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Tribological Testing and Analysis of Ionic Liquids as Candidate Anti-Wear Additives for Next-Generation Engine Lubricants

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I am submitting herewith a thesis written by William Charles Barnhill entitled "Tribological Testing and Analysis of Ionic Liquids as Candidate Anti-Wear Additives for Next-Generation Engine Lubricants." I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Mechanical Engineering.

Feng-Yuan Zhang, Major Professor

We have read this thesis and recommend its acceptance:

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Tribological Testing and Analysis of Ionic Liquids as Candidate Anti-Wear Additives for Next-Generation Engine Lubricants

A Thesis Presented for the
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Degree
The University of Tennessee, Knoxville

William Charles Barnhill
May 2016
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ABSTRACT

In this work, fourteen ionic liquids (ILs) were assayed as potential next-generation engine oil additives. After screenings for corrosion, thermal stability and oil solubility, the candidate additives were subjected to friction and wear tests in both boundary and mixed regime lubrication. While each IL demonstrated friction and wear reduction compared to base oil without any additives, oil-miscible ILs tetraoctylphosphonium bis 2-ethylhexyl phosphate ([P₈₈₈₈][DEHP]) and trioctylammonium bis 2-ethylhexylphosphate ([N₈₈₈₈][DEHP]) were the best performers in bench tests. Their excellent solubility and superior performance was attributed to their symmetric nature and hydrogen bonding in the case of [N₈₈₈₈][DEHP]. The worn specimens generated with these two ILs were chosen for detailed surface analysis, which showed the presence of an amorphous protective tribofilm composed of phosphates and iron oxides. In addition, each of these ILs performed well in experimentally formulated oils as well. [P₈₈₈₈][DEHP] was chosen for full-scale engine fuel economy testing due to its synergy with the common anti-wear additive, zinc dialkyldithiophosphate (ZDDP). The [P₈₈₈₈][DEHP]-containing formulated oil exhibited better fuel economy compared to an oil of the same viscosity containing only ZDDP as the anti-wear additive. Its superior performance was well-correlated with friction and wear bench tests. These results demonstrate the effectiveness of using ILs as engine oil additives and provide a scientific basis for further work towards implementing and optimizing additive packages with ILs.
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INTRODUCTION

Wear and friction are often the limiting factors on the service lifetime of mechanical systems. It is estimated that financial losses in the U.S. due to these factors may sum to 6% of gross domestic product—over one trillion dollars for 2015. More importantly, frequent mechanical maintenance, component replacement and inefficiencies caused by higher friction also have negative consequences for environmental and energy conservation. Lubricants are used to mediate contact forces on mechanical bearing interfaces in an attempt to mitigate friction and wear. Even incremental improvements of lubricants’ friction and wear characteristics can potentially provide massive savings.

Internal combustion (IC) engines are of particular interest considering the sheer number in use in society. The U.S. automotive industry is under pressure to improve IC engine efficiencies both from consumer demand and governmental regulation. Over 10% of the energy generated in an IC engine becomes waste heat due to viscous fluid forces and solid-solid asperity contacts between bearing interfaces. There is an increasing trend to reduce the viscosity of engine oils to improve fuel economy, but doing so causes an increase in wear on engine parts that experience more severe lubricating conditions.

A tribosystem of interacting lubricated surfaces moving relative to one another can be described as being in one of four distinct regimes of lubrication: boundary lubrication (BL), mixed lubrication (ML), elastohydrodynamic lubrication (EHL) or hydrodynamic lubrication (HL). HL and EHL describe a state of complete separation of adjacent surfaces by a lubricant film. Developed friction in these regimes is solely a function of lubricant fluid properties, flowrates and pressure. EHL produces the thinnest lubricant film that completely separates the tribopair with the lowest overall friction. With other factors constant, increasing speed, reducing applied pressure or increasing lubricant viscosity allows a thicker fluid film to develop in the HL regime raising friction (and reducing mechanical efficiency) due to increased fluid shear. As the lubricant film becomes thinner with higher load, lower speed or reduced viscosity, surface asperities begin to come into contact pushing the regime into ML characterized by increasing friction as solid contact area becomes larger. BL occurs when the lubricant film thickness becomes deleteriously less than the average surface roughness. Load bearing in this regime is dominated by solid-solid contact causing elevated wear and friction coefficients usually around 0.1. In more severe cases, the lubricant may be squeezed from the contact area completely causing very high wear and friction due to adhesion and surface scuffing. BL is clearly an undesirable operating condition, but most tribosystems will experience this regime nonetheless, especially during start-stop cycles or reciprocating motion as in a piston-cylinder assembly. The most effective liquid lubricants for systems experiencing a broad range of lubrication regimes provide low fluid shear in EHL and HL via reduced viscosity, and facilitate the formation of a physically adsorbed or chemisorbed tenacious, self-healing thin film, often called a tribofilm or boundary film, that serves to protect the underlying substrate from further material removal and deformation in BL and ML. The presence of surface-active additives in the lubricant in tandem with thermomechanical
stress are usually responsible for the formation and properties of the tribofilm. Understanding the nature of the tribofilm is important when attempting to design a lubricant and additive package for a given mechanical system.

Essentially every commercial lubricating oil contains various types of additives that can be formulated to tailor lubrication performance for a particular application. The most common classes of additives are detergent, dispersant, anti-wear, extreme-pressure, friction-modifying, viscosity-modifying, anti-oxidant, anti-foaming, anti-misting or corrosion-inhibiting additives. Additives typically only constitute 10 wt.% or less of the overall lubricant. The bulk of the lubricant is the base oil or “base stock”, which is normally made up of refined saturated and aromatic hydrocarbons for conventional oils, or alkenes and/or esters for synthetic oils. Next-generation engine oils will offer additive packages robust enough to allow lower viscosity (more efficient) oils to be implemented without loss of the anti-wear functionality of a higher viscosity oil. Achieving this requires that new additive formulations be developed and optimized. One promising new class of additives has provided a fruitful avenue of exploration towards reaching the next-generation of engine oils—ionic liquids (ILs).

ILs are salts that are molten at room temperature consisting solely of positively charged cations and negatively charged anions. This somewhat unique property in a salt is due to ILs’ chemical structures. Most have either a comparatively large cation and/or anion that serves to dilute charge and reduce coordination between the two ions preventing lattice formation. This ionic yet poorly coordinated nature causes properties such as negligible volatility, high thermal stability and reduced combustibility—beneficial properties in a lubricant. Due to their charge, many have very low solubility in conventional and synthetic base oils; however, this problem has been overcome by using ILs with quaternary structure and sufficiently long alkyl groups. These carbon chains facilitate solubility by increasing Van der Waals dispersion forces between the polar IL and non-polar base oil. For an IL to be a viable candidate engine oil additive, it must be sufficiently soluble, thermally stable, non-corrosive and reduce wear and friction in bench and engine tests. The ILs assayed in this work were subject to experiments designed to determine their effectiveness in each of these categories. More in-depth background and literature information for ILs is available in the introduction of each chapter.
CHAPTER I
TERTIARY AND QUATERNARY AMMONIUM-PHOSPHATE
IONIC LIQUIDS AS LUBRICANT ADDITIVES
A version of this chapter was submitted for publication and was currently under editorial review when this thesis was published by William C. Barnhill, Huimin Luo, Harry M. Meyer III, Cheng Ma, Miaofang Chi, Brian L. Papke, and Jun Qu.

I was responsible for performing all tribological tests, making measurements on worn specimens, compiling and analyzing all tribological data, performing open-air corrosion tests, scanning electron microscope micrograph operation, analyzing XPS and TEM data and preparing the manuscript.

Abstract
In this work we investigated the feasibility of five quaternary (aprotic) and four tertiary (protic) ammonium ionic liquids (ILs) with an identical organophosphate anion as lubricant anti-wear additives. Viscosity, oil solubility, thermal stability, and corrosivity of the candidate ILs were characterized and correlated to the molecular structure. Two aprotic ILs and one protic IL were selected for tribological testing, and each IL led to friction and wear reductions when added to a base oil or formulated engine oil. The protic 1-H-trioctylammonium di(2-ethylhexyl)phosphate ([N\textsubscript{888}H][DEHP]) outperformed the others in both oil solubility and anti-wear behavior. The thickness, nanostructure, coverage and composition of the tribofilm formed by [N\textsubscript{888}H][DEHP] were revealed to gain mechanistic understanding of the tribochemical interactions between the protic ammonium-phosphate IL and metal surface. Results provide fundamental insights of the correlations among the molecular structure, physiochemical properties and lubricating performance for ammonium-phosphate ILs.

Introduction
Energy, material and monetary losses caused by friction and wear are a constant problem plaguing many industries and consumers globally. These losses can be reduced by using more effective lubricants. The US automotive industry in particular strives to improve lubrication performance to comply with increasingly stringent regulatory requirements on both fuel economy and emission control. [1] Internal combustion (IC) engine operation involves reciprocating sliding surface interactions that constantly shift the lubrication regime between boundary, mixed and elastohydrodynamic lubrication. This variation poses a problem when minimizing friction and wear. Higher viscosity lubricant serves to better protect engine components from wear in boundary and mixed regime lubrication, but a lower viscosity lubricant increases engine mechanical efficiency and fuel economy by reducing hydrodynamic drag or shear force within the lubricant film. New anti-wear additives that retain the wear reduction but allow the use of lower viscosity oil may provide a solution to this issue.

Room temperature ionic liquids (ILs) have been researched for their usefulness in lubrication since 2001. [2] ILs generally possess low volatility and flammability and have high decomposition temperatures—ideal lubricant properties. Initial work involved ILs
with imidazolium cations and fluorine-containing anions [3-6], but IL research in lubrication since has diversified [7-9]. Although most earlier studies focused on the feasibility of using ILs as base or neat lubricants [10], a few tried polar base oil stocks to overcome ILs’ inherent insolubility in common non-polar oils [11-13] while others tested oil-IL emulsions or very low concentrations of ILs in non-polar base oil. [14-19] Oil-miscible phosphonium-organophosphate ILs were later developed and have demonstrated excellent friction and wear reductions when used as oil additives in both tribological bench [20-23] and engine dynamometer [24] tests.

Ammonium-based ILs caught our interest because they have already found widespread applications in many industries and are produced economically in quantities on the order of tons per year as solvents, gas capture agents, phase-transfer catalysts, coating materials, surfactants, metal extracting agents and anti-microbial agents. [25, 26] Within the realm of lubrication, a related class of salts of alkylated ammonium phosphates has been used as corrosion inhibitors and ashless anti-wear additives for years. [27, 28] Some ammonium-based ILs have been examined as neat lubricants or additives more recently. [15, 29-34] Other recent work has revealed the merits of protic ILs. [35-40]

However, there is lack of fundamental understanding of the correlations between the molecular structures of ammonium cations and the ILs’ physiochemical properties and lubricating performance. Thus, in this work, we synthesize, characterize and test a group of ILs composed of various tertiary and quaternary ammonium cations and an identical organophosphate anion for potential use as engine oil additives. Results provide a scientific basis for future development and optimization.

**Experimental Details and Materials**

**IL Synthesis**

Nine tertiary (protic) and quaternary (aprotic) ammonium cation ILs with organophosphate anions were synthesized in this study whose structures are located in Figure 1. The five aprotic ILs include tetraethylammonium bis(2-ethylhexyl) phosphate ([N$_{2222}$][DEHP]), tetrabutylammonium bis(2-ethylhexyl) phosphate ([N$_{4444}$][DEHP]), tetrahexylammonium bis(2-ethylhexyl) phosphate ([N$_{6666}$][DEHP]), tetraoctylammonium bis(2-ethylhexyl) phosphate ([N$_{8888}$][DEHP]), and trioctylmethylammonium bis(2-ethylhexyl) phosphate ([N$_{8881}$][DEHP]). The four protic ILs are triethylammonium bis(2-ethylhexyl) phosphate ([N$_{222H}$][DEHP]), tributylammonium bis(2-ethylhexyl) phosphate ([N$_{444H}$][DEHP]), trihexylammonium bis(2-ethylhexyl) phosphate ([N$_{666H}$][DEHP]), and trioctylammonium bis(2-ethylhexyl) phosphate ([N$_{888H}$][DEHP]). The synthesis of each IL is described below. Nuclear magnetic resonance (NMR) analysis was carried out using a Bruker MSL-400 NMR spectrometer operating at 400.13 MHz for proton and 100.61 MHz for carbon.
Tetraethylammonium di(2-ethylhexyl)phosphate [N\textsubscript{2222}][DEHP]: A solution of [N\textsubscript{2222}]OH in methanol was prepared from 2 g of [N\textsubscript{2222}]Cl (1.2 mmol) using a Dowex Monosphere 550A (OH) anion exchange resin. 3.87 g of HDEHP (1.2 mmol) were added to the [N\textsubscript{2222}]OH solution. The mixture was then stirred at room temperature for 6 h until the solution became neutral. The methanol and water were distilled off, and the product was dried at 70 °C under vacuum for 12 h to yield [N\textsubscript{2222}][DEHP] as a viscous liquid (5.15 g, 11.4 mmol, yield: 95%). The water content of [N\textsubscript{2222}][DEHP] was 1.9%.

Tetrabutylammonium di(2-ethylhexyl)phosphate [N\textsubscript{4444}][DEHP]: This IL was prepared in the similar procedure as above from [N\textsubscript{4444}]Cl (2.78 g, 10.0 mmol) and HDEHP (3.22 g, 10.0 mmol). [N\textsubscript{4444}][DEHP] was obtained as a colorless viscous liquid (5.29 g, 9.4 mmol, yield: 94%).

Tetrahexylammonium di(2-ethylhexyl)phosphate [N\textsubscript{6666}][DEHP]: This IL was prepared in the similar procedure as above from [N\textsubscript{6666}]Br (4.0 g, 9.2 mmol) and HDEHP (2.97 g, 9.2 mmol). [N\textsubscript{6666}][DEHP] was obtained as a viscous liquid (5.95 g, 8.8 mmol, yield: 96%). The water content of [N\textsubscript{6666}][DEHP] was 0.8%.

Tetraoctylammonium di(2-ethylhexyl)phosphate [N\textsubscript{8888}][DEHP]: This IL was prepared in the similar procedure as above from [N\textsubscript{8888}]Br (5.46 g, 10.0 mmol) and HDEHP (3.22 g, 10.0 mmol). [N\textsubscript{8888}][DEHP] was obtained as a viscous liquid (7.41 g, 9.4 mmol, yield: 94%). The water content of [N\textsubscript{8888}][DEHP] was 0.3%.
Trioctylmethylammonium bis(2-ethylhexyl)phosphate [N\textsubscript{8881}][DEHP]: This IL was prepared in the similar procedure as above from [N\textsubscript{8881}]Cl (4.04 g, 10.0 mmol) and HDEHP (3.22 g, 10.0 mmol). [N\textsubscript{8881}][DEHP] was obtained as a colorless viscous liquid (6.35 g, 9.2 mmol, yield: 92%).

1-H-triethylammonium di(2-ethylhexyl)phosphate [N\textsubscript{222}H][DEHP]: The product was formed by neutralization of equal molar ratio of triethylamine (1.15 g, 11.3 mmol) and Di(2-ethylhexyl)phosphoric acid (HDEHP, 3.64 g, 11.3 mmol) at room temperature for 2 hours. The mixture became more viscous upon stirring. The water content of [[N\textsubscript{222}H][DEHP] was 0.09%.

1-H-tributylammonium di(2-ethylhexyl)phosphate [N\textsubscript{444}H][DEHP]: The product was formed by neutralization of equal molar ratio of tributylamine (1.92 g, 10.4 mmol) and Di(2-ethylhexyl)phosphoric acid (HDEHP, 3.34 g, 10.4 mmol) at room temperature for 2 hours. The mixture became more viscous upon stirring. The water content of [[N\textsubscript{444}H][DEHP] was 0.12%.

1-H-trihexylammonium di(2-ethylhexyl)phosphate [N\textsubscript{666}H][DEHP]: The product was formed by neutralization of equal molar ratio of trihexylamine (2.27 g, 8.44 mmol) and Di(2-ethylhexyl)phosphoric acid (HDEHP, 2.70 g, 8.44 mmol) at room temperature for 2 hours. The mixture became more viscous upon stirring. The water content of [[N\textsubscript{666}H][DEHP] was 0.08%.

1-H-trioctylammonium di(2-ethylhexyl)phosphate [N\textsubscript{888}H][DEHP]: The product was formed by neutralization of equal molar ratio of trioctylamine (2.37 g, 6.69 mmol) and Di(2-ethylhexyl)phosphoric acid (HDEHP, 2.16 g, 6.69 mmol) at room temperature for 2 hours. The mixture became more viscous upon stirring. The water content of [[N\textsubscript{888}H][DEHP] was 0.10%.

**Blending and Characterization**

Viscosities of selected ILs were measured with a Petrolab MINIVIS II falling ball viscometer (OK, US). Three measurements were taken at each data point (23, 40 or 100 degrees Celsius) to ensure a standard deviation below 1%. [N\textsubscript{888}H][DEHP] was selected for thermogravimetric analysis (TGA) to determine decomposition temperature in both air and nitrogen environments. A TA Instruments (DE, USA) TGA-2950 was used for TGA at a 10° C/min heating rate.

A low viscosity (4 cSt at 100 °C) base oil (BO) and an experimentally formulated (EF) engine oil without anti-wear (AW) additive were provided by Shell Global Solutions (TX, US) and served as the base lubricants in this study.

IL solubility in the base oil was determined by combining an IL with base oil starting at 1:1 ratio and shaking vigorously by hand for one minute. These shaken samples were
then placed into a centrifuge at 13,000 rpm for 10 minutes. Any observed separation or cloudiness under bright lighting indicated insolubility. If separation or cloudiness was evident, the ratio was incrementally decreased until solubility was reached.

**Corrosion Testing**

Ambient air corrosion tests were completed by placing a drop of each IL directly onto a 25.4 × 25.4 mm² CL35 cast iron surface and left for 49 days. The ILs’ low volatility prevented evaporation from being a concern. Electrochemical corrosion experiments were performed on [N₈₈₈][DEHP] at room temperature using the potentiodynamic polarization technique with a three-electrode electrochemical cell. A cast iron disk (1 cm² exposed area) served as the working electrode, which was immersed in the electrolyte ([N₈₈₈][DEHP]) for 15 min prior to testing. A Pt wire was the counter electrode, and Ag/AgCl (4M KCl solution) was the reference electrode. The sample was polarized at potentials from -1.0 to +1.50 V versus open circuit potential at a scanning rate of 0.166 mV/s in aerated conditions. The electrochemical test was conducted using a CHI 700C device (CH Instruments, Inc., Austin, TX, USA).

**Friction and Wear Testing**

A Plint TE77 (Phoenix Tribology Ltd., UK) tribometer was used to evaluate the lubricant performance in boundary lubrication. This device produced a reciprocating sliding motion using a 10 mm AISI 52100 steel ball against a CL35 cast iron flat (Metal Samples Company, AL) submerged in candidate lubricants. Cast iron specimens were polished with 600-grade silicon carbide abrasive paper producing a lay perpendicular to the sliding direction. Interacting surfaces were cleaned with isopropyl alcohol and air dried before submersion in lubricant. Each test was performed at 100ºC under a 100 N load with an oscillation frequency of 10 Hz and a 10 mm stroke. Three replicate experiments were performed for each lubricant to determine repeatability. Balls and flats were cleaned in acetone and then isopropanol after testing. A Veeco (now Bruker, TX) Wyko NT9100 optical interferometer was used for measuring wear volumes.

**Surface Analysis**

A Hitachi S-4800 (Tokyo, Japan) scanning electron microscope (SEM) was used to study the worn surface. Cross-sectional makeup and nanostructure was examined with a Hitachi HF-3300 transmission electron microscope (TEM) (300kV, 1.3 Å resolution) equipped with a Bruker solid-state EDS detector. The TEM specimen was prepared using a Hitachi NB5000 focused ion beam (FIB) machine with a gallium ion source to extract a thin cross-section of the tribofilm. A carbon film and then a tungsten layer were deposited onto the wear scar before the FIB process to preserve the tribofilm. A Thermo Scientific (MA, USA) K-Alpha x-ray photoelectron spectrometer (XPS) was applied to assess the chemical makeup of the selected tribofilm. The x-rays were monochromatic Al-ka photons. Photo emitted electrons were analyzed with a hemispherical energy analyzer.
Surface compositions were calculated by computing peak areas of the primary core levels for all elements present and normalizing using tabulated sensitivity factors. Composition-depth profiles were obtained by Ar ion sputtering under 1 kV ion beam energy at high current.

**Results**

**Solubility and Physical Properties**

Oil solubility results of the set of ammonium-organophosphate ILs are listed in Table 1. Since each IL has the same anion, difference in solubility is solely due to the cation structure. Each aprotic IL ([Nnnnn][DEHP] and [N_8881][DEHP]) consistently showed less than 1 wt.% solubility in the base oil for n=2, 4, 6, or 8. In contrast, protic ILs ([NnnnH][DEHP]) displayed a trend of increasing solubility from <1 wt.% for n = 2 to >10 wt.% for n=8. Increasing solubility with larger alkyl moieties can be explained by a corresponding increase in dispersion forces coupled with a dilution of charge within the ion pair. The protic IL series’ improved solubility is most likely a result of hydrogen bonding between the cation and anion to form a quasi-neutral molecule that is more compatible with the non-polar neutral base oil. Such hydrogen bonding is not present in the aprotic ILs. The maximum treat rate of each IL was calculated based on the upper limit of the phosphorous content (800 ppm, regulated by International Lubricants Standardization and Approval Committee GF-5 specifications) as shown in Table 1.

**Table 1. IL molecular weight, oil solubility, target concentration and dynamic viscosity.**

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Molecular weight</th>
<th>Solubility in base oil (wt%)</th>
<th>Solubility in EF w/o AW (wt%)</th>
<th>IL max treat rate in oil (wt%)</th>
<th>Viscosity (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N_2222][DEHP]</td>
<td>452</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.17</td>
<td>667</td>
</tr>
<tr>
<td>[N_4444][DEHP]</td>
<td>568</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.46</td>
<td>1292</td>
</tr>
<tr>
<td>[N_6666][DEHP]</td>
<td>676</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.75</td>
<td>192</td>
</tr>
<tr>
<td>[N_8888][DEHP]</td>
<td>792</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>2.04</td>
<td>256</td>
</tr>
<tr>
<td>[N_8881][DEHP]</td>
<td>694</td>
<td>&gt;3, &lt;5</td>
<td>&gt;3, &lt;5</td>
<td>1.78</td>
<td>32.7</td>
</tr>
<tr>
<td>[N_222H][DEHP]</td>
<td>427</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>1.09</td>
<td>667</td>
</tr>
<tr>
<td>[N_444H][DEHP]</td>
<td>511</td>
<td>&gt;5</td>
<td>&gt;2, &lt;5</td>
<td>1.31</td>
<td>1292</td>
</tr>
<tr>
<td>[N_666H][DEHP]</td>
<td>595</td>
<td>&gt;5</td>
<td>&gt;2, &lt;5</td>
<td>1.53</td>
<td>192</td>
</tr>
<tr>
<td>[N_888H][DEHP]</td>
<td>676</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>1.74</td>
<td>178</td>
</tr>
</tbody>
</table>
TGA results for the protic IL series are shown in Figure 2. ILs in this series with fewer carbons per alkyl chain show lower onset decomposition temperatures than their larger-alkyl counterparts.

![Figure 2. Thermal decomposition curves of protic ILs in N₂.](image)

**Corrosion Behavior**

In open air corrosion tests the cast iron surface showed some pits for aprotic ILs ([Nnnnn][DEHP] where N=2,4,6,8) by day 14, but the corrosion features had no propagation between days 14 and 49. This implies that corrosion is likely caused by the impurities in the ILs, such as residue of Cl⁻ or Br⁻ from the feedstocks, instead of the ILs themselves.

On the other hand, the protic ILs ([Nₘₘₘₘₘ][DEHP] n=2,4,6,8) showed no signs of corrosion in the open air tests. [N₈₈₈₈₈][DEHP] was then chosen for electrochemical measurement. Figure 3 shows the potentiodynamic polarization curve that clearly shows active-passive behavior with strong passivation at a current density on the order of 10⁻⁴ A/cm. No morphology change on the cast iron surface was evident after testing.
ILs in Base Oil

Three ILs were chosen for tribological testing as additives in the base oil: [N₈₈₈₈][DEHP], [N₈₈₈₁][DEHP] and [N₈₈₈₉][DEHP] with treat rates of 2.04, 1.78, and 1.74 wt%, respectively. Although [N₈₈₈₈][DEHP] and [N₈₈₈₁][DEHP] have true oil solubility less than 1 wt% upon centrifuging, they are able to suspend in the oils at the above described treat rates for a short period (hours). The oils containing the two aprotic ILs were shaken well prior to tribo-testing. Friction and wear results for each of these ILs in base oil and formulated oil are shown in Figure 4 and Figure 5. During the initial 25 m of sliding, the friction coefficient for the base oil rose sharply indicating a more severe break-in compared to the IL-containing lubricants. The base oil’s average friction coefficient dropped after break-in but remained elevated throughout the tests compared to IL-containing oils. All three ILs demonstrated friction-reducing capability when blended with the base oil. Each lubricant in this series generated similar friction traces with only slight differences in steady-state friction (~4%) with the [N₈₈₈₉][DEHP] blend slightly outperforming the others.

In addition to friction reduction, each IL induced a significant reduction in wear compared to the base oil (by 82% to 96%) with the protic [N₈₈₈₉][DEHP] generating the least amount of wear. The neat base oil experienced elevated wear associated with scuffing for two out of three tests producing a large error bar. Steel ball wear was consistently two orders of magnitude smaller than that of the softer cast iron flats in all tests.
Figure 4. Wear and friction results for the base oil + IL tests. Each wear data point and friction trace represents an average of three repeated tests. Ball wear volume is shown but is too small to be visible atop the flat wear volume bars.
Figure 5. Wear and friction results for the experimental formulation (EF) + IL tests. Each wear data point and friction trace represents an average of three repeated tests. Ball wear volume is shown but is too small to be completely visible atop the flat wear volume bars.
**ILs in Experimentally Formulated Engine Oil**

The same three ILs were added to the experimentally formulated engine oil without AW for further tribological evaluation. Among the two aprotic ILs, \([\text{N}_{8888}][\text{DEHP}]\) slightly reduced the friction while \([\text{N}_{8881}][\text{DEHP}]\) had little impact. The protic \([\text{N}_{888H}][\text{DEHP}]\)-additized EF oil showed the lowest steady-state friction coefficient by a larger margin compared with the EF oil without AW or with either aprotic IL. In terms of wear, each IL provided benefit compared to the EF oil without AW. The protic IL, \([\text{N}_{888H}][\text{DEHP}]\), again demonstrated better wear protection than the two aprotic ILs.

**Scanning Electron Microscopy**

Owing to its superior friction- and wear-reducing properties, the wear scar generated on a cast iron flat by BO + 1.74% \([\text{N}_{888H}][\text{DEHP}]\) was chosen for more detailed surface analysis beginning with SEM top surface morphology examination. Figure 6 shows two SEM micrographs for wear scars generated by both the neat base oil without and with 1.74% \([\text{N}_{888H}][\text{DEHP}]\). The base oil produced a wear scar with many tightly spaced longitudinal grooves. In contrast, the scar generated by the IL-containing oil is much narrower and shallower. Grooving is sparser with interspersed darker patches that appear relatively smooth.

![Figure 6. SEM micrographs of wear scars lubricated by BO and BO + 1.74% \([\text{N}_{888H}][\text{DEHP}]\).](image-url)
Transmission Electron Microscopy

Assisted by FIB milling, cross-sectional TEM imaging, EDS elemental mapping and electron diffraction were completed from the wear scar produced by the BO containing 1.74% [N\text{888H}][\text{DEHP}] (Figure 7). TEM micrographs reveal the presence of a protective tribofilm up to approximately 350 nm thick. EDS results appear to show a double-layer film with by P, O, and Fe rich in the top layer, suggesting a mixture of iron phosphates and oxides and an interlayer likely predominantly consisting of iron oxides. It should be noted that this double-layer structure is not necessarily representative of the entire tribofilm as lower magnification micrographs in previous work [23] of a phosphonium-organophosphate IL clearly show transitions between single- and double-layer films around valleys in the substrate. N is indicated sparsely throughout both layers of the film. Excluding the C signals from the uppermost layer (a protective film for FIB processing) and from the substrate, C appears to be present in relatively small amounts in the tribofilm, suggesting low contents of organic compounds. Within each layer, P, Fe and O are dispersed rather uniformly. Electron diffraction indicates that the film is amorphous and populated with many small (<10 nm) nanocrystals.

XPS Core Level Spectra

XPS core level spectra of the worn cast iron flat lubricated with BO + 1.74% [N\textsubscript{888H}][\text{DEHP}] is shown in Figure 8. The spectra were recorded after 60 s of ion sputtering of the surface. The C 1s spectrum shows dominating C-C bonding peak (285 eV). Organic carbon is present within the film likely originating from undecomposed IL constituents. The P 2p spectrum suggests the presence of phosphates, commonly observed tribochemical components, due to the strong P-O binding energy peak (133.7 eV), but this does not preclude other iron-phosphorous compounds. Additionally, a small amount of P-metal bonds are revealed. Fe core level spectrum suggests a mixture of ferrous, ferric and metallic iron. The presence of metallic iron along with the carbide peak in C 1s spectrum are a result of substrate exposure (tribofilm removed by ion sputtering) and unreacted wear debris inclusion in the tribofilm. O 1s core level spectrum confirms the presence of oxides and phosphates.
Figure 7. Cross-sectional TEM micrographs, EDS elemental mapping and electron diffraction of tribofilm on the cast iron flat lubricated by BO + 1.74% [N₈₈₃H][DEHP].
Figure 8. XPS core level spectra of the tribofilm on the cast iron flat lubricated by BO + 1.74% \( [N_{s,s,H}]\{DEHP\} \). Signals collected after 60 s of ion sputtering.
Conclusions

This study investigated the potential of using aprotic and protic ammonium-organophosphate ILs as lubricant additives. Four tertiary (protic) ammonium cation ILs and five quaternary (aprotic) ammonium cation ILs with identical organophosphate anions were synthesized, characterized and tested. The protic group exhibits higher solubility in non-polar hydrocarbon lubricating oils than the aprotic group. This is likely attributable to the hydrogen bonding between protic ammonium cations and organophosphate anions to form quasi-neutral cation-anion pairs, which are more compatible with neutral oil molecules. Longer alkyl chains lead to better oil solubility by reducing the charge density. Limited pitting was observed on the cast iron surface exposed to the aprotic ILs, possibly due to impurities. All protic ILs show no corrosion attack on cast iron with strong surface passivation. For the protic series, longer alkyls moderately increases the thermal stability. When tested as oil additives, the protic IL [N₈₈₈₈H][DEHP] consistently outperformed two aprotic ILs ([N₈₈₈₈][DEHP] and [N₈₈₈₁][DEHP]) in terms of both friction reduction and wear protection. Comprehensive characterization of the worn surface lubricated by [N₈₈₈₈H][DEHP] indicated the presence of a tribofilm up to 350 nm thick in a double-layer structure with a top layer composed of iron phosphates and oxides and an interlayer dominated by iron oxides. The encouraging results of this work provide a scientific basis for further development of ammonium-based ILs as lubricant additives.
References

CHAPTER II
PHOSPHONIUM-ORGANOPHOSPHATE IONIC LIQUIDS AS LUBRICANT ADDITIVES: EFFECTS OF CATION STRUCTURE ON PHYSICOCHEMICAL AND TRIBOLOGICAL CHARACTERISTICS
Previous work suggested great potential for a phosphonium-organophosphate ionic liquid (IL) as an anti-wear lubricant additive. In this study, a set of five ILs were carefully designed and synthesized, with identical organophosphate anions but dissimilar phosphonium cations, to allow systematic investigation of the effects of cation alkyl chain length and symmetry on physicochemical and tribological properties. Symmetric cations with shorter alkyl chains seem to increase the density and thermal stability due to closer packing. On the other hand, either higher cation symmetry or longer alkyl moieties induces a higher viscosity, though the viscosity index is dependent more on molecular mass than on symmetry. While a larger cation size generally increases an IL’s solubility in non-polar hydrocarbon oils, six-carbon seems to be the critical minimum alkyl chain length for high oil miscibility. Both the two ILs, that are mutually oil miscible, have demonstrated promising lubricating performance at 1.04% treat rate, though the symmetric-cation IL moderately outperformed the asymmetric-cation IL. Characterizations on the tribofilm formed by the best-performing symmetric-cation IL revealed the film thickness, nanostructure, and chemical composition. Results here provide fundamental insights for future molecular design in developing oil-soluble ILs as lubricant additives.

Introduction

With over a billion registered vehicles in the world, there exists a clear benefit to increasing internal combustion (IC) engine efficiency and longevity. IC engines extract power from a piston and cylinder assembly in a way that necessitates prolonged sliding interaction between surfaces. Engine lubricants are required to mediate the contact pressure between engine bearing interfaces, such as piston rings against cylinder liners, to minimize wear and friction. More than 10% of the energy produced by combustion is dissipated by hydrodynamic drag induced by shearing the lubricant film at the bearing
interfaces. (1) Although this loss cannot be totally eliminated, minimizing it via advanced lubricants can result in significant energy savings.

When relative motion exists between two adjacent lubricated surfaces, the interaction can be categorized as being in boundary, mixed, elastohydrodynamic, or hydrodynamic lubrication. A piston in an IC engine is constrained to reciprocating, linear motion; therefore, it must cease movement before reversing direction. The regions in which this reversal occurs are under boundary lubrication conditions and are prone to wear due to more frequent asperity contacts. Higher viscosity engine oils generate a thicker lubricant film at the interface, and generally provide better wear protection near top and bottom dead centers of the stroke. Conversely, the piston–cylinder interface is within the elastohydrodynamic and hydrodynamic regimes for the majority of a stroke. There is virtually no wear in these regimes; thus, it is desirable to use lower viscosity oils to reduce irreversibilities associated with elastohydrodynamic drag to increase energy efficiency. These conflicting ideas can be reconciled through implementation of more effective additive packages that allow the use of lower viscosity oil while retaining antiwear functionality.

Ionic liquids (ILs) have been utilized in a diverse array of applications over the past half-century with majority use as “customizable” solvents or electrolytes. Generally, ILs possess low volatility, low combustibility, and high thermal stability. Since 2001, research interest in ILs has expanded into lubrication. (2) Early work was centered on ILs containing imidazolium cations with various fluorine-containing anions. (3-7) Much work of using ILs as lubricant additives involved oil–IL emulsions or very low concentrations of ILs in base oils due to many ILs’ inherent insolubility in nonpolar hydrocarbon oils. (8-15) Some applied polar base stocks to facilitate solubility. (16, 17)

In 2012, we reported trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P66614][DEHP]) with mutually miscible properties in nonpolar hydrocarbon oils and promising antiwear characteristics as a lubricant additive for steel–cast iron contacts. (18-20) Later studies from a couple of other groups (21, 22) reinforced the concept of using [P66614][DEHP] as an antiwear additive by confirming the oil miscibility and demonstrating effective wear protection in lubricating steel–aluminum (21) and steel–steel (22) contacts. Several other phosphorus-containing ILs (19, 21, 22) have since been explored as lubricant additives, and the group of alkylphosphonium-organophosphate ILs demonstrated superior lubricating performance compared to a conventional antiwear additive (20) and other phosphorus-containing groups. (21) However, there is lack of fundamental understanding of the correlations between the ion structures and the IL’s physicochemical and tribological properties.

In this study, we carefully designed and synthesized five alkylphosphonium-organophosphate ILs containing identical anions but different cations, including [P66614][DEHP] and four new ILs. Particularly, the two ILs containing symmetric cations are newly invented and patent pending. (25) Such a group of ILs allowed a systematic
investigation of the effects of cation symmetry and alkyl chain length on the ILs’ oil solubility, density, viscosity, thermal stability, corrosion behavior, and lubricating properties. While most of the literature paid more attention to the anion chemistry, (19, 21-24) results here clearly suggest that the cation structure plays an important role as well.

Experimental Details and Materials

Synthesis

Five quaternary phosphonium-organophosphate ionic liquids with different cation structures but the same anion structure were investigated in this study. They are tetraoctylphosphonium bis(2-ethylhexyl) phosphate ([P_{8888}][DEHP]), [P_{66614}][DEHP], tributyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P_{44414}][DEHP]), tributylbutylphosphonium bis(2-ethylhexyl)phosphate ([P_{4444}][DEHP]), and tetrabutylphosphonium bis(2-ethylhexyl) phosphate ([P_{4444}][DEHP]). The ionic structures of these ILs are shown in Figure 9, and their physical properties are listed in Table 2.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Molecular Weight</th>
<th>Density (g/cm^3)</th>
<th>Viscosity of neat IL (cP) 23°C</th>
<th>Viscosity Index</th>
<th>Solubility in BO (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[P_{8888}][DEHP]</td>
<td>805.26</td>
<td>0.91</td>
<td>&gt;1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P_{66614}][DEHP]</td>
<td>805.26</td>
<td>0.86</td>
<td>611.8</td>
<td>68.2</td>
<td>188</td>
</tr>
<tr>
<td>[P_{44414}][DEHP]</td>
<td>721.10</td>
<td>0.88</td>
<td>1045</td>
<td>49.5</td>
<td>177</td>
</tr>
<tr>
<td>[P_{4448}][DEHP]</td>
<td>636.94</td>
<td>0.89</td>
<td>711.4</td>
<td>25.2</td>
<td>128</td>
</tr>
<tr>
<td>[P_{4444}][DEHP]</td>
<td>580.83</td>
<td>0.94</td>
<td>788.6</td>
<td>30.5</td>
<td>147</td>
</tr>
</tbody>
</table>

*Above the upper limit of the measurement range.

The synthesis of [P_{66614}][DEHP] had been reported in our earlier work, (18) and [P_{4444}][DEHP] was kindly provided by Cytec Industries Inc., Niagara Falls, ON, Canada. The purity of [P_{66614}][DEHP] and [P_{4444}][DEHP] was determined using titration at Cytec to be 98% and 97%, respectively.

[P_{8888}][DEHP], [P_{44414}][DEHP], and [P_{4448}][DEHP] were newly synthesized and characterized at ORNL, and the detailed procedures are described as follows. Proton nuclear magnetic resonance (NMR) analysis was carried out using a Bruker MSL-400 at 400 MHz. Spectra were obtained in CDCl₃ with reference to TMS (0 ppm) for ^1^H. Details for [P_{8888}][DEHP] follow: Tetraoctylphosphonium bromide ([P_{8888}]Br, 40.58 g, 72.0 mmol) and bis(2-ethylhexyl)phosphoric acid (HDEHP, 23.2 g, 72.0 mmol) were mixed in 90 mL of deionized water (DI H₂O, 18.2 MΩ cm) and 100 mL of hexanes. To this stirred suspension was added a solution of sodium hydroxide (NaOH, 2.88 g, 72.0
Figure 9. Molecular structures of selected phosphonium-organophosphate ILs.
mmol) in 75 mL of DI H₂O dropwise at room temperature. The white suspension became clear after the addition of NaOH was completed. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with DI H₂O four times to ensure removal of NaBr. Solvents were distilled off by rotary evaporator, and the product was dried at 70 °C under vacuum for 4 h to yield [P₈₈₈₈][DEHP] as a viscous liquid (57.0 g, 70.8 mmol, yield: 93.8%). The water content of [P₈₈₈₈][DEHP] was 0.1%. Proton nuclear magnetic resonance (¹H NMR, CDCl₃, ppm): 0.85–0.87 (m, 24H, 8CH₃), 1.27–1.36 (m, 56H, 28CH₂), 1.44 (m, 2H, 2CH), 1.67 (m, 8H, 4CH₂), 3.31 (m, 8H, 4NCH₂), 3.80 (m, 4H, 2OCH₂). ¹³C NMR (CDCl₃, ppm): 10.81 (2CH₃), 13.96 (4CH₃), 14.02 (2CH₃), 22.02 (4CH₂), 22.52 (4CH₂), 23.04 (2CH₂), 23.09 (4CH₂), 26.28 (4CH₂), 28.92 (2CH₂), 29.06 (4CH₂), 29.87 (4CH₂), 31.64 (4CH₂), 40.09 (2CH), 58.84 (4NCH₂), 67.82 (2OCH₂).

Details for [P₄₄₄₁₄][DEHP] follow: Tributyltetradecylphosphonium chloride ([P₄₄₄₁₄]Cl, 36.47 g, ∼49% in aqueous solution, 41.1 mmol) and bis(2-ethylhexyl)phosphoric acid (HDEHP, 13.26 g, 41.1 mmol) were mixed in 58 mL of hexanes. To this stirred mixture was added a solution of sodium hydroxide (NaOH, 1.64 g, 41.1 mmol) in 45 mL of DI H₂O (18.2 MΩ cm) dropwise at room temperature. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with DI H₂O four times to ensure removal of NaCl. Solvents were distilled off by rotary evaporator, and the product was dried at 70 °C under vacuum for 4 h to yield [P₄₄₄₁₄][DEHP] as a viscous liquid (29.1 g, 40.4 mmol, yield: 98.3%). The water content of [P₄₄₄₁₄][DEHP] was 0.3%. ¹H NMR (CDCl₃, ppm): 0.85–0.90 (m, 24H, CH₃), 1.24–1.31 (m, 36H, CH₂), 1.50–1.55 (m, 18H CH₂ and CH), 2.45 (m, 8H, PCH₂), 3.72 (m, 4H, OCH₂). ¹³C NMR (CDCl₃, ppm): 10.94 (CH₃), 13.48 (CH₃), 14.09 (CH₃), 18.44 (CH₂), 18.91 (CH₃), 21.91 (CH₂), 22.61 (CH₂), 23.13 (CH₂), 23.31 (CH₂), 23.88 (CH), 29.04 (CH₂), 29.27 (CH₂), 29.56 (CH₂), 30.11 (CH₂), 31.63 (CH₂), 40.45 (CH₂), 67.30 (2CH₂).

Details for [P₄₄₄₈][DEHP] follow: Tributyloctylphosphonium chloride ([P₄₄₄₈]Cl, 10.96 g, 31.3 mmol) and bis(2-ethylhexyl)phosphoric acid (HDEHP, 10.08 g, 31.3 mmol) were mixed in 40 mL of hexanes. To this stirred mixture was added a solution of sodium hydroxide (NaOH, 1.25 g, 31.3 mmol) in 30 mL of DI H₂O (18.2 MΩ cm) dropwise at room temperature. The mixture continued to be stirred at room temperature overnight. The upper organic phase was separated and washed with DI H₂O four times to ensure removal of NaCl. Solvents were distilled off by rotary evaporator, and the product was dried at 70 °C under vacuum for 4 h to yield [P₄₄₄₈][DEHP] as a viscous liquid (17.68 g, 27.8 mmol, yield: 88.8%). The water content of [P₄₄₄₈][DEHP] was 0.3%. ¹H NMR (CDCl₃, ppm): 0.85–1.00 (m, 24H, CH₃), 1.28–1.40 (m, 24H, CH₂), 1.49–1.54 (m, 18H CH₂ and CH), 2.42 (m, 8H, PCH₂), 3.74 (m, 4H, OCH₂). ¹³C NMR (CDCl₃, ppm): 10.90 (CH₃), 13.44 (CH₃), 14.05 (CH₃), 18.40 (CH₂), 18.67 (CH₃), 21.65 (CH₂), 22.50 (CH₂), 23.09 (CH₂), 23.27 (CH₂), 23.85 (CH), 28.91 (CH₂), 29.01 (CH₂), 30.06 (CH₂), 31.62 (CH₂), 40.40 (CH₂), 67.39 (2CH₂).
A low viscosity gas-to-liquid 4 cSt base oil (BO 4) was provided by Shell Global Solutions (TX) and used as the base stock in this research. The BO 4 was synthesized via the Fischer–Tropsch process that produces alkanes from carbon monoxide and hydrogen obtained from natural gas.

All ILs in this work contain phosphorus. International Lubricants Standardization and Approval Committee (ILSAC) GF-5 specifications limit phosphorus content in engine oils to 800 ppm. Guided by this restriction, the five ILs were blended with BO 4 to the maximum allowable phosphorus content resulting in treat rates of 0.75–1.04 wt %, as shown in Table 3.

Table 3. IL treat rates in the base oil and viscosities of the oil-IL blends.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Target IL Conc. (wt.%)</th>
<th>P Conc. (wt.%)</th>
<th>Viscosity of BO-IL blend (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO 4</td>
<td>0</td>
<td>0</td>
<td>29.92 15.11 3.28</td>
</tr>
<tr>
<td>BO 4 + [P8888][DEHP]</td>
<td>1.04</td>
<td>0.08</td>
<td>29.97 15.08 3.25</td>
</tr>
<tr>
<td>BO 4 + [P66614][DEHP]</td>
<td>1.04</td>
<td>0.08</td>
<td>30.02 15.04 3.26</td>
</tr>
<tr>
<td>BO 4 + [P44414][DEHP]</td>
<td>0.93</td>
<td>0.08</td>
<td>30.13 15.14 3.27</td>
</tr>
<tr>
<td>BO 4 + [P4448][DEHP]</td>
<td>0.82</td>
<td>0.08</td>
<td>Not measured</td>
</tr>
<tr>
<td>BO 4 + [P4444][DEHP]</td>
<td>0.75</td>
<td>0.08</td>
<td>30.04 15.06 3.27</td>
</tr>
</tbody>
</table>

Characterization

Each IL’s oil solubility was determined by incrementally decreasing combinations of IL and BO 4 from a 1:1 ratio until solubility was reached. The solute and solvent were mixed and vigorously shaken for 1 min. The samples were then placed in a centrifuge for 3 min at 13 000 rpm. The oil–IL blends were examined under bright lighting for evidence of separation or cloudiness right after centrifuge and 24 h after. Thermogravimetric analysis (TGA) was performed on the ILs in air (allowing oxidation) using a TA Instruments (DE) TGA-2950 at a 10 °C per minute heating rate.

Viscosities of the neat ILs and oil-IL blends at 23, 40, and 100 °C were measured using a Petrolab (OK) MINIVIS II viscometer (falling ball technique). At least four measurements were conducted for each fluid to ensure a standard deviation less than 1%.
Corrosion and Tribological Testing and Analysis

Open-air corrosion testing was performed by placing a drop of each candidate IL directly onto a 25.4 × 25.4 mm\(^2\) CL35 cast iron surface in an ambient environment for 7 days. Evaporation was not a concern due to ILs’ low volatility. Electrochemical corrosion tests were carried out on the two oil-miscible ILs, \([P_{8888}][\text{DEHP}]\) and \([P_{66614}][\text{DEHP}]\), at room temperature, using the potentiodynamic polarization technique with a three-electrode electrochemical cell. A disk of cast iron with 1 cm\(^2\) exposed area was used as the working electrode, which was immersed in the electrolyte for 15 min before starting the experiment. A 20 mL portion of the IL to be tested served as the electrolyte. A Pt wire was used as the counter electrode, and Ag/AgCl (4 M KCl internal solution) was the reference electrode. The sample was polarized at potentials from −1.0 to +1.50 V versus open circuit potential at a scanning rate of 0.166 mV/s under aerated conditions. All electrochemical tests were conducted in the ambient environment using a potentiostat model CHI 700C (CH Instruments, Inc., Austin, TX).

Tribological wear and friction testing was performed on a Phoenix Tribology Ltd. (Hampshire, U.K.) Plint TE77 reciprocating sliding tribometer. A ball-on-flat geometry was chosen using an AISI 52100 steel ball against a CL35 (Metal Samples Company, AL) gray cast iron flat. The cast iron flats were first polished using 600 grit silicon carbide grinding paper producing a lay perpendicular to the sliding direction. All interacting surfaces were cleaned with isopropyl alcohol and air-dried before testing. The Plint TE77 obtains friction data in situ by taking tangential force measurements using a piezoelectric load cell. All lubricant blends were well-shaken before use. Testing for all specimens was carried out at 100 °C under a normal load of 100 N for a total sliding distance of 1000 m. The ball reciprocated at 10 Hz with a stroke of 10 mm against the flat. At least three replicate tests were performed for each IL–oil blend and the base oil to assess repeatability. After tribological testing, balls and flats were cleaned with acetone and then isopropyl alcohol. Wear volumes were measured using a Veeco (now Bruker, TX) Wyko NT9100 white light interferometer.

A Hitachi S-4800 (Tokyo, Japan) scanning electron microscope (SEM) equipped with an EDAX SDD energy-dispersive spectroscopy (EDS) system was used to analyze the worn surface from the top. Cross-sectional composition and nanostructure were examined using a Hitachi HF-3300 transmission electron microscope (TEM) (300 kV, 1.3 Å resolution) bundled with a Bruker solid-state EDS detector. TEM samples were prepared using a Hitachi NB5000 focused ion beam (FIB) system with a gallium ion source to extract a thin cross-section of the tribofilm of interest. A carbon film and then a tungsten layer were deposited onto the wear scar before the FIB process to protect the tribofilm. A Thermo Scientific (MA) K-Alpha X-ray photoelectron spectrometer (XPS) was used for chemical analysis of the selected tribofilm. The X-rays used were monochromatic Al Kα photons, and photoemitted electrons were analyzed with a hemispherical energy analyzer. Surface compositions were calculated by measuring peak areas of the primary core levels for all elements present and normalizing the peak areas using tabulated sensitivity factors.
Composition-depth profiles were obtained under 1 kV ion beam energy at high a current setting.

Results and Discussion

Oil Solubility

Due to the identical anion structure among the five ILs, changes in oil solubility are governed solely by the cation structures. We hypothesized that more carbon atoms in the alkyl groups on the cation would improve the oil solubility by (1) diluting the charge density thus decreasing ion coordination, and (2) increasing intermolecular London dispersion forces between lipophilic moieties of the cations with the base oil molecules. ILs with long alkyl chain cations may possess interesting physicochemical properties, (26) and the effects of the anion chemistry and alkyl structure and chain length on the IL’s oil solubility had been discussed elsewhere. (19, 21, 23, 24)

Table 1 and Figure 2a show the oil solubility for each candidate IL. [P66614][DEHP] and [P8888][DEHP] are mutually miscible (>50 wt %) in the BO 4 cSt base oil. The remaining ILs have marked lower oil solubility: [P44414][DEHP], [P4448][DEHP], and [P4444][DEHP] showing solubility limits of ~1, <1, and <1 wt %, respectively. Similar solubility was observed for the five ILs in a poly-α-olefin (PAO) 4 cSt base oil. The prevailing trend from this data strongly supports our hypothesis of longer alkyl chains improving oil solubility. The abrupt drop in oil solubility due to shorter alkyl chains either on the cation (from [P66614] to [P44414]) or on the anion (from [DEHP] to dibutyl phosphate as observed in our previous study (19)) implies that six carbons could be the critical minimum alkyl chain length for phosphonium-organophosphate ILs to achieve high oil miscibility.

Density, Viscosity and Thermal Stability

Densities (ρ), viscosities, and viscosity indices of the five ILs are compared in Table 3 and Figs. 10(b-d). The ILs’ densities are moderately affected by changes in cationic alkyl groups. As illustrated in Fig. 10b, closer packing and thus higher density seems to be achieved by reducing the size of the hydrocarbon chains.

The cationic alkyl groups’ effect on viscosity (η) seems twofold: (1) more carbons per chain increase interionic interaction, (2) and higher symmetry causes closer packing and thus more interaction, as shown in Fig. 10c. Both effects cause increased resistance to shear flow and higher viscosity. For example, η ([P66614][DEHP]) > η ([P44414][DEHP]), η ([P8888][DEHP]) > η ([P4444][DEHP]), and η ([P8888][DEHP]) > η ([P66614][DEHP]). For [P44414][DEHP] vs.[P4448][DEHP], the former has a slightly larger cation but the latter has a slightly higher symmetry, and, as a result of the competition between these two effects, the viscosities of these two ILs turn out to be similar. Evidently for [P44414][DEHP] vs.[P4444][DEHP], the effect of cation symmetry was more significant.

30
The viscosity index (VI) is a measure of the variation in viscosity over an arbitrary temperature range. Reference temperatures of 40 and 100 °C are typically used in the automotive industry. Higher viscosity indices indicate more stable lubrication performance over this temperature range. Contrary to viscosity, the viscosity index generally seems to relate to IL mass but is little affected by the cation symmetry, as shown in Figure 10d. For instance, [P₈₈₈₈][DEHP] and [P₆₆₆₄][DEHP] both have identical mass and the highest mass of the five ILs but have different cation symmetry. These two ILs also possess higher viscosity indices than the other three ILs. Except that of [P₄₄₄₄][DEHP], the VIs of the remaining four ILs appeared to be proportional to their respective masses.

Figure 10. Effects of the cation structure on ILs’ (a) oil-solubility, (b) density, (c) viscosity, and (d) viscosity index
**Corrosion Behavior**

No evidence of pitting or other hints of corrosion were present on any of the cast iron surfaces that were exposed to the five ILs in open-air tests. Figure 11 shows the potentiodynamic polarization curves obtained for cast iron in neat [P$_{8888}$][DEHP] and [P$_{66614}$][DEHP]. Both showed classic active-passive behavior with strong passivation at a current density in the order of $10^{-4}$ A/cm$^2$. No corrosion damage or morphology change was observed on either of the iron surfaces electrochemically tested in the two ILs.

![Potentiodynamic polarization curves](image-url)

**Figure 11. Potentiodynamic polarization curves of cast iron in the two oil-miscible ILs.**

**Friction and Wear Results**

Because of the questionable oil solubility of [P$_{44414}$][DEHP], [P$_{4448}$][DEHP], and [P$_{4444}$][DEHP] at the target concentrations (see Table 2), only [P$_{8888}$][DEHP] and [P$_{66614}$][DEHP], mutually miscible in the BO 4 base oil, were selected for tribological testing and analysis.

Each friction trace in Figure 12 represents the average of three repeated tests. The baseline oil, BO 4, exhibited a rapidly increasing friction coefficient during the initial 25 m of sliding, an indication of scuffing.(27, 28) Neither BO 4 + 1.04% [P$_{8888}$][DEHP] nor BO 4 + 1.04% [P$_{66614}$][DEHP] had such a rapid friction increase in the beginning of the tests. And, each blend reduced the average steady-state friction coefficient by $\sim 10\%$ compared to BO 4.
Figure 12. Friction coefficient traces of the base oil without and with IL additives.

Addition of either [P$_{8888}$][DEHP] or [P$_{66614}$][DEHP] at the 1.04 wt % treat rate into the base oil significantly reduced the wear for the cast iron flat and steel ball (Table 4). Wear results here are an average of three replicates for each lubricant. Wear on the reciprocating steel ball specimens was consistently 2 orders of magnitude smaller than that on the cast iron flats. Two out of three repeats for BO 4 without additive revealed scuffing and associated high wear, leading to a high standard deviation between tests. It is interesting to note the moderately better performance of BO 4 + 1.04 wt % [P$_{8888}$][DEHP] than that of BO 4 + 1.04 wt % [P$_{66614}$][DEHP] (Table 4). Phosphates have been used for years in lubricants and are known to be facilitators of protective tribofilm formation. Additionally, antiwear characteristics of ILs are thought to be more sensitive to changes in the anion. [P$_{8888}$][DEHP] and [P$_{66614}$][DEHP] share the identical organophosphate anion and have the same molecular weight, and differ only in their distribution of alkyl groups about the central phosphorus atom in their cations. Thus, the difference in wear performance may be attributed to the symmetry of the quaternary phosphonium cation. We hypothesize that the symmetric structured cation might allow better mobility for [P$_{8888}$][DEHP] in the base oil to reach and interact with the surface asperities upon collisions to be more readily available in forming the protective tribofilm. Such hypothesis warrants further investigation.
Table 4. Summary of wear results in the base oil without and with IL additives.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Flat wear volume (mm$^3$)</th>
<th>Ball wear volume (mm$^3$)</th>
<th>Total wear volume (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO 4</td>
<td>$1.12^{\pm 0.61}$</td>
<td>$0.51^{\pm 0.25} \times 10^{-2}$</td>
<td>$1.17^{\pm 0.61}$</td>
</tr>
<tr>
<td>BO 4 + [P$_{8888}$][DEHP]</td>
<td>$0.10^{\pm 0.05}$</td>
<td>$0.10^{\pm 0.02} \times 10^{-2}$</td>
<td>$0.10^{\pm 0.05}$</td>
</tr>
<tr>
<td>BO 4 + [P$_{66614}$][DEHP]</td>
<td>$0.18^{\pm 0.05}$</td>
<td>$0.09^{\pm 0.02} \times 10^{-2}$</td>
<td>$0.18^{\pm 0.05}$</td>
</tr>
</tbody>
</table>

**Wear Scar Examination and Tribofilm Analysis**

All wear scars were first examined using SEM for morphology imaging and using EDS for element detection. More comprehensive three-dimensional characterization \(^{(29)}\) was then conducted on the tribofilm on the cast iron surface lubricated by BO 4 + 1.04 wt % [P$_{8888}$][DEHP]. Aided by FIB, cross-sectional examination was carried out using TEM for film thickness measurement, using electron diffraction for phase identification, and using EDS for elemental mapping. XPS was used to analyze the tribofilm composition and ion sputtering allowed layer-by-layer analysis for revealing the composition variation of the tribofilm from top to bottom.

**Top Surface Morphology SEM Examination and EDS Elemental Analysis**

Representative SEM micrographs of the worn flat surface for each lubricant along with the corresponding EDS spectra are shown in Figure 13. The baseline lubricant (BO 4) caused adhesive wear and plastic deformation as demonstrated by the deep grooves formed along the entire width and length of the scar. BO 4 + 1.04% [P$_{66614}$][DEHP] generated a smoother wear track with some shallower grooves. BO 4 + 1.04% [P$_{8888}$][DEHP] produced even less surface damage with the smoothest worn surface with fewest grooves in a more random pattern. The level of surface damage correlates well with the wear results described above.

In addition to the carbon, iron, and silicon peaks, EDS spectra in Figure 13 show prominent oxygen signal on the cast iron worn surfaces suggesting metal oxidation during the wear process. The wear tracks produced with the two oil–IL blends contain phosphorus as shown by the small peaks just above 2 keV, indicative of IL-induced tribofilms on the worn surfaces.
Cross-Sectional TEM Nanostructure Examination and EDS Elemental Mapping

Tribofilms formed by asymmetric-cation IL [P_{66614}][DEHP] (blended in PAO 4 cSt base oil) on cast iron surfaces were previously examined. (18, 20) In this study, the tribofilm examination was focused on the new symmetric-cation IL [P_{8888}][DEHP] due to its superior wear protection (Table 4). Aided by FIB milling, cross-sectional TEM micrographs, EDS element mapping, and electron diffraction pattern of the tribofilm on the cast iron flat lubricated by BO 4 cSt base oil, BO 4 + [P_{8888}][DEHP], and BO 4 + [P_{66614}][DEHP] were obtained (Figure 14). This tribofilm appears to be single layered with a thickness varying from 10 to 200 nm. The diffraction pattern implies an amorphous matrix populated with nanocrystalline inclusions. The size of these inclusions is determined to be 1–10 nm by high magnification TEM imaging. EDS elemental maps show relatively uniform distribution of oxygen, iron, and phosphorus and discrete areas containing carbon (excluding the carbon signals across the top that are from FIB processing) throughout the thickness of the tribofilm. This tribofilm appears similar compared to that of the single-layer tribofilm

Figure 13. SEM micrographs and EDS spectra. From top to bottom, wear scars lubricated by BO 4 cSt base oil, BO 4 + [P_{8888}][DEHP], and BO 4 + [P_{66614}][DEHP]. SEM micron bar: 50 μm.
Figure 14. Cross-sectional TEM micrographs and electron diffraction pattern and EDS elemental maps of the tribofilm on the cast iron surface lubricated by BO 4 + $\text{[P}_{8888}\text{][DEHP]}$. 
from \([P_{66614}][DEHP]\) reported in ref 18 differing from the two-layer tribofilm observed in ref 20. Table 5 compares the tribofilm characteristics (based on cross-sectional TEM/EDS examination) between this work on \([P_{8888}][DEHP]\) and our previous studies on \([P_{66614}][DEHP]\). \((18, 20)\) Although mixed with different base oils, at different treat rates, against different sliders, and under different test conditions, the tribofilms formed on cast iron surfaces by these two ILs seem to have similar nanostructure and chemical composition. The only notable distinction is the double-layer structure (with a discrete oxide interlayer) observed in ref 20, which might be attributed to the combined higher load (240 N) and elevated temperature (100 °C) compared to ref 18 (160 N and 23 °C) and this work (100 N and 100 °C). Under the higher thermomechanical stresses in ref 20, more significant oxidation may occur on surface asperities in collision to grow pads of oxides during wear-in before sufficient IL ions decomposed to become available to form the IL tribofilm on top of the oxide layer.

Table 5. Comparison of tribofilms formed by \([P_{8888}][DEHP]\) and \([P_{66614}][DEHP]\) observed in three studies.

<table>
<thead>
<tr>
<th>IL</th>
<th>Reciprocating sliding test (10 Hz oscillation with 10 mm stroke)</th>
<th>Tribofilm (cross-sectional TEM/EDS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base oil, IL treat rate</td>
<td>Substrate (slider)</td>
</tr>
<tr>
<td>([P_{8888}][DEHP])</td>
<td>BO 4 cSt, 1.04 wt%</td>
<td>Cast iron (52100 steel ball)</td>
</tr>
<tr>
<td>(this study)</td>
<td></td>
<td>100 N, 100 °C, 1000 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe, O, P, C, 10-200, Single layer</td>
</tr>
<tr>
<td>([P_{66614}][DEHP])</td>
<td>PAO 4 cSt, 5.0 wt%</td>
<td>Cast iron (Mo-coated piston ring)</td>
</tr>
<tr>
<td>(Ref. 18)</td>
<td></td>
<td>160 N, 23 °C, 1000 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe, O, P, C, 120-180, Single layer</td>
</tr>
<tr>
<td>([P_{66614}][DEHP])</td>
<td>PAO 4 cSt, 1.0 wt%</td>
<td>Cast iron (Mo-coated piston ring)</td>
</tr>
<tr>
<td>(Ref. 20)</td>
<td></td>
<td>240 N, 100 °C, 4320 m</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fe, O, P, C, 60-220, Double-layer</td>
</tr>
</tbody>
</table>

*L – normal load, T – lubricant bulk temperature, SD – sliding distance*

Layer-by-Layer XPS Chemical Analysis

XPS core level spectra of key elements of the worn cast iron surface lubricated by BO 4 + \([P_{8888}][DEHP]\) are shown in Figure 15. The red spectra represent binding energies for the initial 2–3 nm of the surface including the top of the tribofilm and any lubricant residue (even though all wear scars were carefully cleaned by solvents after wear testing).
Figure 15. XPS core level spectra of key elements for the tribofilm on the cast iron surface lubricated by BO 4 + [P$_{8888}$][DEHP].
The green spectra were produced after 60 s of ion sputtering of the tribofilm to eliminate the surface contaminants.

As compared in the core level spectra, iron on the top surface of the tribofilm is primarily in the Fe$^{3+}$ oxidation state (710.5 eV binding energy, BE) while Fe$^{2+}$ (709.7 eV BE) becomes the major peak after 60 s sputtering. The ferric iron on the top surface is likely manifested as iron(III) oxide that developed during storage (several weeks) before XPS analysis. The phosphorus 2p spectra show a dominating P–O bond (133.7 eV BE) suggesting phosphates. The O 1s shows two distinct features: a peak at ~531.5 eV BE is assigned to O–P bonding (excluding P–O–Fe), and another at 530.3 eV is attributed to O–Fe/P–O–Fe bonds. The higher amount of O–P detected on the top surface is possibly introduced by the IL residue, and the stronger O–Fe/P–O–Fe signal after 60 s of ion sputtering suggests most O atoms are bonded with iron phosphates and oxides. The same C 1s spectra (both before and after 60 s of sputtering) show a dominant peak at 285.0 eV BE assigned to C–C bonding. This indicates that the carbon content in the tribofilm might be from residue hydrocarbon chains on the partially decomposed organophosphate anions. The metallic Fe and carbide peaks after 60 s ion sputtering may be introduced by two sources: (1) iron substrate exposed by ion sputtering and (2) iron wear debris within the tribofilm. On the basis of binding energy analyses, the tribofilm formed by [P$_{8888}$][DEHP], similar to that by [P$_{66614}$][DEHP], is believed to be a composite of iron phosphates (or polyphosphates) and iron oxides.

The deconvoluted composition-depth profile (from 60 to 1790 s of ion sputtering) is shown in Figure 16a. As revealed in the cross-sectional TEM/EDS images in Figure 14, the thickness of the tribofilm varies (10–200 nm in a 2 μm-long TEM sample), and Fe, O, and P have relatively uniform distributions in the tribofilm from the top surface to the interface with the substrate. Therefore, the rising signals of metallic iron and carbide and dropping signals of tribofilm elements along the sputtering time are largely a consequence of substrate exposure from material removal during ion sputtering. Assuming minimal metallic iron and carbide is embedded in the tribofilm (both less than 1 at % on the surface survey scan), we removed these two substrate signals, renormalized other elements, and replotted the profile in Figure 16b. This mitigates the bias from the increasingly exposed substrate and better reflects the composition change through the thickness of the tribofilm. The ratios of O(O–P):P and O(O–Fe/P–O–Fe):Fe(ion) are relatively constant throughout the film thickness, though the oxygen contents are somewhat higher than expected. Results indicate two possibilities: (1) phosphates gradually decrease while iron oxides increase inside the tribofilm from the top surface to the interface with the substrate, and (2) preferential sputtering removes phosphates faster than oxides.

The carefully designed group of five ILs with identical phosphate anions but different phosphonium cations allowed a systematic study of the effects of cation alkyl chain length and symmetry on critical physicochemical and tribological properties, which
Figure 16. XPS composition-depth profile of the tribofilm on the cast iron surface lubricated by BO 4 + \([P_{8888}]\)[DEHP].
provide fundamental insights for future cation design in developing the promising phosphonium-phosphate ILs as lubricant additives. A new U.S. patent application (25) has recently been filed for the phosphonium-organophosphate ILs containing symmetric cations. Results suggest oil-soluble phosphonium-phosphate ILs as potentially candidate lubricant additives in friction and wear control, which may help allow the use of lower viscosity engine and industrial oils to improve machinery efficiency and durability.

**Conclusions**

This study systematically investigated the effects of cation alkyl chain length and symmetry for quaternary phosphonium-organophosphate ILs to correlate between the cation structure and critical physicochemical and lubricating properties. Five ILs containing an identical anion but different cations, \([\text{P}_{8888}]\text{[DEHP]}, \ [\text{P}_{66614}]\text{[DEHP]}, \ [\text{P}_{44414}]\text{[DEHP]}, \ [\text{P}_{44448}]\text{[DEHP]},\) and \([\text{P}_{44444}]\text{[DEHP]}\), were designed, synthesized, characterized, and evaluated as antiwear additives in a BO 4 cSt base oil. As expected, larger cations proved to be more soluble in the base oil with six carbons per alkyl chain being a critical minimum for oil miscibility in this case. Symmetry and smaller alkyl chain lengths on the cation seemed to increase density and thermal stability due to closer packing, and more planes of symmetry and/or longer alkyls served to increase IL viscosity. No corrosive attack by any IL on cast iron was observed in open-air or electrochemical tests. Both the two oil-miscible ILs \([\text{P}_{8888}]\text{[DEHP]}\) and \([\text{P}_{66614}]\text{[DEHP]}\) provided effective wear protection when added to the base oil at a treat rate of 1.04 wt %. Characterization results revealed a 10–200 nm thick amorphous-nanocrystalline tribofilm, consisting primarily of iron phosphates and oxides, on the worn cast iron surface lubricated by the BO 4 + 1.04% \([\text{P}_{8888}]\text{[DEHP]}\). The symmetric-cation \([\text{P}_{8888}]\text{[DEHP]}\) moderately outperformed the asymmetric-cation \([\text{P}_{66614}]\text{[DEHP]}\). The hypothetical explanation for this observation of symmetry allowing higher ion mobility throughout the oil warrants further investigation.
References

CHAPTER III
TRIBOLOGICAL BENCH AND ENGINE DYNAMOMETER TESTS OF A LOW VISCOSITY SAE 0W-16 ENGINE OIL USING A COMBINATION OF IONIC LIQUID AND ZDDP AS ANTI-WEAR ADDITIVES
A version of this chapter was originally published by William C. Barnhill, Hong Gao, Bassem Kheireddin, Brian L. Papke, Huimin Luo, Brian H. West, and Jun Qu:


I was responsible for performing boundary friction and wear tests, making measurements on worn specimens, compiling and analyzing all tribological data, scanning electron microscope/EDS operation, analyzing engine test data and preparing the manuscript.

**Abstract**

We have previously reported an oil-miscible phosphonium-organophosphate ionic liquid (IL) with effective anti-wear functionality when added to a base oil by itself or combined with a conventional zinc dialkyldithiophosphate (ZDDP) for a synergistic effect. In this research, we investigated whether this synergy manifests in formulated engine oils. An experimental SAE 0W-16 engine oil was generated using a combination of IL and ZDDP with equal phosphorus contribution. The prototype engine oil was first evaluated using tribological bench tests: anti-wear performance in boundary lubrication and friction behavior (Stribeck curves) in elastohydrodynamic, mixed, and boundary lubrication. The forthcoming standard Sequence VIE engine dynamometer test was then conducted to demonstrate improved fuel economy. Results were benchmarked against those of another experimental engine oil with almost the same formulation except using ZDDP only without the IL (similar total phosphorus content) and a baseline SAE 20W-30 engine oil. The IL-ZDDP formulation consistently outperformed the ZDDP-only formulation and the results from the bench and engine tests are well correlated.

**Introduction**

Reducing friction and wear is a persistent issue facing many industries, consumers and societies around the world. The US automotive industry in particular faces increasing governmental regulation (1) and consumer demand (2) to improve the effectiveness of lubricants. Incremental improvements in lubricants can not only reduce financial losses associated with component failure, but can also conserve material, energy and the environment. Frictional energy dissipation in internal combustion (IC) engines may cost the US nearly 1.3 billion barrels of oil annually (3) with engine bearing irreversibilities costing 10% to 15% of total engine energy production (4). Power production in IC engines depends on reciprocating, sliding surface interactions that continually vary the lubrication regime between boundary lubrication (BL), mixed lubrication (ML), elastohydrodynamic lubrication (EHL) and hydrodynamic lubrication (HL). This range of lubrication behavior presents a twofold problem when minimizing energy dissipation at the most important piston ring cylinder liner interface: 1) higher viscosity engine oil can better counter the tendency for lubricant films to become deleteriously thinner as sliding...
speed decreases and temperature rises (i.e. in ML or BL) near the top ring reversal region of a stroke, but 2) most of a piston stroke has little to no asperity contact (i.e. in EHL or HL); therefore, a lower viscosity lubricant would be preferable to reduce parasitic friction, but posts a challenge for wear protection. Novel lubricant additive formulations that allow lower viscosity engine oils while retaining anti-wear (AW) benefits are a logical path for researchers to follow in order to resolve these issues.

Since the seminal work in 2001 (5), exploration of ILs as lubricants and lubricant additives has proliferated. These room-temperature molten salts offer low volatility, high thermal stability with ashless decomposition and can be tailored for specific properties via changes in alkyl structures. Early works involved ILs with imidazolium cations and fluorine- (6-8) or borate-containing anions (9, 10), but ILs in lubrication since then have become more diverse (11-13). Progress on ILs as lubricant additives has been varied with some employing polar base stocks (14, 15) to overcome most ILs’ inherent insolubility in non-polar oils and others using immiscible IL emulsions or very low concentrations of ILs in non-polar base oil (16-21). Others explored using ILs as neat lubricants (22). ILs with quaternary alkylphosphonium cations and various anions have been investigated for beneficial tribological properties by several groups (23-30). Fully oil-miscible alkylphosphonium-organophosphate ILs were recently developed in our chemistry lab (31-35) and found to effectively decrease friction and wear in BL and ML, as confirmed later by other research groups (36, 37). Additionally, this family of ILs was shown to be non-corrosive and have decomposition temperatures above hydrocarbon base oils and common AW additives, such as zinc dialkyldithiophosphate (ZDDP) (38).

More recently, we discovered remarkable synergistic effects when using a phosphonium-organophosphate IL and ZDDP together as a hybrid AW additive in gas-to-liquid (BO) base oil (39). In this work, we investigated the tribological impact of a combination of IL+ZDDP in a prototype fully-formulated engine oil using both tribological bench tests and full-scale Sequence VIE engine dynamometer tests.

Experimental Methods and Materials

The IL of interest in this work, tetraoctylphosphonium bis(2-ethylhexyl) phosphate ([P888][DEHP]), was synthesized in an organic chemistry lab at ORNL using the method outlined in our previous work (31) with a 93.8% yield and a water content of 0.1%. Oil solubility assessment for this IL was conducted by combining it with 4 cSt base oil (BO) up to a 1:1 ratio and shaking it for one minute. The combination was then placed into a centrifuge for three minutes at 13,000 rpm. No separation was evident. A commercial secondary ZDDP was provided by Lubrizol (OH) with a zinc content of 11.0 wt.% and phosphorous content of 10.0 wt.%. Characterization and chemical structures related to both AW additives in this work are shown in Table 6 and Figure 1 respectively. The viscosities were measured using a Petrolab MINIVIS II viscometer and the standard deviation was controlled to be less than 1%.
Table 6. Characterization of neat anti-wear additives used. Decomposition temperature was measured in air.

<table>
<thead>
<tr>
<th>Anti-Wear Additive</th>
<th>Density (g/cm³)</th>
<th>Decomposition Temp. (ºC)</th>
<th>P Content (wt. %)</th>
<th>Zn Content (wt. %)</th>
<th>KV (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Secondary ZDDP</td>
<td>1.20</td>
<td>189</td>
<td>10</td>
<td>11</td>
<td>407.6</td>
</tr>
<tr>
<td>[P8888][DEHP]</td>
<td>0.86</td>
<td>290</td>
<td>7.7</td>
<td>0</td>
<td>711.4</td>
</tr>
</tbody>
</table>

Figure 17. Structures of tetraoctylphosphonium bis(2-ethylhexyl) phosphate and zinc dialkyldithiophosphate.

The experimental engine oil formulation (EF) in this work is a blend of 4 cSt and 8 cSt BO with a package of additive components provided and blended by Shell Global Solutions (TX) that includes detergent, dispersant, viscosity modifier (VM), anti-oxidant (AO), friction modifier (FM), pour-point depressant (PPD), anti-foam (AF) and AW additives that are detailed in Table 7. The EF is a result of a systematic study of compatibility between the IL and each additive in the package (to be reported in a separate publication). Three lubricants were tested: EF w/o AW, EF + 0.8 wt% ZDDP, and EF + 0.52 wt% IL + 0.4 wt% ZDDP. Lubricants were blended to adhere to International Lubricants Standardization and Approval Committee (ILSAC) GF-5/6 specifications such that phosphorus concentrations do not exceed 800 ppm. The measured phosphorus contents in EF + 0.8 wt% ZDDP, and EF + 0.52 wt% IL + 0.4 wt% ZDDP are 723 and 705 ppm, respectively. It should be noted that EF + 0.52% [P8888][DEHP] + 0.4% ZDDP was blended so each AW additive contributes roughly equal phosphorus concentration. The high temperature-high shear (HTHS) viscosity was measured using a
tapered bearing simulator (Tannas Co.) and the kinematic viscosity (KV) was measured using a CAV-2100 automatic viscometer (Cannon Instrument Co.). The cold-cranking simulator (CCS) viscosity measurement was performed using a G-109-CCS-2100 model viscometer (Cannon Instrument Co.). Table 8 details the density, rheological properties, and concentrations of phosphorus and zinc for each lubricant.

Table 7. Experimental formulation (EF) additive composition. Percentages are on a mass basis.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Det.</th>
<th>Disp.</th>
<th>VM</th>
<th>AO</th>
<th>FM</th>
<th>PPD</th>
<th>AF</th>
<th>AW</th>
<th>ZDDP</th>
<th>[P8888][DEHP]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF w/o AW</td>
<td>3%</td>
<td>2%</td>
<td>2.4%</td>
<td>1%</td>
<td>0.8%</td>
<td>0.3%</td>
<td>0.03%</td>
<td>0%</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>EF + ZDDP</td>
<td>3%</td>
<td>2%</td>
<td>2.4%</td>
<td>1%</td>
<td>0.8%</td>
<td>0.3%</td>
<td>0.03%</td>
<td>0.8%</td>
<td>0%</td>
<td></td>
</tr>
<tr>
<td>EF + IL + ZDDP</td>
<td>3%</td>
<td>2%</td>
<td>2.4%</td>
<td>1%</td>
<td>0.8%</td>
<td>0.3%</td>
<td>0.03%</td>
<td>0.4%</td>
<td>0.52%</td>
<td></td>
</tr>
</tbody>
</table>

A Plint TE77 (Phoenix Tribology Ltd.) tribometer was used to obtain in situ friction data and to produce wear tracks. The machine is arranged to produce an alternating sliding motion against a test material immersed in lubricant. Wear tracks were created on 25.4 mm × 25.4 mm × 3.175 mm CL35 cast iron flats (Metal Samples Company, AL) rubbing against 10 mm AISI 52100 steel balls. Cast iron test specimens were polished with 600-grade silicon carbide abrasive paper with a unidirectional lay at 90º to the sliding axis. Both steel balls and cast iron flats were cleaned with isopropanol and allowed to dry before submersion in lubricant. Each test was performed at 100°C with a normal load of 100 N for an overall sliding distance of 1000 m. Scars were formed under fully sliding conditions with a 10 mm stroke at 10 Hz. The point-contact ensures test conditions completely within the BL regime. Two tests were executed for each lubricant. After wear testing, balls and flats were cleaned in acetone and then isopropanol. Wear measurements were taken with a Veeco (now Bruker, TX) Wyko NT9100 optical interferometer.

Table 8. Density, P and Zn content, viscosity indices and rheological data for each lubricant.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Density (g/cm³)</th>
<th>P Content (ppm)</th>
<th>Zn Content (ppm)</th>
<th>Viscosity Index</th>
<th>HTHS @150 C (cP)</th>
<th>CCS (cP)</th>
<th>KV (cSt) @40°C</th>
<th>KV (cSt) @100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>EF w/o AW</td>
<td>0.84</td>
<td>0</td>
<td>0</td>
<td>155</td>
<td>2.4</td>
<td>6214</td>
<td>38.9</td>
<td>7.3</td>
</tr>
<tr>
<td>EF + 0.8% ZDDP</td>
<td>0.84</td>
<td>723</td>
<td>836</td>
<td>157</td>
<td>2.4</td>
<td>NM</td>
<td>38.5</td>
<td>7.3</td>
</tr>
<tr>
<td>EF + 0.52% IL + 0.4% ZDDP</td>
<td>0.84</td>
<td>705</td>
<td>392</td>
<td>155</td>
<td>2.4</td>
<td>NM</td>
<td>38.8</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Scanning electron microscopy (SEM) and top-surface elemental analysis was completed using a Hitachi S-4800 (Tokyo, Japan) scanning electron microscope with EDAX (NJ) silicon drift detector energy dispersive x-ray spectroscopy (EDS) capability. EDS was completed at a potential of 5.0 kV over a time span of one minute for each measurement. Two sets of Stribeck curves for EF + 0.8% ZDDP, EF + 0.52% IL + 0.4% ZDDP and SAE 20W-30 reference oil without friction modifier or viscosity improver (same baseline oil as Sequence VIE standard) were produced using ball-on-disc rolling-sliding on a PCS Instruments (UK) Mini Traction Machine 2 (MTM). Both the ball and the disc were made of hardened AISI 52100 bearing steel. The ball had a diameter of 19.5 mm and hardness of 64 $R_c$. The disc had a hardness of 62.5 $R_c$. Test parameters for both test sets are given in Table 9 with slide-roll ratio $(\text{SRR}) = \frac{\Delta U}{U_e}$, and $\Delta U = U_1 - U_2$ is the sliding velocity and $U_e = \frac{(U_1 + U_2)}{2}$ is the mean velocity. Arithmetic average surface roughness $(R_a)$ was quantified for both sets of tests using the Wyko NT9100 for the balls and a Dektak XT stylus profilometer for the discs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>MTM Method 1 (Figure 5)</th>
<th>MTM Method 2 (Figure 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed Step Size (mm/s)</td>
<td>250</td>
<td>200</td>
</tr>
<tr>
<td>Number of Scans</td>
<td>20 over entire range per scan</td>
<td>5</td>
</tr>
<tr>
<td>Approx. Time per Step (s)</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Load (N)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Temperature ($^\circ$C)</td>
<td>100</td>
<td>120</td>
</tr>
<tr>
<td>Slide-Roll Ratio (%)</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Fuel economy improvement due to the addition of IL was further assessed using FEI 1 of the impending ILSAC GF-6 Sequence VIE engine dynamometer test at Intertek Automotive Research (TX). The Sequence VIE is an update to the standard Sequence VID test (ASTM D 7589 (40)) with increased fuel economy limits and change of the test engine to a 2012 GM Malibu 3.6 L engine. This standard testing procedure compares a test lubricant’s performance with that of a SAE 20W-30 baseline lubricant over six different stages of engine operation. Each lubricant was first aged over 16 hours of
engine operation at 2250 rpm and 120°C oil temperature. The first six-stage measurements (FEI 1) are then made at the conditions outlined in Table 10.

Table 10. Sequence VIE engine test fuel economy test conditions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
<th>Stage 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torque (N•m)</td>
<td>105.0 ± 0.1</td>
<td>105.0 ± 0.1</td>
<td>105.0 ± 0.1</td>
<td>20.0 ± 0.1</td>
<td>20.0 ± 0.1</td>
<td>40.0 ± 0.1</td>
</tr>
<tr>
<td>Speed (rpm)</td>
<td>2000 ± 5</td>
<td>2000 ± 5</td>
<td>1500 ± 5</td>
<td>695 ± 5</td>
<td>695 ± 5</td>
<td>695 ± 5</td>
</tr>
<tr>
<td>Oil Gallery Temperature (°C)</td>
<td>115 ± 2</td>
<td>65 ± 2</td>
<td>115 ± 2</td>
<td>115 ± 2</td>
<td>35 ± 2</td>
<td>115 ± 2</td>
</tr>
<tr>
<td>Nominal Power (kW)</td>
<td>22.0</td>
<td>22.0</td>
<td>16.5</td>
<td>1.5</td>
<td>1.5</td>
<td>2.9</td>
</tr>
<tr>
<td>Weight Factor</td>
<td>0.300</td>
<td>0.032</td>
<td>0.310</td>
<td>0.174</td>
<td>0.011</td>
<td>0.172</td>
</tr>
<tr>
<td>Lubrication Regime</td>
<td>EHL/HL Dominant</td>
<td>More BL/ML</td>
<td>Some BL/ML</td>
<td>More BL/ML</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Results and Discussion

*Boundary Lubrication Wear and Friction*

Ball-on-flat reciprocating wear tests were performed in the BL regime to compare the wear protection performance between the IL-ZDDP combination and the ZDDP-only lubricant. As shown in Fig. 18, EF + 0.52% [P₈₈₈₈][DEHP] + 0.4% ZDDP produced the lowest wear, at roughly 90% reduction over EF w/o AW and about 9% reduction over EF + 0.8% ZDDP. Each data point represents an average of two repetitions per lubricant. Due to the hardness disparity between the balls and flats, ball wear volumes are on the order of two magnitudes less than flat wear volumes.

Friction results from the reciprocating-sliding bench test are also shown in Figure 18 and represent an averaged performance over two repetitions. The lubricant without AW had the highest steady-state friction coefficient with a final value above 0.10. EF + 0.52% [P₈₈₈₈][DEHP] + 0.4% ZDDP produced the lowest friction coefficient for the first 500 m of sliding, after which, both lubricants containing AW showed a similar friction coefficient around 0.08.
Wear Scar Morphology Examination and Chemical Analysis
The wear scars produced by the two lubricants containing either ZDDP only or ZDDP+IL were examined using SEM for top-surface morphology imaging and EDS for chemical analysis. Figure 19 consists of the SEM micrographs and EDS spectra of the surface pair lubricated with EF + 0.8% ZDDP. The steel ball shows an elliptical wear pattern with relatively evenly dispersed parallel scratch patterns. The worn surfaces appear covered by dark tribofilms with some patchy areas of exposed substrate. EDS spectra provide further evidence of the tribofilms: on a surface lubricated by a ZDDP-containing oil, both mating surfaces show the presence of zinc, phosphorus and sulfur—elements which could only have originated from ZDDP in the lubricant. Increased amounts of these elements on the cast iron flat may indicate a more substantial film with better coverage on this surface compared to that of the ball. Calcium is also present in trace amounts at the surface originating from the detergent in the EF. It has been shown that calcium phosphates form in a separate phase in ZDDP tribofilms whenever calcium-containing detergent is present in the lubricating oil with a detrimental effect on its overall anti-wear characteristic (40).
Figure 20 shows SEM micrographs and EDS spectra of the tribosystem lubricated with EF + 0.52% [P₈₈₈₈][DEHP] + 0.4% ZDDP. The morphologies of these surfaces are visually similar to those shown in Figure 19. The elliptical ball wear scar is slightly smaller than the previous, and both ball scars show oblique wiping marks—artifacts of cleaning. The worn cast iron flat lubricated with EF + 0.52% [P₈₈₈₈][DEHP] + 0.4% ZDDP EDS spectrum shows a marked reduction of zinc and sulfur on the surface and an increased ratio of phosphorous to zinc suggesting both AW constituents are participating in tribofilm growth. Again, a high iron peak on the ball is observed indicating a thinner tribofilm on the steel ball. A similar amount of calcium is present compared to that in Figure 19.

Figure 19. SEM micrographs of worn surfaces lubricated with EF + 0.8% ZDDP. Top: Steel ball surface with corresponding EDS. Bottom: Cast iron flat surface with corresponding EDS.
Figure 20. SEM micrographs of worn surfaces lubricated with EF + 0.52% [P8888][DEHP] + 0.4% ZDDP. Top: Steel ball surfaces with corresponding EDS. Bottom: Cast iron flat surface with corresponding EDS.

**Mini Traction Machine Stribeck Curves**

Having verified synergy between the IL and ZDDP in the formulated oil in boundary wear and friction, we shift attention to friction behavior in a broader survey of lubrication regimes. MTM full-range speed scans generated Stribeck curves are shown in Figure 21, subject the tribosystem to mostly ML with some BL and EHL at a temperature of 100ºC. The SAE 20W-30 reference oil and EF + 0.8% ZDDP display very similar behavior in terms of how friction evolves as each repetition is executed. The first scan for each produced the lowest friction and the last showed the highest. A pattern emerges for these two blends of increasing friction as the tribofilm develops with increasing number of scans though EF + 0.8% ZDDP increases within a narrower band than the 20W-30 baseline oil. An opposite trend was observed for EF + 0.52% IL + 0.4% ZDDP as it, for the most part, showed slightly decreasing friction as the tribofilm develops and the number of scans increases. As a result, the steady-state friction curve, an average of the last 3 of 20 scans, for EF + 0.52% IL + 0.4% ZDDP is substantially lower than the other two lubricants as shown in the summary chart. EF + 0.52% IL + 0.4% ZDDP exhibits the highest advantage over EF + 0.8% ZDDP in the ML regime, but as EHL is approached, the friction curves tend to convergence as expected for lubricants of the same viscosity grade.
The second set of Strubeck scans was completed with the sliding speed varied over three separate ranges as opposed to one scan over a broader range as in the previous tests. As shown in Figure 22, a similar pattern of increased friction as the tribofilm is built is noted here in both the SAE 20W-30 baseline and EF + 0.8% ZDDP except in the third and fastest test range (EHL) in which all lubricants showed minimal variation as more repeats were completed. EF + 0.52% IL + 0.4% ZDDP again showed the lowest friction overall and a reduced friction coefficient as the tribofilm developed. For the average of final three scans, an even more distinct improvement was observed in ML as a result of the IL’s presence.
Figure 22. MTM representative Stribeck curves for ring-on-liner method. Only 5 scans in each speed range are shown for clarity. The summary represents the average of the final three scans for each lubricant.

Surface roughness for balls and discs produced in both MTM Stribeck scan sets is quantified in Table 11. Both methods show excellent correlation with the friction results in Figures 21 and 22. EF + 0.52% IL + 0.4% ZDDP produced smoother surfaces on both balls and discs in each case.
Table 1. Measured arithmetic average surface roughness of balls and discs for each set of MTM results.

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>MTM Data Set 1 (Figure 5)</th>
<th>MTM Data Set 2 (Figure 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Disc, $R_a$ (nm)</td>
<td>Ball, $R_a$ (nm)</td>
</tr>
<tr>
<td>EF + 0.8% ZDDP</td>
<td>22.8 ± 5.4</td>
<td>22.3 ± 0.9</td>
</tr>
<tr>
<td>EF + 0.52% IL + 0.4% ZDDP</td>
<td>10.2 ± 4.1</td>
<td>21.4 ± 1.1</td>
</tr>
</tbody>
</table>

With very encouraging results for the IL-additized formulated oil in the previous boundary wear and friction tests and in both MTM Stribeck scan experiments, we moved forward with full-scale, multi-cylinder, fired engine fuel economy evaluation.

**Sequence VIE Fuel Economy Engine Dynamometer Test (FEI 1)**

Sequence VIE fuel economy engine test FEI 1 results are shown in Table 12. In agreement with bench test friction measurements, EF + 0.52% IL + 0.4% ZDDP demonstrated improved fuel economy in all six stages of the Sequence VIE compared with the baseline by 2.12% and EF + 0.8% ZDDP by 0.25%, respectively. Stages 4, 5 and 6, which constitute 35.7% of the final weighted score, subject the test engine to increased levels of BL and ML regimes; under these conditions there is more pronounced benefit as a result of adding the IL (0.76%, 0.48% and 0.79% for Stages 4, 5 and 6 respectively) compared to ZDDP only. On the other hand, Stages 1, 2 and 3 show smaller IL-induced improvements because EHL and HL are the dominant lubrication regime. These test results indicate that an IL such as $[P_{8888}][DEHP]$ can function in tandem with ZDDP in an anti-wear context and reduce the friction between engine components in the Sequence VIE assessment thus improving fuel economy across a spectrum of engine operating conditions.
Table 12. ASTM D7589 Sequence VIE engine test fuel economy test results

<table>
<thead>
<tr>
<th>Stage</th>
<th>Stage 1</th>
<th>Stage 2</th>
<th>Stage 3</th>
<th>Stage 4</th>
<th>Stage 5</th>
<th>Stage 6</th>
<th>Weighted FEI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lubrication Regime</td>
<td>EHL/HL Dominant</td>
<td>More BL/ML</td>
<td>Some BL/ML</td>
<td>More BL/ML</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EF + 0.8% ZDDP vs. baseline</td>
<td>2.36%</td>
<td>2.84%</td>
<td>1.66%</td>
<td>3.72%</td>
<td>5.98%</td>
<td>3.03%</td>
<td>1.87%</td>
</tr>
<tr>
<td>EF + 0.4% ZDDP + 0.52% IL vs. baseline</td>
<td>2.54%</td>
<td>2.91%</td>
<td>1.77%</td>
<td>4.48%</td>
<td>6.46%</td>
<td>3.81%</td>
<td><strong>2.12%</strong></td>
</tr>
<tr>
<td>IL-induced Improvement</td>
<td>0.17%</td>
<td>0.07%</td>
<td>0.11%</td>
<td>0.76%</td>
<td>0.48%</td>
<td>0.79%</td>
<td>0.25%</td>
</tr>
</tbody>
</table>

**Conclusions**

In this work we have demonstrated the effectiveness of applying an oil-miscible phosphonium-organophosphate IL in conjunction with a secondary ZDDP to fulfill an anti-wear and friction-reducing role as an additive in an experimentally formulated SAE 0W-16 engine oil. Through boundary lubrication bench tests, we have shown that the combination of the IL and ZDDP in formulated oil is more effective than using ZDDP-only. Two types of Stribeck friction curve measurements showed marked IL-induced improvement in the mixed and boundary regimes. The full-scale engine fuel economy dynamometer experiments provided direct evidence of fuel economy improvement as a result of adding IL in formulated oil in a Sequence VIE test with weighted FEI of 2.12% and 0.25% over the reference oil and ZDDP-only formulation, respectively. The strong correlation between the bench and engine test results suggests promising potential for the ionic liquid additive technology.
References


CONCLUSION

In this work, fourteen ILs were assessed as potential next-generation engine oil additives. These ionic liquids were first screened through corrosion, decomposition and oil solubility studies. The remaining five candidates were tribologically tested to determine their effectiveness as anti-wear and friction-reducing engine oil additives. The worn specimens generated by the most effective ionic liquid-containing lubricants were then studied in detail via SEM, EDS, XPS, and TEM, which provided qualitative and quantitative chemical and structural information about the protective tribofilms. Contrary to the common belief that the anion is the only important aspect of an IL in lubrication, we discovered that the cation can serve an important function by promoting solubility in non-polar oils. For phosphonium-organophosphate ILs, six carbons per cation alkyl seems to be the critical number for increased solubility in oils. The overall best performing ionic liquids were [P8888][DEHP] and [N888H][DEHP], which demonstrated significant friction and wear reductions compared to the base oil. Both tribofilms were composed primarily of phosphates and iron oxides. [N888H][DEHP]’s superior performance compared to other ammonium ILs in base oil and formulated oil was attributed to hydrogen bonding, which is not present in the other ammonium ILs. Utilizing the previously discovered synergy between phosphonium-organophosphate ILs and ZDDP, we combined [P8888][DEHP] and ZDDP in an experimentally formulated engine oil. This oil was then placed in a full-scale engine for Sequence VIE fuel economy testing. The ionic liquid-containing oil outperformed the ZDDP-only oil by 0.25% in terms of fuel economy improvement. Substantial IL-induced friction and wear reductions were observed in boundary and mixed lubrication regime bench tests compared to the ZDDP-only oil. This research demonstrates the potential improvements that ILs can bring when applied as a lubricant additive either with or without ZDDP. Optimizations of these ILs with other common engine oil additives would bring additional improvements, and this work provides a foundation through which these improvements can be achieved.
VITA

William Charles Barnhill was born in Franklin, TN to parents William Keith and Alisa Dawn Barnhill in 1989. Upon graduating from Spring Hill High School in 2008, he attended Tennessee Technological University in Cookeville, TN and obtained his Bachelor of Science degree in mechanical engineering. After earning his diploma, he became a research intern working at Oak Ridge National Laboratory in Oak Ridge, TN with a focus in tribology and lubrication science. While performing research at ORNL, he decided to pursue a Master of Science degree in mechanical engineering at the University of Tennessee in Knoxville, TN.