-based formulated oil w/o AW
IL-A	>10%	>10% (no color change)	>10% (no color change)
IL-B	>10%	>10% (no color change)	>10% (no color change)
IL-C	>10%	>10% (no color change)	>10% (no color change)
IL-D	>10%	>10% (no color change)	>10% (no color change)

Corrosion tests

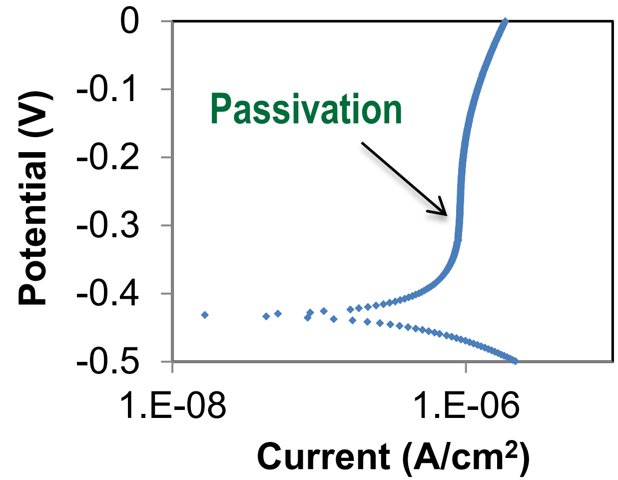
Pitting test on CL35 grey cast iron at RT

Day 1

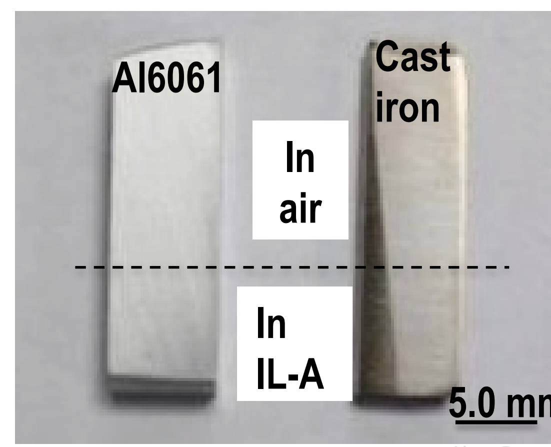
Day 14



Potentialdynamic polerization curve of cast iron in IL-A



HT (135 °C) exposure for 7 days



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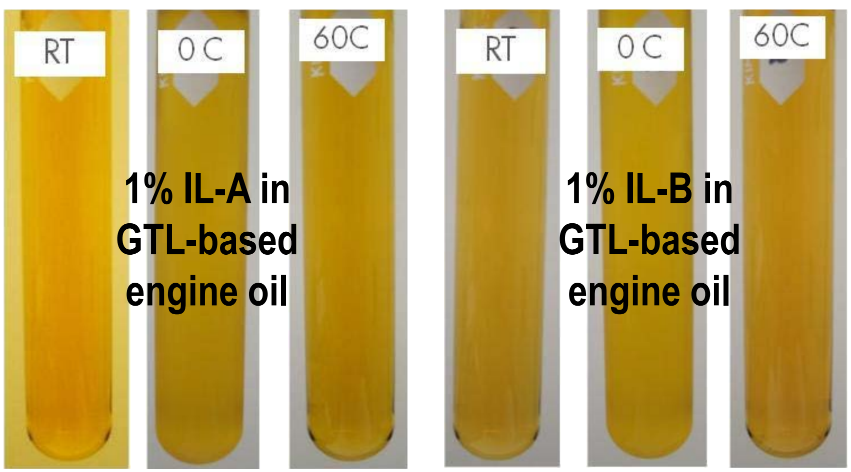
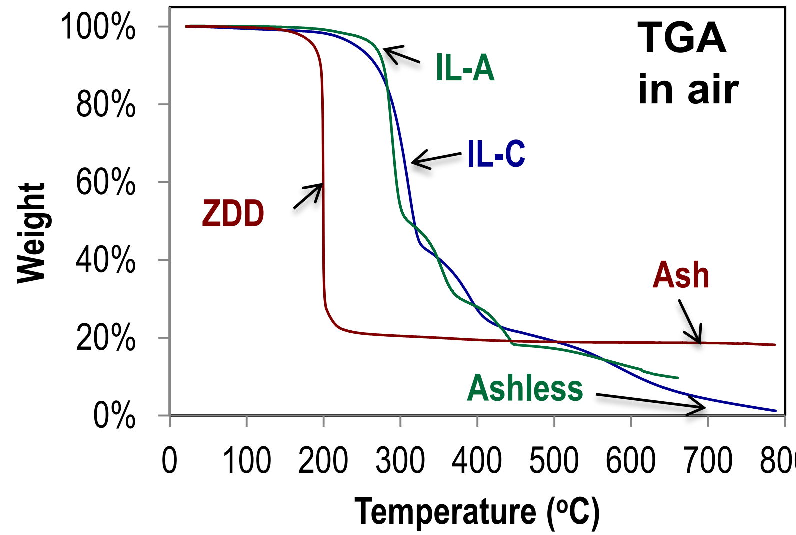
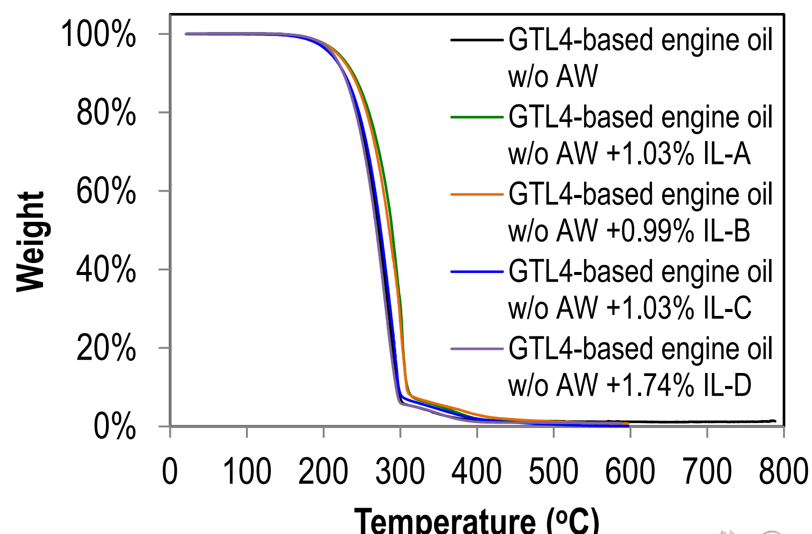
Storage and thermal stabilities

- IL-A and IL-B have passed the 3-month Shell storage stability tests at 0 °C, RT, and 25 °C.
  - No color change and no precipitates
- TGA tests revealed ashless and higher thermal stability and anti-oxidation of ILs compared to ZDDP.
- No premature thermal degradation when adding ILs into the formulated engine oil.







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ILs' concentrations in GF-5 engine oils

ILSAC GF-5

3.a <u>Catalyst Compatibility</u>

Phosphorus Content, ASTM D4951	0.08% (mass) maximum
Phosphorus Volatility, ASTM D7320 (Sequence IIIGB, phosphorus retention)	79% minimum
Sulfur Content, ASTM D4951 or D2622	
0W-XX, 5W-XX	0.5% (mass) maximum
10W-30	0.6% (mass) maximum

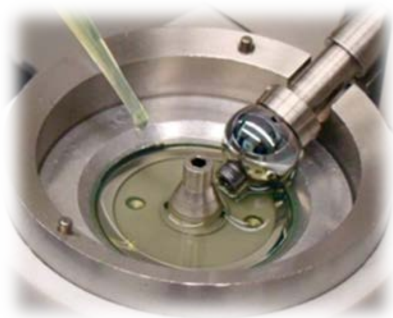
3.b <u>Wear</u>

Phosphorus Content, ASTM D4951	0.06% (mass) minimum

Little change in oil viscosity by IL additives at these concentrations

	Molecular weight	P (wt%)	S (wt%)	Zn (wt%)	Allowable concentration
ZDDP (Octyl)	771	8.04	16.6	8.43	0.75 - 0.99 wt%
IL-A	804	7.71	0	0	0.78 - 1.03 wt%
IL-B	772	8.03	0	0	0.75 - 0.99 wt%
IL-C	804	7.71	0	0	0.78 - 1.03 wt%
IL-D	675	4.59	0	0	1.31 - 1.74 wt%

Tribological bench tests



- **Ball-on-disc rolling-sliding test for Stribeck curves (BL-ML-EHL)**
  - PCS Mini-Traction Machine (MTM2)
  - Ball: AISI E52100 steel (19 mm dia)
  - Disk: AISI E52100 steel
  - Temperature: 100, 120 ^{o}C
  - Load: 30 N
  - Rolling speed: 0.01-3 m/s (50% slip)

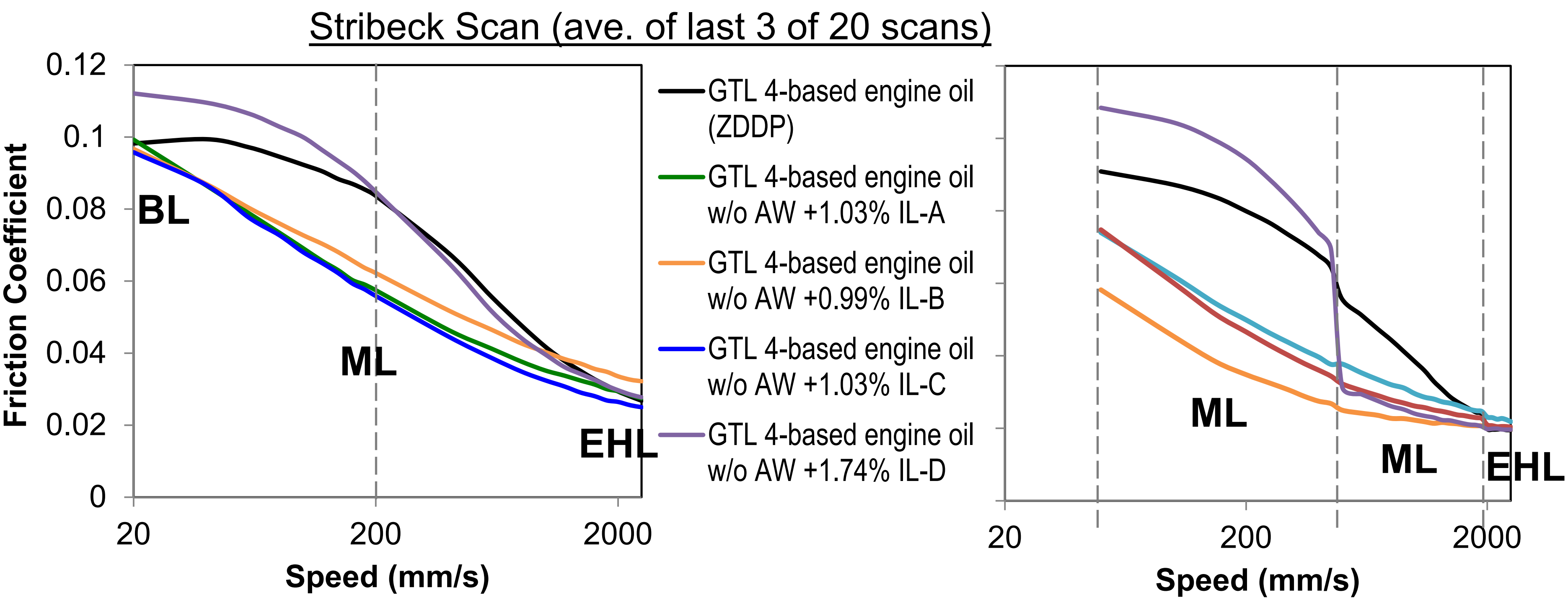
- **Ball-on-flat reciprocating sliding test for boundary lubrication friction and wear**
  - Plint TE-77 and TE-90 machines
  - Ball: AISI E52100 steel (10 mm dia)
  - Flat: CL35 grey cast iron (1”x1”x1/8”)
  - Temperature: 100 ^{o}C
  - Load: 50 or 100 N and speed: 0.2 m/s (ave)
  - Sliding distance: 1000 m

	As-is	+IL	+IL+ZDDP
GTL 4 cSt			
GTL 4+ full additive package w/o AW			
GTL 4+ full additive package			

*Additive concentration: 0.8-1.8 wt% (to approach the max allowable phosphor content 0.08 wt%)

IL additives reduce friction in mixed lubrication (rolling-sliding tests at Shell)

- **Full Stribeck scan: 25-35% friction reductions in mixed lubrication when IL-A, IL-B, or IL-C replacing ZDDP in the engine oil.**
- **Sectioned Stribeck scan: 40-50% friction reductions in mixed lubrication when IL-A, IL-B, or IL-C replacing ZDDP in the engine oil.**



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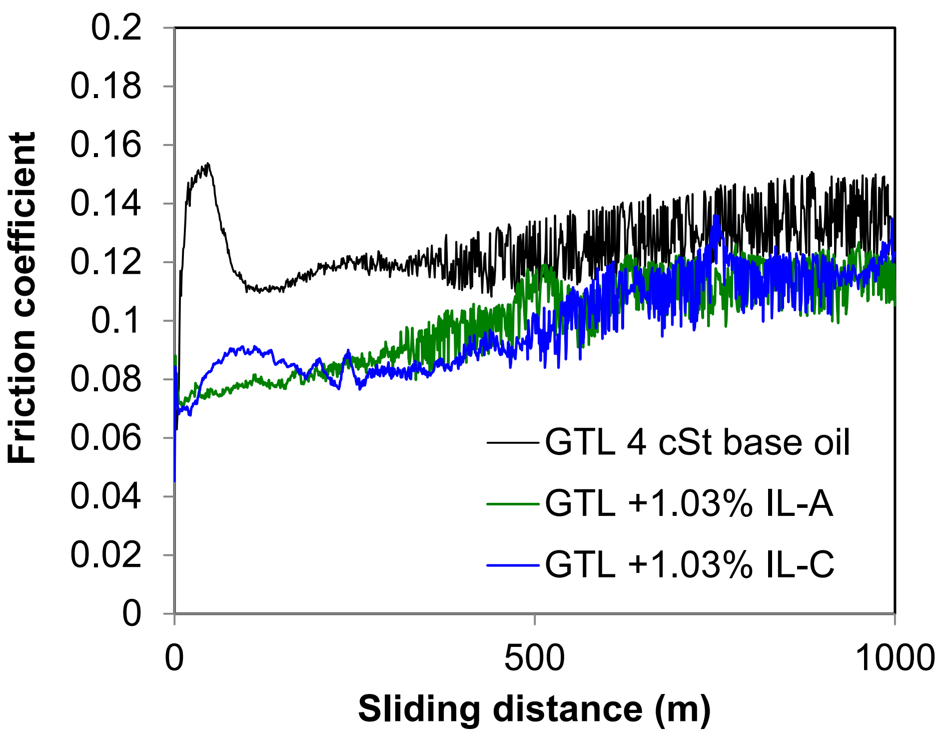
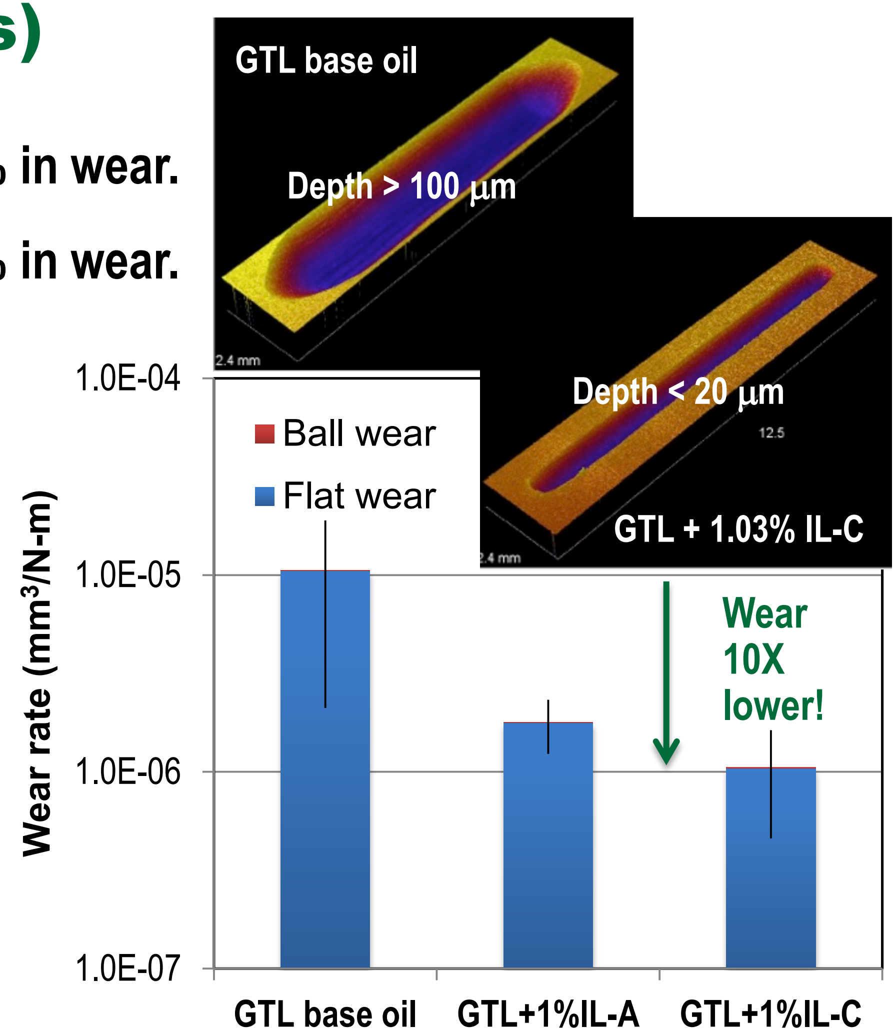
IL additives reduce friction and wear in boundary lubrication
(reciprocating sliding tests)

- **IL-A: reductions of 17% in friction and 83% in wear.**
- **IL-C: reductions of 16% in friction and 90% in wear.**





Collaboration

- **3-year CRADA (NFE-12-03876) between ORNL and Shell Global Solutions**

RASIC Roles & Recommendations (LEGEND: **R**= Responsible, **S**= Support, **C**= Consult)

ROLE / WHAT	R	S	C
Task 1. Design, synthesis, and optimization of oil-soluble ILs	ORNL		Shell
Task 2. Characterization of physical/chemical properties of ILs	ORNL	Shell	
Task 3. Standard additive evaluation for ILs and lubricant formulation	Shell	ORNL	
Task 4. Tribological bench tests and analyses	ORNL Shell		
Task 5. Investigation and modeling of lubrication mechanism of IL additives	ORNL	Shell	
Task 6. Instrumented single-cylinder motored engine tests	ORNL		Shell
Task 7. Instrumented single-cylinder fired engine tests with emission analysis	ORNL		Shell
Task 8. Multi-cylinder fired engine fuel efficiency dynamometer tests (ASTM D 7589 Sequence VI)	*Vendor**	Shell	ORNL
Task 9. Initial field tests	Shell		ORNL

**Through a subcontract to a commercial vendor.*

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Future work

April 2013 – March 2014

- Tailor the molecular structures of ILs to optimize the physical/chemical properties and lubricating performance.
- Complete tribological bench tests and analyses of single base oil-IL blends and simple ZDDP-replacement IL-additized engine oils.
- Carry out standard additive evaluations for candidate ILs.
- Achieve initial engine lubricant formulation using top-performing IL additives.
- Conduct systematic tribological bench tests and analyses.
- Investigate and model the lubrication mechanisms of IL additives.
- Initiate single-cylinder fired engine tests for durability and emission analysis.

Summary

- **Program management**
  - Three-year CRADA signed between ORNL and Shell Global Solutions on July 23, 2012.
  - Project kick-off meeting at ORNL on Aug. 6-7, 2012
  - First quarterly face-to-face meeting at Shell on Nov. 13, 2013.
  - Progress teleconferences in each month.
- **Technical progress**
  - Several groups of ILs with 3D quaternary structures designed/synthesized.
  - Four oil-miscible, non-corrosive ILs selected for systematic evaluations, and storage stability and thermal decomposition/oxidation tests conducted.
  - Ranges of ILs' concentrations in GF-5 engine oils determined, and oil-IL blends with maximum allowable IL contents prepared and characterized.
  - Tribological bench tests designed and test matrix defined.
  - Initial results of rolling-sliding tests showed 25-50% friction reduction in mixed lubrication when using ILs as a replacement of ZDDP in a formulated oil.
  - Initial results of reciprocating sliding tests showed >15% friction reduction and >80% wear reductions in boundary lubrication when adding Ils into a GTL base oil.

Technical Back-up Slides

Viscosity

- **Little change in viscosity caused by IL additives.**

Viscosity (cSt)	23 °C	40 °C	100 °C
Shell GTL 4	36.6	18.5	4.01
Shell GTL 4 + 1.03% IL-A	36.8	18.4	3.98
Shell GTL 4 + 1.03% IL-C	36.7	18.5	3.99
Shell GTL 4 + 0.99% IL-B	36.6	18.5	3.97
Shell GTL 4 + 1.74% IL-D	36.6	18.4	3.95
Shell GTL 4-based engine oil	93.4	42.0	7.99
Shell GTL 4-based engine oil w/o AW	94.8	42.8	8.12
Shell GTL 4-based engine oil w/o AW+1.03% IL-A	94.5	42.6	8.04
Shell GTL 4-based engine oil w/o AW+1.03% IL-C	95.9	43.2	8.10
Shell GTL 4-based engine oil w/o AW+1.74% IL-D	93.8	42.9	8.05