# Using Ionic Liquid Additive to Enhance Lubricating Performance for Low-Viscosity Engine Oil

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## Abstract

Energy efficient lubricants are essential for sustainable transportation and the trend is to develop and implement lower viscosity lubricants with more effective additives. Ionic liquids (ILs) have been reported as candidate additives with superior friction and wear reducing capabilities. Unlike most literature relying on bench-scale testing of simple oil-IL blends, this study produced low-viscosity (SAE 0W-12) fully-formulated engine oils using a phosphonium-organophosphate IL as an antiwear additive and evaluated them in both bench-scale tribological testing and full-scale fired engine dynamometer testing. The experimental formulation containing a combination of ZDDP and IL outperformed the formulations using either ZDDP or IL alone as well as a commercial SAE 0W-20 engine oil in terms of mitigating boundary friction, wear, and contact fatigue-induced micropitting. Racing engine dynamometer tests demonstrated 3-4 °C lower oil temperature, 4-5 ft-lbs higher horsepower output, and 9.9% better fuel economy for the IL-containing SAE 0W-12 experimental oil compared with selected commercial SAE 5W-30 and 0W-20 engine oils.

Keywords: low viscosity engine oil, micropitting, ionic liquid, fully formulated oil, engine test

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## Introduction

Frictional energy dissipation in internal combustion (IC) engines may cost the US nearly 1.3 billion barrels of oil annually. <sup>1</sup>Highly efficient and protective lubricants have been tireless pursued by the automotive industry to improve the fuel economy, enhance reliability, and reduce exhaust emissions for sustainable transportation. An important approach has been developing more effective lubricant additives to allow the reduction of oil viscosity. A commercial engine oil contains multiple categories of additives, including anti-wear, friction modifier, viscosity modifier, antioxidant, detergent, dispersant, etc <sup>2</sup>

Ionic liquids (ILs) are molten salts with melting points at or below 100 °C and possess high thermal stability, low volatility and flammability. <sup>3, 4</sup> After the first introduction of alkylimidazolium tetrafluoroborates IL as neat lubricant in 2001, exploration of ILs has become of interest in lubrication. <sup>5</sup> Since then, researchers have been using ILs as neat lubricant and/or lubricant additives to the base oil<sup>6-8</sup>. A diverse group of cations and anions are being explored. Commonly used IL cations are imidazolium,<sup>9</sup> ammonium,<sup>10, 11</sup> and phosphonium,<sup>12</sup> whereas halogen,<sup>13</sup> borate,<sup>14</sup> phosphate,<sup>15</sup> containing complexes uses as anions. Most of the early research of ILs with non-polar base oil have been limited to addition of very low concentrations of ILs to mitigate the solubility issues with base oil or applied as oil-IL emulsions.<sup>11, 16</sup>

In early 2012, we first reported phosphonium-based ILs that are fully miscible in non-polar hydrocarbon oils like polyalphaolefins and possess excellent anti-wear characteristics when used as lubricant additives <sup>12, 17</sup> Most recently, we discovered a synergistic effect between zinc dialkyldithiophosphates (ZDDP) and phosphonium-organophosphate ILs (e.g., [P<sub>8888</sub>][DEHP]) to reduce both friction and wear more effectively than using either the ZDDP or IL alone.<sup>18</sup> We proposed the formation of a new compound ZOTP (zinc alkyl phosphate alkyldithiophosphate) by anion exchange between the IL and ZDDP. The concentration of ZOTP was found to be significantly higher at the oil interface meaning more anti-wear agents available to react with the contact area for tribofilm formation. The ZDDP and IL synergized tribofilm evidently showed higher contents of zinc and iron phosphates and lower metal sulfides than the conventional ZDDP tribofilm, which was believed to be responsible for the more effective friction and wear reduction.<sup>18</sup> Further, we developed a prototype GF-5 compatible SAE 0W-

16 engine oil by replacing half of the ZDDP content with  $[P_{8888}]$ [DEHP].<sup>19</sup> While the IL+ZDDP formulation demonstrated reduced friction and improved engine fuel economy, little synergy was observed in wear protection, which suggested the lubricant formulation was far from optimized. In addition, the ashless phosphonium-organophosphate ILs have shown less adverse impact effects on the emission catalysts compared to the conventional ZDDP and therefore replacing half the amount of ZDDP potentially reduces the exhaust emissions.<sup>20</sup> Our recent study on the effect of ILs on rolling contact fatigue (RCF) revealed suppression of RFC surface damage and associated vibration noise by introducing a phosphonium-organophosphate IL to the gear oil.<sup>21</sup>

The objective of this research is to continue to develop IL-additized engine oils by further reducing the oil viscosity grade to SAE 0W-12 and optimizing the oil formulation by understanding the compatibilities between the IL+ZDDP combination and other additives including friction modifiers, detergents, dispersants, and anti-oxidants. A couple dozen of GF-6 compatible experimental formulations were designed for using the hybrid IL+ZDDP anti-wear additives and screened using bench-scale tribological testing and analysis. Based on the friction and wear behavior, a top-performing formulation was selected for systematic evaluation and engine dynamometer demonstration as presented below. The IL-additized high-performance low viscosity engine oil expects to enhance the automotive sustainability by (a) improved engine efficiency for less fuel consumption and lower  $CO_2$  emission, (b) improved engine durability and reliability, and (c) extended oil drain intervals.

#### Material and methods

*Lubricants:* A commercially available Mobil 1 SAE 0W-20 engine oil was used as the baseline. A matrix of IL-additized experimental formulations (EFs) in a target viscosity grade of SAE 0W-12, in compliance with International Lubricant Specification Advisory Committee (ILSAC) GF-6 specifications, were prepared by Driven Racing Oil (DRO) company. A secondary ZDDP was used as an antiwear additive and a tetraoctylphophonium bis(2-ethylhexyl) phosphate IL ( $[P_{8888}]$ [DEHP]) were used to replace a half of the ZDDP. The chemical structures of the ZDDP, IL and their abbreviation are presented in Figure 1.

The synthesis of [P<sub>8888</sub>][DEHP] has previously been reported. <sup>22</sup> A variety of friction modifiers, detergents, dispersants, and anti-oxidants were used to test the compatibility with the [P<sub>8888</sub>][DEHP]+ZDDP combination. Three versions of experimental formulation (EF) oils were prepared for comparison by changing the type of the antiwear additives while keeping the rest of the additives the same. (1) EF(ZDDP): containing 0.8 wt% ZDDP as the only antiwear additive (2) EF(IL): containing 1 wt% IL as the sole antiwear additive, and (3) EF(ZDDP+IL): containing 0.4 wt% ZDDP and 0.52 wt%IL as the antiwear additives. Thus, the only difference in the above three EF oils is the antiwear additives while all three had the same phosphorus content of 800 ppm (upper limit defined by ILSAC GF-6). These three-formulations allowed us to distinguish the performance of ZDDP and [P<sub>8888</sub>][DEHP] from their synergistic combination in fully formulated oils (FFOs). Based on screening tribological bench-scale tests, one of the top performing formulations was selected for systematic bench-scale testing study and engine dynamometer testing. The viscosities of these particular EF blends and the commercial baseline were measured using a Petrolab MINIVIS II viscometer and data are shown in Table 1. Additionally, the lubricants' viscosity at 150 °C was calculated using the method similar to the ASTM D341 for comparison, as shown in Supporting Information Table S1.

Lubricant	Viscosity (cP)				
	Temperature (°C)				
	23	40	100		
EF(ZDDP+IL) 0W-12	58.5	28.8	5.6		
EF(ZDDP) 0W-12	59.6	29.2	5.6		
EF(IL) 0W-12	57.0	28.1	5.5		
Mobil 1 0W-20	73.8	35.7	6.9		

Table 1. Viscosities of selected EF oils and a commercial baseline.

*Bench-scale tribological tests*: Boundary lubrication tests were conducted to examine the lubrication behavior of the EFs containing ZDDP, IL and combination of ZDDP+IL. The tribological tests were conducted on a Plint TE-77 tribotester using ball-on-flat reciprocating sliding configuration. An AISI 52100 steel ball was used to slide against a CL35 gray cast iron or AISI 52100 steel flat. All flat surfaces were

polished to a roughness ( $R_a$ ) of 60-80 nm. Tests were carried out at 100 and 150 °C under 100 N at 10 Hz for 20 km of sliding (or ~27 hours of sliding time). Friction force was captured in-situ by measuring the tangential force using a piezoelectric load cell. Wear volumes of both ball and flat specimens were quantified using a 3D optical profiler (Wyko NT9100 white light interferometer) aided by Vision (version 4.10) software. Cylindrical and spherical curvature fittings were applied to flat and ball surfaces in the wear volume calculations, respectively.

*Engine dynamometer tests*: Engine dynamometer tests were conducted at EFI University at Arizona utilizing a GM 6.2 Liter V8 LT1 engine. Four lubricants were tested for comparison: SN SAE 5W-20, Mobil 1 SAE 0W-20, EF(ZDDP) and EF(ZDDP+IL). Engine dynamometer tests were designed to have four running stages of 15 minutes each with different rpm and torque settings as follows: step (1) at 1500 rpm, 140 ft-lbs, (2) at 2900 rpm, 140 ft-lbs, (3) from 1750 to 4500 rpm, 100 ft-lbs, (4) 4500 rpm, 175 ft-lbs.

*Characterization*: A Hitachi S4800 scanning electron microscope (SEM) equipped with energy-dispersive spectroscopy (EDS) was used for the wear scar morphology and elemental composition analysis. Focused ion beam (FIB) milling was used to lift out thin cross-sections of the wear scar of interest using a Hitachi NB5000 FIB equipped with a gallium ion source. A thin carbon layer was deposited onto the wear scar before the FIB process to protect the tribofilm. The tribofilm cross-sections were then analyzed using a JEOL JEM 2200-AC scanning transmission electron microscope (STEM) coupled with a Bruker solid-state EDS detector.



Figure 1. Chemical structures of [P<sub>8888</sub>][DEHP] and ZDDP. R represents an alkyl group and typically range from C4-C12

## **Results and Discussion**

#### **Results of Bench-Scale Tribological Tests**

The friction and wear performance of three EF versions are shown in Figure 2. However, individual (a) friction traces (b) wear track (c) wear volumes can be found in the Supporting Information section of Figure S1, Figure S2, and Table S2, respectively. The test of EF(ZDDP) showed unstable friction behavior (with random frictional spikes), with COF ranging from 0.05 to 0.09. The EF(IL) showed a relatively higher, but more stable COF with an initial friction spike to COF of 0.11 and then dropdown before increasing to a final COF of 0.10-0.12. The EF oil contains both IL and ZDDP as antiwear additives, EF(ZDDP+IL), exhibited low and stable friction behavior, with COF stabilized at around 0.05 after the initial 1 km of running-in for the rest of 19 km of sliding. The EF(ZDDP+IL) also had an excellent performance in wear protection with the wear volume ( $4.3 \times 10^7 \mu m^3$ ) reduced by nearly half, compared with EF(ZDDP) or EF(IL). This observation confirmed the synergetic interaction between ZDDP and IL in the EF oil.

In addition, it was a little surprising to observe micropitting on the cast iron flat lubricated by EF(ZDDP), as shown in dark pits on Figure 2c(iii). Although micropitting is common in rolling and rolling/sliding contacts, it was rarely reported for pure sliding. During the 20 km sliding in this study, the wear track on the cast iron surface experienced 2 million cycles of repeated contact. This had evidently led to localized contact fatigue failure when lubricated by EF(ZDDP), but not for the lubricants containing IL. This suggests that the tribofilm composition significantly influences the mechanical properties of the contact surface zone.



**Figure 2.** Friction traces (a) and wear volumes of the cast iron flats (b) lubricated by EF(ZDDP), EF(IL), and EF(ZDDP+IL) at 100 °C. (c) Wear scar morphology of the cast iron flat lubricated by (i) EF(ZDDP+IL), (ii) EF(ZDDP), and (iii) EF(IL) at 100 °C.

Mobil 1 SAE 0W-20 was used as a baseline to compare with EF(ZDDP+IL) to lubricate the steel-cast iron contact at both 100 and 150 °C. The friction coefficient for Mobil 1 0W-20 at 100 °C oscillate between 0.047-0.080 , whereas the COF at 150 °C fluctuated in a range of 0.07-0.11 at 150 °C, as shown in Figure 3a and Figure S3. The EF(ZDDP+IL) performed well with COFs around 0.05 at both 100 and 150°C, about 30% friction reduction from the Mobil 1. In average, 50% better wear protection was obtained for EF(ZDDP+IL) compared with the commercial baseline at 100 °C, but the improvement was much less at 150 °C.

It should be noted that the commercial Mobil 1 0W-20 engine oil produced micropitting on the cast iron wear tracks at both 100 (2 out of three samples) and 150 °C (1 out of 2 samples), as shown in Figures 3c(ii) and (iv). In contrast, little to no micropitting damage was observed when lubricated by the EF(ZDDP+IL) at both temperatures. The detailed results of individual tests are available in Figure S3, Figure S4 and Table S3 of the Supporting Information section.



Figure 3. Friction traces (a) and wear volumes of the cast iron flats (b) lubricated by Mobil 1 0W-20 and EF (ZDDP+IL) at 100 and 150 °C. (c) Wear scar morphology of the cast iron flat lubricated by (i) EF(ZDDP+IL), (ii) Mobil 1 0W-20 at 100 °C, (iii) EF(ZDDP+IL) at 150 °C, and (iv) Mobil 1 0W-20 at 150 °C.

Figure 4 shows the worn surfaces of the cast iron flats lubricated with EF(ZDDP+IL), EF(ZDDP), EF(IL), and Mobil 1 0W-20. While the worn surfaces lubricated with Mobil 1 0W-20 and EF(ZDDP) clearly had micropitting, the EF(IL) and EF(ZDDP+IL) were able to mitigate the micropitting.

The worn surface of cast iron flat lubricated by the Mobil 1 engine oil contains Mg, Zn, P, and S/Mo based on EDS analysis. Mo is likely derived from a Mo-containing friction modifier. Mg and Ca should be originated from the detergent(s) and Zn, P and S are believed to be supplied by ZDDP. The worn surface lubricated by the EF(IL) did not contain Zn (as expected) or Mg (suggesting exclusion of Mg-based detergent). The EF(ZDDP) and EF(ZDDP+IL) produced wear scars appeared to have similar compositions except the ratio of P to S/Mo being higher for EF(ZDDP+IL). This agrees with our previous report that the tribofilm formed by this synergistic ZDDP+IL pair held a relatively higher P/S ratio.<sup>18</sup>



Figure 4. Wear scar SEM images and EDS spectra of the cast iron flats lubricated by (a) EF(ZDDP+IL),(b) EF(ZDDP), (c) EF(IL), and (d) Mobil 1 0W-20.

Figure 5 presents the cross-sectional STEM images and EDS elemental maps of the cast iron flats lubricated by EF(ZDDP+IL) and Mobil 1 0W-20 at 100 °C. The tribofilm generated by EF(ZDDP+IL) was as thick as 450 nm, as shown in Figure 5a. In contrast, a much thinner tribofilm (up to 50 nm) was produced

by the Mobil 1, as shown in Figure 5b. The EDS elemental maps show the distribution of Zn, S, P and Ca in the tribofilms. The EF(ZDDP+IL) tribofilm appeared to have higher contents of P and Zn but lower content of S compared with the Mobil 1 tribofilm, which is line with the observations for ZDDP+IL versus ZDDP alone as reported previously<sup>18</sup>.

The P compounds in tribofilm could be attributed to the ZDDP or IL. Zn content was clearly provided by ZDDP. The S could be contributed by ZDDP or other additives such as detergent or friction modifier. Most S compounds were found to be deposited at the bottom of the tribofilm when lubricated with Mobil 1, while the EF(ZDDP+IL) tribofilm showed iron-sulfur clusters in both top and bottom layers. Ca was likely associated with the detergent in additive package and evidently actively participated in the tribofilm formation.<sup>23-25</sup> The EF(ZDDP+IL) clearly produced a significantly thicker tribofilm with a higher ratio of P/S than the commercial Mobil 1 oil, which is believed to be responsible for its superior lubricating performance.





**Figure 5**. Cross-sectional STEM images and EDS elemental maps of the tribofilms on the cast iron flats lubricated by (a) EF(ZDDP+IL) and (b) Mobil 1 0W-20 at 100 °C for 20 km.

Is the superior lubricating performance of this EF(ZDDP+IL) low-viscosity oil applicable for other contact materials such as steel on steel? To answer the question, self-mated AISI 52100 bearing steel ballon-flat tests were conducted in lubrication of EF(ZDDP+IL) in the same testing conditions as those for steel against cast iron as described above (100 N load, 10 Hz, 10 mm stroke, 100 °C, and 20 km sliding distance). The friction and wear results are shown in Figure 6. For reference, friction traces, wear tracks, and wear volumes of each test were included in the supporting information section of Figure S5, Figure S6, and Table S4, respectively. The test lubricated with the Mobil 1 had an initial high friction stage but gradually dropped down to 0.07 after 7.5 km sliding and maintained at that level for the rest of the test. The EF(ZDDP+IL) showed a more stable COF of ~0.07 throughout the 20 km sliding. The EF(ZDDP+IL) also performed well in wear protection with 40% lower wear than that of the Mobil 1 (refer to Figure 6b). The Mobil 1 0W-20 oil produced moderate micropitting on both the steel ball and flat, as indicated by dark color patches in Figure 6c(i). While a few isolated micro-pits were observed on the ball and flat worn surfaces lubricated by the EF(ZDDP+IL) [Figure 6c(ii)], but the severity (size and number of pits) was significantly less than that of Mobil 1, which presumably is correlated to the less wear losses.



**Figure 6.** Friction traces (a) and wear volumes (b) of self-mate AISI 52100 contacts lubricated with EF(ZDDP+IL) and Mobil 1 0W-20 oils at 100 °C for 20 km. (c) Wear scars morphology of the AISI 52100 steel ball and flat lubricated with (i) Mobil 1 0W-20 and (ii) EF(ZDDP+IL), at 100 °C.

## Results of engine dynamometer tests

Encouraged by the superior friction and wear performance in the bench-scale tribological tests, the EF(ZDDP+IL) was further evaluated using a fired multi-cylinder engine dynamometer test at EFI University utilizing a GM 6.2 Liter V8 LT1 engine. Results are shown in Table 2, including oil temperature, torque output, and fuel consumption. It seems that using the IL helped to maintain the oil temperature 3-4 °C lower and improved the horsepower output by 4-5 ft-lbs compared with EF(ZDDP) and other two commercial baseline engine oils, Mobil 1 SAE 0W-20 and SN SAE 5W-30. The EF(ZDDP), because of its lower viscosity, showed a fuel economy improvement (FEI) of 4.4% in comparison to the commercial SN SAE 5W-30 oil. The addition of IL (replacing a half amount of ZDDP) further improved the FEI by another 5.5%, which resulted in a total FEI 9.9%. The additional 5.5% FEI correlates well with the reduced boundary friction as observed in the bench-scale tribological testing (see Figures 2 and 3). Please note that this dramatic FEI was achieved under harsh engine operating conditions, designed for racing cars. In such operations, boundary and mixed lubrication accounts for a significant share and the synergistic IL+ZDDP combination had fundamentally proven to reduce the friction at boundary and mixed regimes most effectively. Analysis of the four lubricant oils after the engine tests showed similar Fe and Cu counts in the used EF(ZDDP+IL) to those in the used EF(ZDDP) and Mobil 1 and less than those in the used SN SAE 5W-30, implying satisfactory wear protection for piston-cylinder assembly. The Al counts presented a moderate increase for a reduced oil viscosity, from 1 for SAE 5W-30 to 2 for SAE 0W-20 then to 3 for SAE 0W-12, corresponding to increased boundary lubrication at the connecting rod's Al alloy sleeve bearings, as expected.

Table 2.	Engine	dynamomete	er test ar	id post	oil a	nalysis	results	comparison	for 1	EFs and	l comme	rcial	base
line.													

Lubricant	Lubricant	Torque	Fuel	FEI vs SN	Met	Metal in used	
	temp.(°C)	(±1 ft-lbs)	consumption	5W-30	oil (±1ppm)		
					Fe	Cu	AI
SN SAE 5W-30	121	n/a	31.85	-	5	6	1
Mobil 1 SAE 0W-20	121	506	n/a	n/a	3	0	2
EF(ZDDP) (SAE 0W-12)	120	505	30.4	4.4%	2	1	3
EF(ZDDP+IL) (SAE 0W-12)	117	510	28.7	9.9%	3	1	3

## **Discussion of Micropitting in Pure Sliding**

Micropitting is a sign of contact fatigue and commonly observed on rolling contacts, e.g., gear teeth.<sup>26</sup> There are several factors that influence the crack initiation and propagation, such as material composition, surface roughness, load, temperature, relative velocity, lubricant viscosity and chemistry, and slide-to-roll ratio. It was reported that the applied load has a major effect on micropitting initiation, whereas speed and slide-to-roll ratio have dominant effects on micropitting propagation.<sup>27</sup> To the best of our knowledge, this study is the first time reporting contact fatigue micropitting produced in pure sliding. During the 20 km sliding (significantly longer than the typical range of sliding distances of 100-1000 m in the literature), each location of the wear track on the cast iron flat experienced 2 million cycles of contact under a contact stress of as high as 1.68 GPa (Hertzian contact pressure) at the beginning of the test and gradually decreasing to several tens to a few hundred MPa (depending on the wear scar size) by the end of the test. As shown in Figures 2c,3c and 4, microcracks seemed to originate from the boundaries between iron grains and graphite flakes and multiple cracks coalesced to form micropits.

The better resistance to micropitting by the IL-containing lubricants, EF(IL) and EF(ZDDP+IL), than EF(ZDDP) and Mobile 1, as shown in Figures 3, 4, and 6, suggests that the tribofilm composition significantly influences the mechanical properties of the contact surface zone. Literature<sup>26-29</sup> reported both beneficial and detrimental effects for antiwear additives on micropitting. Some observed enhanced

micropitting resistance by additives containing sulfur and phosphorus compounds while others showed adverse effects.<sup>28,29</sup> EDS composition analysis in Figures 4 and 5 showed more sulfur compounds in the tribofilms when lubricated by EF(ZDDP) and Mobil 1 than in the tribofilms formed by the EF(IL) and EF(ZDDP+IL). Sulfur diffusion through grain boundaries are known to cause surface embrittlement and ZDDP produced sulfur-rich tribofilm had been found to be prone to fracture and delamination.<sup>30</sup> On the other hand, the EF(ZDDP+IL) tribofilm contained more phosphorus and less sulfur, as shown in Figures 4 and 5.

The EF(ZDDP+IL) tribofilm's good resistance to contact fatigue micropitting may be attributed to two factors: (i) high content of phosphates and low content of sulfides and (ii) higher thickness (450 nm) to provide a better cushion upon contact. Phosphorus compounds are known to be wear-resistant whereas sulfur compounds could have a detrimental effect on the tribofilm.<sup>30, 31</sup>The synergistic interaction between ZDDP and IL brings a higher concentration of triboactive elements to the solid-oil interface to form a thick zinc and phosphorus rich but sulfur-less tribofilm. Mechanical properties of the ZDDP, IL and (ZDDP+IL) generated tribofilms were previously determined by nanoindentation.<sup>32</sup> The (ZDDP+IL) tribofilm was found to have a substantially lower ratio of hardness to stiffness squared than either the ZDDP or IL tribofilm,<sup>18,32</sup> which may be attributed to its higher phosphate content and polymerization level.<sup>30</sup> The lower ratio of hardness to stiffness squared of the (ZDDP+ IL) tribofilm would allow the surface to shear and deform more easily<sup>33</sup> (less brittle), and could absorb more energy upon surface asperity impact (cushion effect) to reduce microfracture or micropitting.

#### Conclusions

Experimental formulations of ILSAC GF-6 compatible SAE 0W-12 engine oils were produced using a ZDDP alone, a phosphonium-phosphate IL alone, and combination of ZDDP+IL as the antiwear additives. In bench-scale tribological testing, the EF oil containing both the ZDDP and IL was found to be more

effective in friction and wear reductions as well as resistance to contact fatigue-induced micropitting compared with the EFs using either the ZDDP or IL alone. The EF(ZDDP+IL) also outperformed the commercial Mobil 1 0W-20 engine oil for both steel-cast iron and steel-steel contacts. Tribofilm characterization showed formation of a thicker protective tribofilm with a higher P/S ratio when lubricated by EF(ZDDP+IL) compared with the tribofilms produced by the commercial baseline oil. Engine dynamometer testing further demonstrated 3-4 °C lower oil temperature, 4-5 ft-lbs higher horsepower output, and 9.9% better fuel economy for the EF(ZDDP+IL) SAE 0W-12 oil compared with commercial SN SAE 5W-30 and Mobil 1 SAE 0W-20 engine oils. The improved fuel economy and higher horsepower make the IL-enhanced low-viscosity lubricant technology promising in sustainable transportation.

## **ASSOCIATED CONTENT**

## **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/ Friction traces, wear volumes and wear scar images of the cast iron flats, AISI 52100 flats and AISI 52100 balls surfaces

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# REFERENCES

- 1. Holmberg, K.; Andersson, P.; Erdemir, A., Global energy consumption due to friction in passenger cars. *Tribology International* **2012**, *47*, 221-234, doi:10.1016/j.triboint.2011.11.022
- 2. Rudnick, L.R. (2003). Lubricant Additives: Chemistry and Applications, CRC Press.
- 3. Zhigang, L.; Biaohua, C.; Yoon-Mo,K.; Douglas, M.,Introduction: Ionic Liquids. *Chemical Reviews* **2017**, *117* (10), 6633-6635, doi:10.1021/acs.chemrev.7b00246
- 4. Wang, B.; Qin, L.; Mu, T.; Xue, Z.; Gao, G., Are Ionic Liquids Chemically Stable? *Chemical Reviews* **2017**, *117* (10), 7113-7131. doi:10.1021/acs.chemrev.6b00594
- 5. Ye, C.; Liu, W.; Chen, Y.; Yu, L., Room-temperature ionic liquids: a novel versatile lubricant. *Chemical Communications* **2001**, (21), 2244-2245. doi:10.1039/B106935G
- 6. Bermúdez, M.-D.; Jiménez, A.-E.; Sanes, J.; Carrión, F.-J., Ionic Liquids as Advanced Lubricant Fluids. *Molecules* **2009**, *14* (8), 2888-2908. doi:10.3390/molecules14082888
- 7. Zhou, F.; Liang, Y.; Liu, W., Ionic liquid lubricants: designed chemistry for engineering applications. *Chemical Society Reviews* **2009**, *38* (9), 2590-2599, doi:10.1039/B817899M
- 8. Jiménez, A. E.; Bermúdez, M. D.; Iglesias, P.; Carrión, F. J.; Martínez-Nicolás, G., 1-N-alkyl -3methylimidazolium ionic liquids as neat lubricants and lubricant additives in steel–aluminium contacts. *Wear* **2006**, *260* (7), 766-782, doi:10.1016/j.wear.2005.04.016
- 9. Phillips, B. S.; Zabinski, J. S., Ionic Liquid Lubrication Effects on Ceramics in a Water Environment. *Tribology Letters* **2004**, *17* (3), 533-541, doi:10.1023/B:TRIL.0000044501.64351.68
- Qu, J.; Blau, P. J.; Dai, S.; Luo, H.; Meyer, H. M.; Truhan, J. J., Tribological characteristics of aluminum alloys sliding against steel lubricated by ammonium and imidazolium ionic liquids. *Wear* 2009, 267 (5), 1226-1231. doi:10.1016/j.wear.2008.12.038
- 11. Qu, J.; Truhan, J. J.; Dai, S.; Luo, H.; Blau, P. J., Ionic liquids with ammonium cations as lubricants or additives. *Tribology Letters* **2006**, *22* (3), 207-214, doi:10.1007/s11249-006-9081-0

- Yu, B.; Bansal, D. G.; Qu, J.; Sun, X.; Luo, H.; Dai, S.; Blau, P. J.; Bunting, B. G.; Mordukhovich, G.; Smolenski, D. J., Oil-miscible and non-corrosive phosphonium-based ionic liquids as candidate lubricant additives. *Wear* 2012, 289, 58-64, doi:10.1016/j.wear.2012.04.015
- Ma, K.; Somashekhar, B. S.; Nagana Gowda, G. A.; Khetrapal, C. L.; Weiss, R. G., Induced Amphotropic and Thermotropic Ionic Liquid Crystallinity in Phosphonium Halides: "Lubrication" by Hydroxyl Groups. *Langmuir* 2008, 24 (6), 2746-2758, doi:10.1021/la703175x
- 14. Chen, Y. M.; Zeng, Z. X.; Yang, S. R.; Zhang, J. Y., The tribological performance of BCN films under ionic liquids lubrication. *Diamond and Related Materials* **2009**, *18* (1), 20-26, doi:10.1016/j.diamond.2008.07.023
- 15. Zhou, Y.; Dyck, J.; Graham, T. W.; Luo, H.; Leonard, D. N.; Qu, J., Ionic Liquids Composed of Phosphonium Cations and Organophosphate, Carboxylate, and Sulfonate Anions as Lubricant Antiwear Additives. *Langmuir* **2014**, *30* (44), 13301-13311, doi:10.1021/la503236
- 16. Schneider, A.; Brenner, J.; Tomastik, C.; Franek, F., Capacity of selected ionic liquids as alternative EP/AW additive. *Lubrication Science* **2010**, *22* (6-7), 215-223, doi:10.1002/ls.120
- Qu, J.; Bansal, D. G.; Yu, B.; Howe, J. Y.; Luo, H.; Dai, S.; Li, H.; Blau, P. J.; Bunting, B. G.; Mordukhovich, G.; Smolenski, D. J., Antiwear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive. *ACS Applied Materials & Interfaces* 2012, 4 (2), 997-1002, doi:10.1021/am201646k
- Qu, J.; Barnhill, W. C.; Luo, H.; Meyer III, H. M.; Leonard, D. N.; Landauer, A. K.; Kheireddin, B.; Gao, H.; Papke, B. L.; Dai, S., Synergistic Effects Between Phosphonium-Alkylphosphate Ionic Liquids and Zinc Dialkyldithiophosphate (ZDDP) as Lubricant Additives. *Advanced Materials* 2015, 27 (32), 4767-4774, doi:10.1002/adma.201502037
- Barnhill, W. C.; Gao, H.; Kheireddin, B.; Papke, B. L.; Luo, H.; West, B. H.; Qu, J., 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. *Frontiers in Mechanical Engineering* 2015, 1 (12),1-8, doi:10.3389/fmech.2015.00012
- Kim, D.; Toops, T. J.; Nguyen, K.; Brookshear, D. W.; Lance, M. J.; Qu, J., Impact of Lubricant Oil Additives on the Performance of Pd-Based Three-Way Catalysts. *Emission Control Science and Technology* 2019, doi:10.1007/s40825-019-00138-x
- Stump, B. C.; Zhou, Y.; Luo, H.; Leonard, D. N.; Viola, M. B.; Qu, J., New Functionality of Ionic Liquids as Lubricant Additives: Mitigating Rolling Contact Fatigue. ACS Applied Materials & Interfaces 2019, 11 (33), 30484-30492, doi:10.1021/acsami.9b10001
- 22. Barnhill, W. C.; Qu, J.; Luo, H.; Meyer, H. M.; Ma, C.; Chi, M.; Papke, B. L., Phosphonium-Organophosphate Ionic Liquids as Lubricant Additives: Effects of Cation Structure on Physicochemical and Tribological Characteristics. *ACS Applied Materials & Interfaces* **2014**, *6* (24), 22585-22593, doi:10.1021/am506702u
- 23. Najman, M.; Kasrai, M.; Michael Bancroft, G.; Davidson, R., Combination of ashless antiwear additives with metallic detergents: interactions with neutral and overbased calcium sulfonates. *Tribology International* **2006**, *39* (4), 342-355, doi:10.1016/j.triboint.2005.02.014
- 24. Thersleff, T.; Jenei, I. Z.; Budnyk, S.; Dörr, N.; Slabon, A., Soot Nanoparticles Generated from Tribofilm Decomposition under Real Engine Conditions for Identifying Lubricant Hazards. *ACS Applied Nano Materials* **2021**, *4* (1), 220-228, doi:10.1021/acsanm.0c02536
- Pereira, G.; Lachenwitzer, A.; Kasrai, M.; Bancroft, G. M.; Norton, P. R.; Abrecht, M.; Gilbert, P. U. P. A.; Regier, T.; Blyth, R. I. R.; Thompson, J., Chemical and mechanical analysis of tribofilms from fully formulated oils Part 1 Films on 52100 steel. *Tribology Materials, Surfaces & Interfaces* 2007, 1 (1), 48-61, doi:10.1179/175158407X189293
- Stump, B. C.; Zhou, Y.; Viola, M. B.; Xu, H.; Parten, R. J.; Qu, J., A rolling-sliding bench test for investigating rear axle lubrication. *Tribology International* 2018, *121*, 450-459, doi:10.1016/j.triboint.2018.01.058
- 27. Oila, A.; Bull, S. J., Assessment of the factors influencing micropitting in rolling/sliding contacts. *Wear* **2005**, *258* (10), 1510-1524, doi:10.1016/j.wear.2004.10.012

- Brechot, P.; Cardis, A. B.; Murphy, W. R.; Theissen, J., Micropitting resistant industrial gear oils with balanced performance. *Industrial Lubrication and Tribology* 2000, *52* (3), 125-136, doi:10.1108/00368790010371762
- 29. Winter, H.; Oster, P. Influence of the Lubricant on Pitting and Micro Pitting (Grey Staining, Frosted Areas) Resistance of Case Carburized Gears: Test Procedures; American Gear Manufacturers Association: Alexandria, VI, USA, 1987
- 30. Zhou, Y.; Weber, J.; Viola, M. B.; Qu, J., Is more always better? Tribofilm evolution and tribological behavior impacted by the concentration of ZDDP, ionic liquid, and ZDDP-Ionic liquid combination. Wear 2019, 432-433, 202951,1-11, doi:10.1016/j.wear.2019.202951
- 31. Kumara, C.; Meyer III, H. M.; Qu, J., Material-Dependent Antagonistic Effects between Soot and ZDDP. Advanced Materials Interfaces 2020, 7 (6), 1901956, doi:10.1002/admi.201901956
- 32. Landauer, A. K.; Barnhill, W. C.; Qu, J., Correlating mechanical properties and anti-wear performance of tribofilms formed by ionic liquids, ZDDP and their combinations. Wear 2016, 354-355, 78-82, doi:10.1016/j.wear.2016.03.003
- 33. Joslin, D. L.; Oliver, W. C., A new method for analyzing data from continuous depth-sensing microindentation tests. *Journal of Materials Research* **1990**, 5 (1), 123-126, doi:10.1557/JMR.1990.0123

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**Synopsis**: Low viscosity automotive engine oil were formulated by replacing a half the amount of ZDDP with ionic liquid to improve the engine performance.