Interactions between ZDDP and an oil-soluble Ionic Liquid additive

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Abstract

Zinc dialkyldithiophosphates (ZDDP) and a P-based ionic liquid (IL) were added in a polyalphaolefin base oil (PAO). Their tribological performance in steel-steel contacts in the boundary (BL) and “starved” elastohydrodynamic (sEHL) lubrication conditions were investigated.

In BL conditions, IL reduces friction at 40°C. It reduces both friction and wear at 100°C. ZDDP reduces wear but has relatively high friction at both temperatures. Synergy between IL and ZDDP is observed only at 100°C, due to the generation of a smoother worn surface and potentially a thicker boundary film.

In sEHL conditions at room temperature, ZDDP, IL and their mixture change the inlet condition and increase lubricant film thickness. No synergy between the two additives is observed.

Keywords Oil-soluble Ionic Liquid; “Starved” EHL; Film formation property; ZDDP, Synergistic effect

1 Introduction

Zinc dialkyldithiophosphates (ZDDPs) are low cost lubricant additives which are widely used since 1940s. They work very well as anti-oxidants, anti-wear additives in extreme pressure (EP additives), and corrosion inhibitors [1,2]. ZDDPs, however, contain phosphorus and sulphur. Significant restrictions on the sulfur and phosphorus content in an engine oil to as low as 0.6% and to within 0.08%, respectively [3] impacts directly on the amount of ZDDPs that engine oils can contain. As a result, alternatives to ZDDPs are urgently needed [4]. One possible alternative is ionic liquids (IL). IL are molten salt at room temperature. Many ILs [5-8] have shown excellent tribological performance as neat lubricants and as additives. Since the development of phosphonium-based ILs which are miscible with non-polar hydrocarbon oils and are non-corrosive to either ferrous or aluminum alloys [9, 10], the potential of oil-miscible ILs as neat lubricants [11, 12, 13] or lubricant additives have attracted extensive attention [14-25]. Lately, several novel oil-soluble ILs in polyalphaolefin (PAO) base oils were developed with excellent tribological performance as multi-functional additives [17, 18]. In the boundary lubrication (BL) regime, many IL additives [15-17, 6, 20] have been shown to be as effective as ZDDP in preventing scuffing, while demonstrating better performance in reducing friction. Mixtures of ILs and ZDDP outperformed their individual constituent alone in PAO [15, 16, 18-21].

Performance of ZDDP or IL can be ascribed to the generation of physically adsorbed films, which may then become chemically reacted films [10, 18, 23]. Properties of tribofilms depend on many factors including shear stress, applied compressive stress, slide-roll ratio and temperature [1, 26-28]. It was widely accepted that ZDDP formed a thick glassy tribofilm which provides wear protection. Thinner IL tribofilms, due to the polar nature of ILs, are believed to have a layered structure. They have low shear strength and prevent direct contact between two contact surfaces [18-24]. This has led to IL tribofilms having better anti-friction property than ZDDP tribofilms. The synergy between IL and ZDDP was attributed to the resulting hybrid tribofilm. Compared to ZDDP tribofilm, the hybrid film has substantially higher contents of zinc and iron phosphates but much less metal oxides and sulfur compounds [15, 22-25]. Note that synergies between IL and other additives have been observed and is chemistry dependent [29, 30].

Recently ZDDP tribofilms have been shown to form in the elastohydrodynamic lubrication (EHL) regime, i.e. under full film conditions [31, 32]. The ZDDP tribofilm has been suggested to hinder

lubricant entrainment into the contact, leading to a reduced EHD film thickness compared to ZDDP-free lubricants [33]. Few research examined properties of neat IL or IL-containing lubricant films in mixed lubrication or EHL regimes [14, 33-37]. The evidence of the existence of IL films in the EHL regime is inconclusive since they may only adsorb weakly on surfaces. Typical surface analytical techniques such as XPS, EDS, TOF-SIMS usually require rigorous cleaning of supernatant liquids. This may remove weakly adhered IL tribofilm films, render their examination difficult. Nevertheless, the use of IL has been shown to impact on the performance of lubricants in the EHL regime. Arora and Cann [34] measured lubricant film thicknesses of 5 neat IL lubricants in the EHL regime using optical interference intensity method. They found that 1-butyl-3-methyl fluids gave anomalously thick, time-dependent films at low speeds (< 0.3 m/s), which they attributed to the formation of shear-induced aggregates in bulk IL liquids. Xiao *et al.* [35] show that long alkyl chain ILs can form thicker films than silicone oils of similar viscosities. This is likely due to IL supramolecular aggregates formed in rubbing contacts, increasing effective viscosities of ionic liquids [32]. On the other hand, P-based IL additives in a group III mineral oil did not affect lubricant film thickness in full film lubrication regime even though improvements in friction reduction were obtained under mixed (ML) and boundary lubrication (BL) regimes at SRR of 50% [14]. Similarly, IL additives generated by lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) in polyethylene glycol in situ only mildly affected friction and film thickness in the EHL regime but reduced friction and metal wear in the ML regime [37].

In the EHL regime, sufficient lubricant is entrained into the contact such that a thin lubricant film fully separates the two rubbing surfaces. The thickness of this lubricant film depends on test conditions and properties of lubricants and rubbing surfaces. A starved elastohydrodynamic lubrication (sEHL) condition refers to the situation when lubricant film instability and film collapse are observed. From the literature, ILs can reduce friction and wear in the mixed and boundary lubrication regimes, without reducing lubricant film thickness in the EHL regime. Thus, IL additives may be beneficial in situations where insufficient lubricant in the contact area may occur intermittently due to fluctuations in operating conditions, leading to the “starved” elastohydrodynamic lubrication (sEHL) regime [38]. Using surface-active additives such as ILs may affect the surface conditions, and thus the entrainment of the lubricant and conditions in which starved EHL occurs. Note that the performance of IL and potential synergies between ZDDP and ILs are base oil dependent. In this study, polyalphaolefin (PAO), a synthetic oil, was the model

base oil. ZDDP and a P-based IL (IL) were used as lubricant additives. Their performance in the boundary and sEHL regimes were investigated. Specifically, we ask the following questions:

1. Does synergy exist between ZDDP and IL in PAO in the BL and sEHL conditions?
2. If so, how does the use of IL affect sEHL film thickness?

2 Materials and Methods

2.1 Test lubricants

PAO4 (PAO) was obtained from Exxon Mobil. A commercial ZDDP additive ZDDP-T202 and an oil-soluble IL (trioctylhexadecyl phosphonium oleate) were used as lubricant additives. ZDDP was purchased from Jinan Saiya Company. IL was synthesized by following the procedures in [10, 39]. 1-Bromohexadecane and sodium oleate used to synthesize the IL were purchased from Energy Chemical. All other chemicals used in the synthesis were analytical grade reagents purchased from J&K Scientific Ltd and were used as received. The molecular structures of PAO, ZDDP-T202 and the synthesized IL are illustrated in Figure 1. Note that ZDDP and our IL contain 8.65 and 3.91 wt.% of P, respectively, and 17.9 wt.% and 0 wt.% of S, respectively.

Figure 1 Molecular structures of (a) PAO, (b) ZDDP and (c) quaternary phosphonium ionic liquid

Four test lubricants were used (see Table 1). They were prepared by mixing the right amount of additives into the base oil with a magnetic stirrer at 40 °C ~ 50 °C for 4 h, followed by sonication for 1 hour at room temperature. All solutions were tested within 72 h after their preparations. Refractive indices of all lubricants at 20 °C were 1.46, as measured by an Abbe refractometer.

Dynamic viscosities and densities were measured using an Anton Paar Modular Compact Rheometer MCR 302 with a shear rate of 1-1000 s⁻¹ at 20 °C, 40 °C and 100 °C. Viscosity index (VI), which measures the sensitivity of the viscosity of a fluid to temperature, was determined according to the ASTM D2270-04 standard. Note that the higher the VI of a fluid, the less the effect of temperature on its viscosity. Table 1 shows that the addition of 1 wt.% additives has minimal effect on the refractive index, viscosity and VI of the base oil.

Lubricants (Compositions wt.%)	Dynamic Viscosity (m Pa·s)			VI	Density at 20 °C (g/cm ³)	Refractive index
	20 °C	40 °C	100 °C			
PAO4	32.2	14.3	3.1	182	0.81	1.46
PAO4 + 1 % ZDDP	34.4	14.8	3.2	188	0.81	1.46
PAO4 + 0.5 % IL + 0.5 % ZDDP	33.8	14.5	3.2	189	0.81	1.46
PAO4 + 1 % IL	28.3	12.7	3.0	189	0.81	1.46

Table. 1 The dynamic viscosity, density and viscosity index of lubricants used in the tests

2.2 Friction and scuffing tests in the boundary lubrication regime

Friction and wear tests were conducted with a commercial four-ball tester (Jinan Shunmao Test Instrument Co, Ltd, China), with a rotating ball pressed against three stationary balls, schematically shown in Figure 2a. The applied load was 196 N, giving an average Hertz contact pressure 2.78 GPa. Test balls were made of bearing steel GCr15. They had a nominal diameter of 12.7 mm, and a hardness of HRC 64. 10 mL of a test lubricant was used in each test such that the balls were fully submerged in the lubricant. The top ball rotated at 600 and 1200 rpm. The test temperature was set at 40 °C and 100 °C. Each test lasted 60 min. 3 repeats were conducted for each condition.

(a) Four ball friction tester

(b) Ball-on-disk film thickness measurement system

Figure 2 Schematic of experimental setups used in this study

The ability of the lubricant to protect rubbing surface was examined by scuffing tests where the applied load increased gradually at 30 s intervals during the test. Frictional force was monitored. Scuffing has occurred when the frictional force increased abruptly and the corresponding applied load is identified as the failure load. The test temperature was set at 100 °C and the rotation speed 800 rpm.

All balls were cleaned prior to testing by firstly immersed in petroleum ether overnight to remove corrosion inhibitors from their surfaces. They were then cleaned in petroleum ether for 2 h, followed by ultrasonication in ethanol, lastly dried by nitrogen. After friction tests, the balls were lightly rinsed in ethanol to remove residual oil on their surfaces for subsequent surface analysis.

2.3 Characterization of worn surface

Wear scars on steel balls were observed under a microscope. The diameter of a wear scar (WSD) was measured at 3 different positions, and averaged to evaluate the amount of wear on a steel ball. Three-dimensional profiles of the wear scars were obtained using a Form Talysurf PGI 800 (Taylor Hobson, UK) with a scan area of $1.1 \times 1.1 \text{ mm}^2$. Scanning electron microscope (SEM) was employed to examine wear scars. Chemical compositions of scar surfaces were examined by energy dispersive x-ray spectroscopy (EDS).

2.4 Lubricant film thickness in “starved” elastohydrodynamic lubrication (EHL) regime

The impact of IL additives on lubricant film thickness in the sEHL condition was investigated using optical interferometry. A home-built ball-on-disc test apparatus, with a contact created by pressing a steel ball (diameter 25.4 mm, RMS surface roughness 25 nm) against a flat glass disc (with a diameter of 150 mm and roughness of 8 nm), was used. To apply optical interferometry, the glass disc was coated with approximately 20 nm of chromium then 200 nm of silica to increase its reflectivity. Two lasers, with wavelengths of 655 nm and 532 nm, were shone through the glass disc into the contact at the same time. The interference fringes produced due to optical phase differences of reflected light from the glass disc and the steel ball, were captured via a CCD camera. A schematic representation of the test setup is shown in Figure 2b. Maps of lubricant film thickness in the contact, with a thickness resolution of 1 nm, were obtained [40-42].

Before the test, steel balls underwent the same cleaning procedure as those for friction tests. Glass discs were cleaned with anhydrous ethanol followed by deionized water and then dried by nitrogen before use. 10 μ L of lubricant was pipetted onto the disc. The glass disk rotated at 1 mm/s without applied load for 30 min to ensure the lubricant was evenly distributed over the rubbing track. The load was then applied so the ball and the disc were pressed against each other. Film thickness measurements were taken at room temperature (23 °C), over a speed range of 0.001 – 0.5 m/s at pure rolling condition. Three repeats were conducted for each lubricant. 10 μ L and 5 μ L of a lubricant were used for EHL and sEHL conditions.

3 Results and Discussion

3.1 Effects of additives on friction in the boundary lubrication regime

The effect of the addition of ZDDP and IL on the friction coefficient of PAO depends on temperature, see Figure 3.

Figure 3 The effect of ZDDP and IL additives on friction coefficient of PAO at (a) 40 °C and (b) 100 °C. The rotational speed was 600 rpm and the applied load was 196 N.

Neat PAO gives a friction coefficient μ_{PAO} of about 0.08 at 40 °C (solid line, Figure 3a). At 100 °C, the viscosity of PAO drops and the lubricant becomes less effective in separating the rubbing surfaces. This leads to a rise in friction and wear. μ_{PAO} increases quickly as soon as rubbing starts (solid line – coincide with the y-axis, Figure 3b). The test was stopped when μ_{PAO} reached 0.25, indicating scuffing has occurred. This shows that neat PAO is unable to protect rubbing surfaces at high temperatures.

The friction coefficient of ZDDP-containing PAO (dash line), μ_{ZDDP} , is higher than μ_{PAO} (solid line) at 40 °C (Figure 3a). Usually the roughness of the surface decreases during the running-in process. This is however prevented by the use of ZDDP [43, 44], an anti-wear additive, giving higher μ_{ZDDP} . μ_{ZDDP} is stable at 100 °C throughout the duration of the test, which shows that ZDDP protects the rubbing surfaces from scuffing at both temperatures. Note μ_{ZDDP} is slightly higher at 100 °C (Figure 3b) than at 40 °C, as previously shown [15].

At 40 °C, the friction coefficient of PAO with IL (dotted line, Figure 3a), μ_{IL} , is lower than μ_{PAO} (solid line). This confirms prior results in the literature [1, 18, 21, 27, 45]. It is believed that IL additives form “viscous” boundary films with layered structure on metal surfaces due to its strong polarity [22, 27, 39]. This film may possess low shear strength, hence the lower μ_{IL} . μ_{IL} fluctuates at the beginning of the test, then stabilizes at ~0.06. The fluctuations in μ_{IL} may be due to the

competition between the formation and removal of the IL film on rubbing surfaces. Note that a stable μ_{IL} may be achieved when an equilibrium between the two processes is reached, giving rise to a stable film. μ_{IL} at 100 °C (dotted line, Figure 3b) is higher and remains relatively constant throughout the test. The more stable μ_{IL} may be due to increased IL film formation rate at higher temperature. The higher μ_{IL} implies this high temperature film is likely to be stronger and more robust against shear, leading to lower removal rate. This shows that the nature and formation kinetics of the IL film is temperature dependent.

For PAO containing both ZDDP and IL, its coefficient of friction $\mu_{ZDDP+IL}$ (dash-dot line) is just below μ_{ZDDP} (dash line) at 40 °C, i.e. no synergy is observed between the two additives (Figure 3a). On the other hand, synergy exists between ZDDP and IL at 100 °C (Figure 3b) as $\mu_{ZDDP+IL}$ (dash-dot line) is lower than μ_{IL} (dotted line). While both μ_{IL} and μ_{ZDDP} at 40 °C are lower than their counterparts at 100 °C, $\mu_{ZDDP+IL}$ at 100 °C is lower than that at 40 °C.

If a constant friction coefficient signifies the establishment of a stable tribofilm, then ZDDP films form more readily than IL films at 40 °C, while the reverse is true at 100 °C. $\mu_{ZDDP+IL}$ and hence the properties of the mixed film, resembles that of the individual component that forms a film the fastest, despite forming at a lower rate.

3.2 Effects of additives on scuffing

Results from scuffing tests conducted at 100 °C were presented in Figure 4. The failure load of PAO is about 440 N (solid line, Figure 4). With additives, the failure load increases. ZDDP, being an anti-wear additive, provides the most protection and gives the highest failure load of 870 N (dash line). The use of IL additives results in a failure load of about 680 N (dotted line). The mixture of ZDDP and IL additives (dash-dot line) results in a failure load in between those of adding ZDDP and IL alone. This result is consistent with the consensus that the anti-scuffing performance of a lubricant improves with the concentration of sulphur, which promotes the formation of anti-sintering sulphides [27, 35].

Figure 4 The effect of ZDDP and IL additives on lubricant failure load of PAO. The rotational speed was 800 rpm. The applied load was 196 N. The test temperature was 100 °C.

3.3 Effect of additives on wear

The diameters of wear scars (WSD), averaged from measurements of 3 wear scars, are presented in Figure 5.

Figure 5 The effect of ZDDP and IL additives of the size of the wear scar (WSD) formed in PAO4 at 196 N and 600 rpm.

The addition of ZDDP, whether it is used alone or in a mixture, reduces WSD and its effect is insensitive to temperature. The use of IL additive alone at 40 °C results in higher WSD than using PAO alone. This may be associated with large fluctuations in μ_{IL} observed in Figure 3a (dotted line). Before a stable IL tribofilm is formed, reactions between IL and the steel surfaces may promote wear. In contrast, the tribofilms of ZDDP and the combination of IL and ZDDP quickly reach steady state, as suggested by their stable friction coefficients. These stable films protect rubbing surfaces and reduce wear. WSD formed in PAO4+ZDDP+IL are similar to that in PAO4+ZDDP at 40 °C. Note that $\mu_{ZDDP+IL} \approx \mu_{ZDDP}$ at this temperature. This supports that the tribofilm formed in PAO+ZDDP+IL at 40 °C is similar to ZDDP tribofilm.

At 100 °C, WSDs from PAO+IL, PAO+ZDDP and PAO+ZDDP+IL are comparable (Figure 5). The morphology of these wear scars is however different, see Figure 6. A rough worn surface was obtained as soon as the test started when PAO was used (Figure 6a, $R_a = 0.49 \mu\text{m}$). PAO+ZDDP gives a smaller wear scar (see Figure 6b) after rubbing for an hour. It possesses shallower scratches and dimpled-like features due to the formation of transverse cracks.

Figure 6 The morphology of wear scars on stationary balls after friction tests at 196 N, 600 rpm, 100 °C. Yellow circles identify wear scars. Note tests with PAO were very short due to scuffing.

Using IL additive (see Figure 6c for PAO+IL; and Figure 6d for PAO+IL+ZDDP) results in smoother wear scars, with PAO+IL giving the smoothest ($R_a = 0.10 \mu\text{m}$). The mixture of IL and ZDDP gives a wear scar with surface roughness in between those lubricated with ZDDP and IL alone. The smoother surface explains the reduced coefficient of friction of PAO when IL additives and IL+ZDDP mixtures are used.

Our results confirm that the effects of ZDDP layer and IL layer differ, with the anti-wear and anti-scuffing properties of ZDDP protecting the rubbing surfaces, while low shear layers of IL give low friction. Their difference in working mechanisms leads to different wear scar morphology, with IL resulting in smoother rubbing surface. At 100 °C, the IL tribofilms forms quickly enough to also reduce wear. For the mixture of the two additives, the effect of ZDDP dominates at 40 °C. At 100 °C, the synergy of ZDDP and IL is displayed by PAO+ZDDP+IL having the lowest friction of all the lubricants tested.

3.4 Chemistry of the tribofilm on rubbing surfaces

Tribofilms on wear scars was examined using EDS, see Table 2. Fe and Cr are expected from the steel surface. As tribofilms are relatively thin, signals of the underlying steel are still detected.

Atomic %	PAO	PAO +ZDDP	PAO +IL	PAO +ZDDP+IL
C	46.67	68.48	68.73	80.42
O	0.00	0.00	0.00	0.00
P	0.00	0.14	0.50	0.28
S	0.00	0.15	0.00	2.19
Cr	0.32	0.45	0.35	0.25
Fe	53.01	30.67	30.42	16.66
Zn	0.00	0.12	0.00	0.19

Table 2 EDS results of wear scars lubricated by PAO, PAO+ZDDP, PAO+IL and PAO+ZDDP+IL. Applied load = 196 N, sliding speed = 600 rpm, test temperature = 100 °C.

Note tests with PAO were very short due to scuffing.

Recall that Zn, S, and P are present in a ZDDP molecule, while P, O and N are in an IL molecule. Results obtained on wear scars formed in PAO+ZDDP and PAO+IL are in line with published work [46-49]. The wear scar formed in PAO+ZDDP+IL has the lowest Fe signal of the four wear scars, suggesting that the mixed film is thicker than those formed in PAO+ZDDP and PAO+IL. The amount of P in the mixed film is in between those formed in PAO+ZDDP and PAO+IL. It has more S and Zn than that formed in PAO+ZDDP. In fact, this mixed tribofilm is much richer in S. As S and Zn can only be from ZDDP, this implies that the mixed tribofilm contains substantial amount of ZDDP related materials although its chemistry has been modified by the addition of IL. If the ratio of P:Zn of the ZDDP-related component of the mixed film is similar to that formed in PAO+ZDDP, then 0.22 and 0.06 atomic % of P originated from ZDDP and IL, respectively. Our results suggest that a small amount of IL in this hybrid tribofilm is sufficient to give the observed results at 100 °C. Alternatively, IL may adhere to rubbing surfaces weakly and is removed and reformed continuously during rubbing. While PAO+ZDDP+IL, PAO+ZDDP and PAO+IL result in similar amount of wear at 100 °C, PAO+ZDDP+IL gives lower friction (see Figures 3b and 5). This shows that the hybrid tribofilm has good load-carrying capacity and is easily sheared.

3.5 Effect of additives on lubricant film thickness in the sEHL regime

Interferometric maps showing the thickness of the lubricant in and around the contact obtained under EHL and sEHL conditions are presented in Figure 7. The darker the color shown in the contact, the lower the lubricant film thickness. The violet dash lines near or at the inlet indicate the locations of the menisci of lubricants formed between rubbing surfaces. All four tested lubricants achieved a fully flooded (EHL) condition with 10 μ L of lubricant when the applied load was 30 N and the entrainment speed is 300 mm/s (see Figure 7a). All rubbing contacts in this condition look similar, and the use of additives has minimal effect on lubricant film thicknesses (see Figure 8a and 8b for minimum and central film thickness respectively). This is expected as lubricant film thickness is governed by the viscosity of the lubricant at the inlet region and all these lubricants have similar viscosities. The distance between the meniscus and the edge of the contact,

d , however, depends on the choice of additive. It is found that d is the smallest when neat PAO is used, Figure 7a. This suggests that the additives have modified the inlet condition and possibly improved lubricant entrainment.

(a) EHL condition – Load = 30 N; Entrainment speed = 300 mm/s

(b) Lightly sEHL condition – Load = 75 N; Entrainment speed = 300 mm/s

(c) Heavily sEHL condition – Load = 75 N; Entrainment speed = 450 mm/s

Figure 7 Interference images of contacts lubricated with PAO, PAO+ZDDP and PAO+IL and PAO+ZDDP+IL, taken at room temperature in (a) EHL conditions, and (b) and (c) sEHL conditions.

Figure 8 (a) Variation of minimum film thickness in contact with speed and (b) central film profile, orthogonal to the rubbing direction, in full film lubrication at room temperature.

With a higher load (to 75 N), a higher speed (to 450 mm/s) or a reduced oil supply (to 5 μ L), starved EHL conditions are observed. Figure 7b and 7c are images of lightly and heavily starved EHL conditions respectively. In both cases, the oil-air interface extends into the contact, indicating that there is insufficient entrained lubricant. As the load and the speed increase, the severity of lubricant starvation increases, as shown by an expansion of the dark region in the rubbing contact. Figure 9 shows the lubricant film thickness profiles taken across the contact at positions shown by the dash-dot lines in Figures 7b and 7c. Using additives increases the thickness of the lubricant film in the sEHL condition. This confirms that these additives modify the contact inlet condition, which promotes lubricant entrainment in our study and impacts on the lubricant film thickness [49].

Figure 9 Central film thickness profiles (orthogonal to the flow direction) at room temperature in (a) lightly and (b) heavily starved EHL conditions.

PAO+IL (dotted line) gives the thickest lubricant film in starved EHL conditions (Figure 9). This is not due to differences in lubricant viscosity as these lubricants have similar viscosity (see Table 1). Our observations are likely stemmed from differences of their tribofilms. The formation of ZDDP tribofilm requires high shear stress. Hence in the EHL and starved EHL conditions, the formation of ZDDP tribofilms is likely to be incomplete [37, 39, 40]. On the other hand, highly polar IL may adsorb on steel surface through electrostatic interaction. Note that some ILs may form aggregates in lubricants which may subsequently be entrained into the contact [34]. This may result in higher film thickness due to aggregate deposition and increased effective lubricant viscosity in the contact. An increase in entrainment speed reduces the lubricant film thickness in all cases, as commonly seen in sEHL conditions [50]. At heavily starved conditions, the effect of IL additives on lubricant film thickness diminishes and differences in the lubricant film thickness of all additised PAO are much smaller than in the slightly sEHL conditions.

Lubricant film thicknesses formed in PAO+ZDDP+IL are similar to PAO+ZDDP and PAO+IL at lightly and severe sEHL conditions respectively. This suggests that no synergy is observed between ZDDP and IL in the sEHL regime. Interestingly in boundary lubrication condition where surface condition dominates, the friction coefficient from PAO+ZDDP+IL is closer to that from PAO+ZDDP at 40 °C (less severe) and PAO+IL at 100 °C (more severe).

4 Conclusions

The effectiveness of ZDDP and a P-based IL in lubricating steel-steel contact in PAO was investigated in this study. For sEHL conditions, the addition of IL, ZDDP and their mixture in PAO improves lubricant entrainment and hence increases lubricant film thickness. Their effect however diminishes at heavily starved EHL conditions. Among them, IL is the most effective. The effect of ZDDP is small since the shear stress is low which hinders the formation of ZDDP tribofilm. No synergy is observed between IL and ZDDP in sEHL condition, with ZDDP and IL controlling the behavior of the mixed additive lubricant at lightly and severely sEHL conditions respectively.

In the boundary lubrication regime, the formation of tribofilms is promoted by friction heating and high stress. These tribofilms may adhere strongly with the metal surface. ZDDP tribofilm is known to have an island-like structure with good carrying capacity and superior antiwear performance. Its surface is however rough and results in a higher friction. In contrast, IL tribofilms are believed to have a layered structure, and have low shear strength which give lower friction. The IL film formed in this study offers little protection against wear at 40 °C, while at 100 °C, it exhibits excellent performance in reducing friction and wear. Our results suggest that our P-based IL is more likely to form a stable tribofilm at high temperature. While the mixture of ZDDP and IL gives rise to a scuffing load that is in between those of ZDDP and IL, the mixed tribofilm shows lower friction coefficient and less wear at 100 °C than using ZDDP and IL alone. This shows that synergy exists between IL and ZDDP at high temperature. The observed synergy may stem from (1) the IL in the mixture giving a smoother worn surface; (2) the ZDDP-related materials in the mixed film providing good wear resistance; and (3) IL altering the nature of the thicker, predominantly ZDDP based tribofilm resulting in lower friction.

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515	List of Figures
516	Figure 1 Molecular structures of (a) PAO, (b) ZDDP and (c) quaternary phosphonium ionic liquid
517	Figure 2 Schematic of experimental setups used in this study
518	Figure 3 The effect of ZDDP and IL additives on friction coefficient of PAO at (a) 40 °C and (b)
519	100 °C. The rotational speed was 600 rpm and the applied load was 196 N.
520	Figure 4 The effect of ZDDP and IL additives on lubricant failure load of PAO. The rotational
521	speed was 800 rpm. The applied load was 196 N. The test temperature was 100 °C.
522	Figure 5 The effect of ZDDP and IL additives of the size of the wear scar (WSD) formed in
523	PAO4 at 196 N and 600 rpm.
524	Figure 6 The morphology of wear scars on stationary balls after friction tests at 196 N, 600 rpm,
525	100 °C. Yellow circles identify wear scars. Note tests with PAO were very short due to scuffing.
526	Figure 7 Interference images of contacts lubricated with PAO, PAO+ZDDP and PAO+IL and
527	PAO+ZDDP+IL, taken at room temperature in (a) EHL conditions, and (b) and (c) sEHL
528	condition.
529	Figure 8 (a) Variation of minimum film thickness in contact with speed and (b) central film
530	profile, orthogonal to the rubbing direction, in full film lubrication at room temperature.
531	Figure 9 Central film thickness profiles (orthogonal to the flow direction) at room temperature in
532	(a) lightly and (b) heavily starved EHL conditions
533	
534	List of Table
535	Table. 1 The dynamic viscosity, density and viscosity index of lubricants used in the tests
536	Table 2 EDS results of wear scars lubricated by PAO, PAO+ZDDP, PAO+IL and
537	PAO+ZDDP+IL. Applied load = 196 N, sliding speed = 600 rpm, test temperature = 100 °C.
538	Note tests with PAO were very short due to scuffing.
539	
540	