

High-Efficiency Low-Toxicity Ionic Liquids as Lubricant Additives

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Oak Ridge National Laboratory, East Tennessee



Great Smoky Mountains

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ORNL Tribology Research Portfolio

Technologies

- Advanced lubrication
 - Ionic liquids (including eco-friendly)
 - Nanolubricants
 - Molten salts
- Surface engineering
 - Superlubricity and wear-resistant coatings
 - Surface functionalization
 - Additive surface compositing & structuring (FSP, LM, BJ)
- Nanomaterials processing
 - Organic/electrochemical synthesis
 - Chemical/physical vapor deposition (CVD/PVD)
- Contact interface investigation
 - Contact mechanics and lubrication modeling
 - Surface/tribofilm characterization
- Bench testing & standardization
 - Application-oriented testing and analysis
 - 4 ASTM standards developed at ORNL

Applications

• Vehicle (IC & EV)

- Energy-efficient engine and gear lubricants
- Superlubricity bearings and seals
- High-efficiency e-motor coolants
- High-conductivity thermal interface material
- Bioenergy
 - Biomass/MSW preprocessing tool wear & mitigation
 - Biomass/MSW fouling & plugging
- Concentrating solar power
 - Wear/corrosion-resistant molten salt pumps
 - Self-lubricating high-efficiency seals
- Hydropower & Hydraulics
 - Eco-friendly tidal turbine lubricants/hydraulic fluids
- Nuclear
 - Grid-to-rod fretting of ATF claddings (PWR)
 - Wear and corrosion in molten salt and gas-cooled reactors
- Building
 - Advanced lubricants and coatings for HVACs

ORNL Tribology Research Capabilities

- Tribosystem analysis for understanding the failure ٠ modes and wear mechanisms
 - **Contact interface modeling**: Contact mechanics, heat transfer, and lubrication modeling
 - *Materials characterization:* Microstructure. composition, morphology, roughness, and mechanical and thermophysical properties
- Materials development for mitigation
 - Novel lubricants and additives: Ionic liquids, molten salts, and nanoparticles
 - Advanced coatings/surface treatments: CNT coatings, oxygen diffusion, friction stir processing, and additive manufacturing
- Tribological testing and analysis for evaluation
 - Various wear modes: Abrasive (2-body & 3-body) wear; Sliding wear; Rolling contact fatigue; Fretting
 - Well-controlled conditions: Ambient, vacuum, or controlled gas; RT - 1000 °C; 0.1 - 1000 N load; 0.1 mm/s – 15 m/s velocity; Dry, wet, & lubricated
- Standardization: 4 ASTM standards for tribo-testing



Standards





ORNL Advanced Lubrication

- Development and evaluation of new lubricant additives (ionic liquids, nanoparticles, molten salts, etc.)
- Recent projects:
 - 1. Organic-modified CNTs as lubricant additives for enhanced lubricity and thermal management of EVs (DOE VTO 2022-26, CRADA w/ Valvoline)
 - 2. Eco-friendly ionic liquids as additives for environmentally-acceptable lubricants (DOE WPTO 2021-25, ORNL TIP 2020-21, DOE VTO 2018-20)
 - 3. Molten salt lubrication for concentrating solar power and nuclear reactors (DOE NE 2021-25, SETO 2018-20)
 - 4. Ionic liquids for lubricating HVAC compressors (DOE TCF 2021-23)
 - 5. Organic-modified nanoparticles as lubricant additives (Hyundai 2019-20, DOE VTO w/ UTK and UCM, 2015-17)
 - 6. Ionic liquids as lubricants or multi-functional lubricant additives to improve fuel economy (Seed and VTO 2005-19, w/ GM, Shell, and DRO)
 - Compatibility of lubricant additives with non-ferrous coatings and alloys (VTO 2013-20)
 - 8. Hyperbranched polymers for improved viscosity and enhanced lubricity (VTO 2014-16, w/ PNNL)
 - 9. Tribological evaluation of aged diesel engine oils (DOE VTO 2002-05)

10. Diesel fuel injectors in ultra low sulfur fuels (DOE VTO 2002-05)







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ORNL Surface Engineering

- Development of new coatings and surface treatments ٠
- Recent projects ٠
 - 1. Surface modifications to enhance printability of US banknotes (BEP 2024-26)
 - 2. Carbon nanotube-based coatings for friction and thermal management (DOE VTO 2022-26, ORNL Seed 2018-19)
 - 3. Tool wear characterization and mitigation in biomass preprocessing (DOE BETO 2018-26, CRADAs with Rawlings and Forest Concepts)
 - 4. Graphite wear in molten salt and gas-cooled reactors (DOE NE 2021-25)
 - 5. Carbon nanotube-coated mesh seal (DOE SETO 2020-24)
 - 6. Grid-to-rod fretting of candidate accident-tolerant fuel claddings (DOE NE FOA 2018-23, CASL 2014-17)
 - 7. Additive manufacturing for tribology (Ford, 2018-20)
 - 8. Advanced diesel engine piston skirt coatings (DOE VTO 2015-16, CRADA w/ Cummins)
 - 9. AIMgB₁₄-based superhard coatings for hydraulic & tooling (DOE ITP 2007-10, w/ Eaton, Greenleaf, and Ames Lab)
 - 10. Surface nanocompositing of aluminum alloys using friction stir processing (ORNL LDRD 2006-08)
 - 11. Oxygen diffusion case-hardening for titanium alloys (DOE VTO 2004-08)
 - 12. Low-temperature carburization of austenitic stainless steels (DOE ITP 2005-08, w/ Swagelok and CWRU)







Nanocomposite surface layet

Metallic or coarse MMC substrate





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Ionic liquids for lubrication (since 2005)

ILs as neat lubricants or base stocks

- High thermal stability (up to 500 °C)
- High viscosity index (120-370)
- Low pressure-viscosity coefficient ightarrow low EHL friction
- − Strong surface adsorption \rightarrow low boundary friction
- Strong tribo-film formation \rightarrow excellent wear protection
- Technical problem: Many earlier ILs corrosive
 - ORNL developed non-corrosive ILs in 2006 (U.S. patent #7,754,664)

• ILs as oil additives for engine/gear lubrication

- Potential multi-functions: AW/EP, FM, etc.
- Ashless \rightarrow low sludge
- Allow the use of lower viscosity oils
- Advantage: cost effective and easier market penetration
- Technical problem: most ILs insoluble in oils (<<1%)
 - ORNL invented 1st group of oil-soluble ILs in 2010 (U.S. patent #9,957,460, 2014 R&D 100 Award)
- ILs as eco-friendly lubricant additives for hydropower/hydraulics
 - Problem: many ILs as toxic as traditional additives
 - ORNL invented eco-friendly ILs in 2019 (U.S. Patent #11,760,766)



Ionic Liquid Anti-wear Additives for Low-Viscosity Engine Lubricants

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









1-alkyl-3-methylimidazolium N-alkylpyridinium ammonium Tetraalkylphosphonium $(R_{1,2,3,4} = alkyl)$

Common Cations

[PF ₆]-	[BF ₄] ⁻	[CH ₃ CO ₂] ⁻
$[(CF_{3}SO_{2})_{2}N]^{-}(Tf_{2}N)$	[CF ₃ SO ₃] ⁻	[CF ₃ CO ₂] ⁻ , [NO ₃] ⁻
[(C ₂ F ₅ SO ₂) ₂ N] ⁻ (BETI)		Br, Cl ⁻ , I ⁻
$[BR_1R_2R_3R_4]^{-1}$		$[Al_2Cl_7]^-, [AlCl_4]^-$
[P(O) ₂ (OR) ₂] ⁻ (phospha	te)	
$[P(O)_2(R)_2]^-$ (phosphina	te)	

Common Anions

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Y. Zhou and J. Qu*, lonic liquids as lubricant additives – a review, ACS Applied Materials & Interfaces 9 (2017) 3209.



2010 Invented oil-miscible ionic liquids as lubricant additives



- 1. J. Qu, et al., *U.S. Patent* #10,435,642.
- 2. J. Qu, et al., ACS Appl. Mater. Interfaces 4 (2012) 997.
- 3. J. Qu, et al., *Advanced Materials* 27 (2015) 4767.



Multiple groups of oil-soluble ILs have been developed



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1. J. Qu, H. Luo, *U.S. Patent* #10,435,642, 2019.

2. J. Qu, H. Luo, Y. Zhou, J. Dyck, T. Graham, U.S. Patent Application 14/444,029, 2014.



Tribofilm by phosphonium-phosphate [P₈₈₈₈][DEHP]



- \succ Iron phosphates (~50 at%),
- Iron oxides (~50 at%), \geq
- Metallic iron (<1 at%). \geq







Tribofilm by ammonium-phosphate [N₈₈₈H][DEHP]



Tribofilm (up to 400 nm) on iron:

- Iron phosphates (30-40 at%),
- Iron oxides (40-50 at%),
- \succ Metallic iron (10-15 at%).



W.C. Barnhill and J. Qu*, et al., Tribology Letters 63 (2016) 22.



Correlating friction and wear performance to the tribofilm chemical composition

- Higher content of metal phosphates
 → lower friction and wear
- Higher content of metal oxides → higher friction and wear





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Correlating to the tribofilm thickness and mechanical properties

- · Thicker tribofilm often leads to lower friction and wear
- · No correlation between tribofilm hardness with friction or wear
- Lower ratio of load to stiffness squared (P/S²) leads to less wear
 - P/S² representing the resistance to plastic deformation
 - Opposite trend to literature reports for bulk or coating materials
 - Attributed to the dynamic, sacrificial and self-healing nature









Understand the IL tribofilm formation process





J. Qu^{*}, et al., *Wear* 332-333 (2015) 1273.
Y. Zhou^{*}, D.N. Leonard, W. Guo, J. Qu^{*}, *Scientific Reports* 7 (2017) 8426.
W. Guo^{*}, Y. Zhou, and J. Qu^{*}, et al., *ACS Applied Materials & Interfaces* 9 (2017) 23152.



Wear debris evolution-based tribofilm growth model for ILs





Y. Zhou* and J. Qu*, et al., *Scientific Reports* 7 (2017) 8426.
 W. Guo*, Y. Zhou, and J. Qu*, et al., *ACS Applied Materials & Interfaces* 9 (2017) 23152.

2013 discovered synergistic effects between phosphonium-phosphate ILs and ZDDPs



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J. Qu, et al., *Advanced Materials* 27 (2015) 4767.

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Prototype IL+ZDDP additized engine oil demonstrated lower boundary and mixed friction





W.C. Barnhill and J. Qu*, et al., Frontiers in Mechanical Engineering, 1 (2015) 12.

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2018 ORNL discovered synergistic effects between ammonium-phosphate ILs and OFM





W. Li, J. Qu*, et al., *Langmuir* 34 (2018) 10711.

Introducing ILs into a fully-formulated lubricant is rather complex...





2013 Demonstrated improved fuel economy in engine dyno tests for IL-additized experimental oil

Sequence VIE (ASTM D7589) FEI 1 fuel economy engine dyno tests at InterTek

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6
Engine condition	2000 rpm,	2000 rpm,	1500 rpm,	695 rpm,	695 rpm,	695 rpm,
Engine condition	105 N-m, 115 ºC	105 N-m, 65 °C	105 N-m, 115 °C	20 N-m, 115 °C	20 N-m, 35 °C	40 N-m, 115 °C
Lubrication regime	Dominated by HD/EHD lubrication			More boundary & mixed lubrication		
0W-16 w/ ZDDP vs. BLB	2.36%	2.84%	1.66%	3.72%	5.98%	3.03%
0W-16 w/ ZDDP+IL vs. BLB	2.54%	2.91%	1.77%	4.48%	6.46%	3.81%
ZDDP+IL vs. ZDDP only	0.17%	0.07%	0.11%	0.76%	0.48%	0.79%

1.77 – 6.46% fuel economy improvement (FEI) for the prototype IL+ZDDP additized experimental oil over the standard baseline

- J. Qu, et al., U.S. Patent #10,435,642 licensed to Driven Racing Oil, 2019.
- J. Qu, et al., 2014 R&D 100 Awards.
- J. Qu, et al., Frontiers in Mechanical Engineering, 1 (2015) 12.







Prototype IL-additized low-viscosity engine oil demonstrated 9.9% increased fuel economy in a racing engine

Engine dyno running stages (V8, 90 mins)

- 1. 15 minutes @ 1,500 RPM 140 ft lbs, Dyno Sweep To 6,000 RPM at max 140-500 ft lbs, stop-start
- 2. 15 minutes @ 2,900 RPM 140 ft lbs, Dyno Sweep To 6,000 RPM
- 3. 15 minutes @ 1,750 to 4,500 RPM (5 second acceleration and 10 second deceleration) 100-300 ft lbs, Dyno Sweep To 6,000 RPM
- 4. 15 minutes @ 4,500 RPM 175 ft lbs, Dyno Sweep To 6,000 RPM

IL replacing half ZDDP with IL to	Oil temp	Torque (Ib-	Fuel consump.	FEI vs. SN	Metal in used oil (ppm)		
maintain P content @ ~800 ppm	D ~800 ppm (°C) ft)		(lb)	5W-30	Fe	Cu	Al
SN SAE 5W-30	121	n/a	31.85	-	5	6	1
Synthetic SAE 0W-20	121	506	n/a	n/a	3	0	2
CPO 334 w ZDDP alone SAE 0W-12	120	505	30.4	4.4%	2	1	3
CPO 334+ZDDP <mark>+IL</mark> SAE 0W-12	117	510	28.7	<mark>9.9%</mark>	3	1	3

Such a significant FEI reflected the benefits of using the IL-additized oil at harsh engine operation conditions when boundary/mixed lubrication friction has high impact.

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C. Kumara* and J. Qu*, et al., ACS Sustainable Chemistry & Engineering 9 (2021) 7198.



ILs as Gear Oil Additives to Improve Durability and Efficiency

Adding 2-5% IL to oil significantly reduced rolling contact fatigue, sliding wear, and vibration



Case 2. Moderate conditions: 165-350 N, 55-120 °C, 3.5 m/s, 1.5% SRR 3.5 hr (2.6 million cycles) 200 Vibration (CLA) 001 (CLA) -VHVI8+2%IL 50 0 180 0 60 120 Testing time (minutes)



Roller tested in





Roller surface Roller surface tested in base oil tested in base oil + 2% IL

2018 Gear dynamometer tests increased 6% of the power output by using an IL-additized gear oil

Oil	Viscosity @ 40 C (cSt)	Viscosity @ 100 C (cSt)	Viscosity index	Iron in used oil (PPM)
80W-90 GL-5, Mineral				13
Valvoline Synpower	100	15	150	3
(Racing) 75W-90				
CPO-818v3	34.7	7.8	210	4





base oil

2020 developed new ILs with much lower toxicity than ZDDP and previous ILs

Survival in acute toxicity test (5 days)				ILs previously developed for automotive engines			
# of survivals	Neat PAG	PAG + 5% IL-1	PAG + 5% IL-2	PAG + 5% [N888H][DEHP]	PAG + 5% [P8888][DEHP]	PAG + 5% ZDDP	
Day 1	10	10	10	10	10	10	
Day 2	10	10	10	6	0	0	
Day 3	10	10	10	0	0	0	
Day 4	10	10	10	0	0	0	
Day 5	10	10	10	0	0	0	

Reproduction in chronic toxicity test (7 days)

# of neonates per				PAG + 5%	PAG + 5%	PAG + 5%
day	Neat PAG	PAG + 5% IL-1	PAG + 5% IL-2	[N888H][DEHP]	[P8888][DEHP]	ZDDP
Day 1	0	0	0	0	0	0
Day 2	0	0	0	0	0	0
Day 3	32	36	45	0	0	0
Day 4	2	0	13	0	0	0
Day 5	91	98	82	0	0	0
Day 6	128	159	141	0	0	0
Day 7	175	201	172	0	0	0
Grand Total	428	494	453	0	0	0



United States Environmental Prot

> Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms

Fourth Edition

October 2002





J. Qu, H.M. Luo, X. He, *U.S. Patent #11,760,766*, 2023.

Eco-friendly ILs for tidal turbine lubrication

- Current lubricants for tidal turbines are basically borrowed from those for wind turbines, however lubricating a tidal turbine are far more challenging:
 - Slower speed and higher force and thus no full-film lubrication, leading to higher wear risk, which largely rely on the protection of the anti-wear additives in the lubricant.
 - Lubricant more prone to a high water/moisture content, causing degraded lubricity.
 - Longer maintenance intervals of up to 6 years, because the difficulties to access and maintenane.
- Conventional gear oils are harmful and pose a significant threat to the marine ecosystems, because they would contaminate the water directly upon spill or leak and violate the U.S. Clean Water Act's 'non-sheening rule'.
- While EPA has approved multiple groups of EAL base fluids, there is lack of additives that are both non-toxic and effective in friction reducing and wear protection.



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Lubricity: ORNL's new ILs demonstrated 50% reduction in friction and wear compared with the baseline gear oil



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Toxicity: ORNL's new ILs can be classified as 'Not Toxic to aquatic organisms' based on on-going sea water toxicity tests





[2] Chemical hazard classification and labeling: comparison of OPP requirements and the GHS, 2004.

Key fundamental questions remained to be answered

- Impact of marine water/moisture content in the lubricant? ٠
 - Marine water/moisture getting into the tidal turbine oil is inevitable during the multi-year operation.
 - What's the impact on the viscosity, lubricity, and corrosion of the ionic liquid-enhanced eco-friendly lubricants in comparison with that on the commercial baseline oils?
- Effects of lubricant aging?
 - The promising results in Phase 1 were from fresh lubricants; however, lubricant aging involving oxidation, decomposition, and reactions with the bearing/gear surfaces, is inevitable in the tidal turbine operation.
 - What's the aging behavior of our ionic liquid-enhanced eco-friendly lubricants in comparison with that of the commercial baseline oils?
- Feasibility of lower-viscosity lubricants?
 - The promising results in Phase 1 were based on the same viscosity grade with the baseline gear oils.
 - A lower oil viscosity is expected to reduce the hydrodynamic drag and environmental impact; however, it inevitably posts a higher risk of wear – would the ionic liquids provide adequate wear protection to allow the use of lower viscosity lubricants?



Team and Collaborators

- My current tribo-team: C. Kumara, T. Grejtak, W. Wang
- Internal collaborators (long term):
 - o CNMS: M. Chi, R. Unocic, K. Xiao, K. An
 - o CSD: S. Dai, H. Meyer, N. Gallego
 - o ESD: T. Mathews, L. Stevenson, P. Ku
 - o MDF: A. Elliot, N. Niyanth, R. Dehoff
 - o MSD: H. Luo, T. Toops, B. West
 - MSTD: P. Blau, J. Keiser, J. Truhan, H. Wang, L. Lin, T.
 Watkins, Z. Feng, H. Bei, M. Lance, D. Leonard, B.
 Armstrong, A. Shaym, D. Pierce, M. Brady, E. Lara-Curzio

• Other national labs:

- ANL: G. Fenske, O. Ajayi
- INL: J. Lacey, M. Kuns, D. Hartley, V. Thompson, D. Thompson
- o NREL: E. Wolfrum, R. Elandar, S. Sheng
- o PNNL: L. Cosimbescu, R. Cavagnaro
- SNLs: M. Dugger, V. Neary

• Academia:

- Central FL: L. An
- PSU: K. Seong
- TAMU: H. Liang
- Temple: F. Ren
- U lowa: H. Ding
- o UTK: B. Zhao

Industrial partners (formal collaborations):

- o Biosynthetic: M. Woodfall, M. Miller
- o Cummins: R. England, C. Wang
- o Danfoss: T. Li, A. Rezaei, N. LaTray
- o Driven Racing Oil: L. Speed, J. Coleman
- o Eaton: D. Zhu, A. Elmoursi, C. Higdon
- Ford: A. Gangopadhyay, H. Ghaednia, D. Uy
- Forest Concepts: D. Lanning, C. McKiernan
- o GM: S. Tung, M. Viola
- Hayward Tyler: K. Oldinski
- o Hyundai: I. Lyo
- Lubrizol: E. Bardasz
- Rawlings: J. Rawlings
- Shell: B. Papke, H. Gao, D. Uy
- o Solvay: J. Dyck, E. Conrad, C. Chretien
- Swagelok: P. Williams
- o Trane: W. Akram, M. Herried, A. Poslinski
- Valvoline: R. England, N. Ren, J. Bonta, E. Murphy
- o Westinghouse: R. Lu, M. Conner

The key to success is collaboration!



Postdoc openings at ORNL

- Postdoc position 1: Surface Science and Engineering
 - <u>https://jobs.ornl.gov/job/Oak-Ridge-Postdoctoral-Research-Associate-Surface-Science-and-Engineering-TN-37830/1085481400/</u>
 - <u>Polymer</u> surface characterization and modification
 - Including but not limited to plasma treatment, as well as investigation and mitigation of adhesion and transfer of third-body material at contact interfaces under pressure and shear
 - Subject to export control requirements: Yes
- Postdoc position 2: Thermal Degradation
 - <u>https://jobs.ornl.gov/job/Oak-Ridge-Postdoctoral-Research-Associate-Thermal-Degradation-TN-37830/1088612800/</u>
 - Organic thermal degradation in energy conversion and storage
 - Development of a unique thermal-sensitive coating for alarming thermal runaway of energy storage systems including electric vehicle batteries
 - Investigation and mitigation of biomass fouling under combined thermal and mechanical stresses in biofuel preconversion
 - Subject to export control requirements: No
- Contact: Jun Qu, Group Leader of Surface Engineering and Tribology, ORNL qujn@ornl.gov

