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Ultra-Low Boundary Lubrication Friction by Three-Way Synergistic Interactions among Ionic Liquid, Friction Modifier, and Dispersant

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ABSTRACT

Interactions among anti-wear additives (AWs), friction modifiers (FMs), and dispersant in a lubricating oil are critical for tribological performance. This study investigates compatibilities of three oil-soluble ionic liquids (ILs, candidate AWs) with a FM, molybdenum dithiocarbamate (MoDTC), and a dispersant, polyisobutene succinimide (PIBSI), under boundary lubrication. Either synergistic or antagonistic effects were observed depending on the IL's chemistry. Adding an aprotic phosphonium-alkylphosphate or phosphonium-alkylphosphinate IL into the oil containing MoDTC and PIBSI showed detrimental impact on the friction and wear behavior. PIBSI was found to preferably interact/react with the aprotic IL to lose its ability to suspend MoDTC and to partially consume or even deplete the IL. In contrast, a protic ammonium-alkylphosphate IL seemed to be able to co-exist with PIBSI and work synergistically with MoDTC, yielding a sustainable, ultra-low boundary friction. A three-stage tribochemical process is proposed to explain how this IL+MoDTC pair interacts with the contact surface to form a chemically-reacted, wear-protective tribofilm supporting a physically-adsorbed, friction-reducing film on top. This study provides fundamental insights of the compatibilities among three common lubricant components, anti-wear, friction modifier, and dispersant, which can be used to guide future lubricant development.

KEYWORDS: Ionic liquids, MoDTC, ZDDP, friction modifier, dispersant, synergistic effect

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1. INTRODUCTION

Lubrication is at the heart of many energy systems, such as transportation vehicles, hydraulics, hydropower turbines, wind turbines, and nuclear power plants. Advances in lubricants have been relentlessly sought by modern society for energy efficiency and durability. It has been estimated that lubrication R&D may lead to savings of one Quad of energy in U.S.¹. Reduction of the lubricant viscosity and employment of friction modifiers (FMs)² are the two main approaches for energy saving ³. A lower oil viscosity reduces the drag (friction) for the moving parts operating under hydrodynamic lubrication as well as the energy consumption for oil pumping ^{4,5}. FMs, on the other hand, decrease the friction in boundary and mixed lubrication ². Using multiple FMs together may have either synergistic or antagonistic interactions whose effects may vary for different contacts and motions ⁶.

Molybdenum-containing compounds for reducing the coefficient of friction (COF) have been used as FMs in engine oils for more than 40 years ⁷⁻⁸. The most commonly used compounds are molybdenum dithiocarbamates (MoDTCs), which have been extensively studied in engine oil lubrication ⁹⁻¹². It's worth mentioning that the functionality of MoDTC is highly affected by its compatibility with the chemistry of the base oil and other additives in the package ¹³⁻¹⁹. Particularly, interactions between FMs and anti-wear additives (AWs) are crucial since these two additives dominate the tribological properties of an engine oil ²⁰. Several studies have investigated the compatibility between MoDTC and a classic AW, zinc dialkyldithiophosphate (ZDDP), and reported synergistic friction or wear results ²¹⁻²⁴, involvement of the two additives in the tribofilm formation ²⁵, and their exchange reactions in different solutions ²⁶.

Ionic liquids (ILs) were first explored for lubrication in 2001 ²⁷ and most earlier studies utilized ILs as neat lubricants ²⁸⁻³⁰. While there were a few attempts of using ILs as lubricant additives ³¹⁻³⁴, truly oilmiscible ILs (5 wt.% or higher solubility in non-polar base oils) were not developed until 2012 ^{35,36} and have since been repeatedly demonstrated as promising AWs ³⁷. Our recent studies revealed interesting synergistic effects between phosphonium-alkylphosphate ILs and a secondary ZDDP ³⁸ and between an ammonium-alkylphosphate IL and an organic FM (OFM) ³⁹ when used together as oil additives. However, to our best knowledge, there is no report on the compatibility between oil-soluble ILs and Mo-based FMs,

e.g., MoDTC, not to mention the influence by dispersants that often are used in engine oils to help suspend insoluble compounds including MoDTCs.

This study deals with a more complex, three-way interaction system among IL, MoDTC, and a polyisobutylene succinimide (PIBSI) dispersant in boundary lubrication for a steel-cast iron contact. Such a lubricant system containing the three surface-active components sets up an interesting platform to allow investigation of the three-way physicochemical interactions among them as well as their combined tribochemical interactions with the metal contact surfaces upon rubbing. The PIBSI was discovered to play a critical role by preferably interacting with an aprotic IL to lose its ability to suspend MoDTC and partially consumed or even depleted the IL. In contrast, a protic IL seemed to able to co-exist with PIBSI and work synergistically with MoDTC, yielding a promising ultra-low friction behavior. While this particular protic IL showed synergistic effects with both OFM ³⁹ and MoDTC, the mechanisms are distinct. The IL-OFM pair did not form any solid tribofilm but solely relied on an adsorption film of a network of the IL ions and OFM molecules ³⁹. In contrast, the IL-MoDTC combination went through a three-stage process to build a chemically-reacted, wear-protective tribofilm with contributions from both the IL and MoDTC and a physically-adsorbed, friction-reducing film on the top of the solid tribofilm.

2 EXPERIMENTS AND MATERIALS

2.1. Materials

A poly alpha olefin 4 cSt (PAO4) base oil, a MoDTC, and a PIBSI were kindly provided by ExxonMobil. A secondary ZDDP was received from Lubrizol, which contains 5-10 wt.% mineral oil for flowability. The phosphorus and zinc contents in this ZDDP product (ZDDP plus 5-10% oil) are 11 and 10 wt.%, respectively. Three ILs, tetraoctylphosphonium bis (2-ethylhexyl) phosphate $[P_{8888}][DEHP]$, trihexyltetradecylphosphonium phosphinate $[P_{66614}][BTMPP]$, trioctylammonium bis(2-ethylhexyl) phosphate $[N_{888}H][DEHP]$, were synthesized in our organic chemical lab using the protocols described in our earlier work 40,41,42 . The molecular structures of the selected ILs, ZDDP, MoDTC, and PIBSI are presented in Figure 1. All three ILs have purity above 98% and are soluble (>5 wt.%) in the PAO4 base oil.

The ILs' basic physicochemical properties and lubricating performance when used as single additives have been reported previously ^{40,41,43}.

Lubricant samples, as listed in Tables 1, were prepared by blending 0.8 wt.% MoDTC alone or together with ZDDP or an IL into PAO4 containing 2 wt.% PIBSI. This particular MoDTC has very limited solubility (<0.2 wt.%) in PAO4, but the PIBSI dispersant helps suspend it well in the oil. The ZDDP and ILs were used at the same molecular concentration, and the corresponding weight concentrations are 0.8 wt.% for ZDDP, 1.04 wt.% for [P₈₈₈₈][DEHP], 0.99 wt.% for [P₆₆₆₁₄][BTMPP], and 0.87 wt.% for [N₈₈₈H][DEHP]. Additional lubricants were prepared for PAO4+IL and PAO4+PIBSI+IL, as listed in Table S1 in the Supporting Information.

Fourier-transform infrared spectroscopy (FTIR) was used to analyze blends of neat additives (without the base oil) to investigate their interactions. The additives were mixed in the same weight ratio as what they were added into the oil, as shown above and listed in Tables 1 and S1. Analyses were carried out on a Bruker Vertex 80 FT-IR spectrometer equipped with a single reflection ATR accessory (Harrick MVP-Pro) and a diamond crystal. The spectral range was 400-4000 cm⁻¹ and each spectrum was an average of 100 scans and has a resolution of 4 cm⁻¹. The incident angle of the IR beam was 45°.



Figure 1. Chemical structures of the selected three ILs, ZDDP, MoDTC, and PIBSI.

2.2. Tribological testing

Tribological tests were carried out on a Phoenix-Tribology Plint TE-77 tribometer using a steel ball reciprocating sliding against a grey cast iron flat. The steel ball was a grade 25 AISI 52100 bearing steel ball with a diameter of 10 mm and a surface roughness of 25-50 nm (R_a). The flat was a CL35 grey cast iron plate with a roughness of about 80 nm (R_a). The alloy compositions and Vickers microindentation hardness values are shown in Table S2. This material pair was used to simulate the common sliding interface for a steel piston ring against a grey cast iron cylinder wall in an actual engine. Tests were conducted at a constant temperature of 100 °C, under a 100 N load and a 10 Hz oscillation with a 10 mm stroke for 1,000 or 10,000 m sliding. At least two replicate tests were performed for each lubricant. Friction force was monitored *in situ* by measuring the tangential force using a piezoelectric load cell. All worn surfaces of cast iron were cleaned with isopropyl alcohol and the wear volumes were quantified using a Wyko NT9100 white light interferometer.

The maximum Hertzian contact stress at the beginning of the test was calculated to be 1.68 GPa, which is higher than the compressive yield strength of the grey cast iron (~800 MPa). As a result, the cast iron flat surface would yield and the actual contact pressure at the beginning of the test would be around 800 MPa and gradually decrease during the wear process due to enlarged contact area. Based on the Hamrock– Dowson formula ⁴⁴, the calculated central thickness *t* of the lubricant film at the ball-flat interface at the beginning of the test is <15 nm. Since the composite roughness was calculated to be >100 nm using the equation $\sigma = \sqrt{R_{q,ball}^2 + R_{q,flat}^2}$, the lambda ratio $\lambda = \frac{t}{\sigma}$ is less than 1 and thus the lubrication regime was determined to be boundary lubrication.

The flash temperature ⁴⁵ of the sliding test has been calculated using the Archard equation ⁴⁶, as detailed in Supporting Information. The calculated flash temperature (see Table S3) is in the range of 10.1 - 30.6°C at the beginning of the test (Hertzian contact) when the nominal contact area is used. When taking the surface roughness into consideration, the flash temperature at the surface asperities in contact would be much higher. Specifically, for the sliding pair of AISI 52100 steel ball against CL35 cast iron flat used in this study, the ratio of the true contact area to the nominal contact area at the beginning of the sliding test has been calculated to be 2.2%. Since the flash temperature is inversely proportional to the radius of the contact area, the flash temperature on the true contact area has been adjusted to 68 - 206 °C, as shown in Table S3. The significant flash temperature likely promotes the chemical reactions among additives and between the additives and the contact surfaces, as observed and discussed in Sections 3 and 4 below.

2.3. Surface characterization

A Hitachi S-4800 field-emission scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDS) was used to characterize the morphology and chemical composition of the tribofilm on the worn surface from the cross section. A scanning transmission electron microscopy (STEM) sample was prepared by using a Hitachi NB5000 focused ion beam (FIB) system with a gallium ion source to extract a thin cross-section of the near-surface zone from the worn surface. Before extraction, a tungsten layer was deposited onto the wear scar to protect the tribofilm from ion milling. The FIB sample was mounted on a Gatan double tilt specimen holder. The tribofilm nanostructure and chemical composition were analyzed using a Hitachi HF-3300 electron microscopy operated at 300 kV. The vacuum chamber was pumped down to $<4x10^{-6}$ Pa, before inserting the sample to ensure stable beam path. STEM images were acquired using High Angle Annular Dark Field (HAADF) detector to improve the image z-contrast. The FIB sample was stable to the electron beam and had no visual deformation over the beam exposure. EDS signals were collected using a built-in Bruker solid state EDS detector and then EDS elemental maps were processed using the Bruker Espirit (version 2) software.

X-ray photoelectron spectroscopy (XPS) was used to further analyze the chemical composition of the tribofilm (Thermo Scientific K-Alpha XPS). Al K_{α} monochromated X-ray source, focused to a 250 µm diameter spot, was used to excite photoelectrons that were measured with a hemispherical electron energy analyzer and a 128-channel detector. A binding energy value of 284.8 for C 1s was used to calibrate binding energies. Low-energy Ar ions and electrons provide a region around the analysis area that compensates for positive or negative charging. Surface compositions were determined by calculating peak areas of the primary core levels for all elements present and normalized using tabulated sensitivity factors. Composition-depth profiles were acquired by an argon-ion sputter gun (2 KeV Ar ions) for up to 500 s of

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sputtering. The sputter rate was assumed to be 8 nm/min based on calibration using silica, but may vary with the compositions and mechanical properties of the tribofilm and substrate material. All XPS data were analyzed using Thermo Scientific Avantage software (v.4.61) that includes tabulated sensitivity factors.

3 RESULTS

3.1. Tribological behavior of different blends

Tables 1 and S1 summarizes the mean coefficient of friction (COF), wear volume of the cast iron flat, and roughness of the wear scar on the cast iron flat for each lubricant. The steel ball wear was consistently two orders of magnitude less than the iron flat wear, and thus is ignored here. Figures 2 and S1 (see Supporting Information) show the friction behavior, wear scar morphology, and worn surface composition. The wear depth profiles of the worn cast iron surfaces are compared in Figure S2 in the Supporting Information.

Table 1. Summary of friction and wear results.				
Lubricant	Mean COF	Wear volume	Roughness <i>R</i> a	
Lubicant		(×10 ⁷ µm³)	(μm)	
Unworn surface of cast iron flat	-	-	0.08 ^{±0.01}	
PAO4 +2% PIBSI	0.113	23.9 ^{±1.1}	1.10 ^{±0.04}	
PAO4 +2% PIBSI +0.8% MoDTC	0.067	4.0 ^{±1.1}	$0.42^{\pm 0.03}$	
PAO4 +2% PIBSI +0.8% MoDTC +0.8% ZDDP	0.099	16.5 ^{±0.2}	$0.40^{\pm 0.02}$	
PAO4 +2% PIBSI +0.8% MoDTC +1.04% [P ₈₈₈₈][DEHP]	0.114	16.3 ^{±1.4}	0.74 ^{±0.18}	
PAO4 +2% PIBSI +0.8% MoDTC +0.99% [P ₆₆₆₁₄][BTMPP]	0.099	9.1 ^{±0.1}	1.28 ^{±0.20}	
PAO4 +2% PIBSI +0.8% MoDTC +0.87% [N888H][DEHP]	0.053	2.7 ^{±0.1}	0.18 ^{±0.08}	
PAO4 +2% PIBSI +0.8% MoDTC +0.87% [N ₈₈₈ H][DEHP], 10,000 m	0.040	6.0	$0.15^{\pm 0.07}$	
PAO4 +2% PIBSI +0.8% MoDTC, 10,000 m	0.057	7.0	1.05 ^{±0.10}	

Due to the poor lubricity of neat PAO4 and the poor solubility of MoDTC in base oil, PAO4 with 2% PIBSI, which was used to assist the dispersion of MoDTC, was chosen as the baseline. It can be seen in Figure 2a that the COF of PAO4+PIBSI experienced an initial spike (0.13) due to the high contact stress and the lack of protective additives. It then quickly dropped to 0.10 due to the decreasing contact pressure

as a result of wear-enlarged contact area, from where the COF gradually climbed up likely due to surface roughening in the wear process (wear scar roughness 1.10 μ m versus the unworn area roughness 0.08 μ m). The wear loss of the grey cast iron flat was 23.9×10⁷ μ m³ after the 1,000 m sliding, as shown in Table 1.

As expected, incorporation of MoDTC effectively alleviated the rubbing process, as shown in Figure 2b: after a fluctuated running-in period (first 400 m sliding), the COF was stabilized at around 0.06, which is in good agreement with earlier studies ¹. In addition, the MoDTC significantly lowered the wear volume to $4.0 \times 10^7 \,\mu\text{m}^3$, an 85% reduction compared to the fluid without MoDTC.

Adding ZDDP into the PAO4+PIBSI+MoDTC fluid increased the mean COF to 0.10, degraded the surface protection yielding a higher wear loss of $16.5 \times 10^7 \,\mu\text{m}^3$. This observation is contrary to some previously reported synergistic effects for MoDTC and ZDDP working together ²¹⁻²⁴. One reason might be the influence of dispersant/detergent that had been reported to significantly affect the interactions between MoDTC and ZDDP ²³ and certain dispersants ^{47,48} including PIBSI ⁴⁹ could react with ZDDP to cause antagonistic effects. Most literature ²¹⁻²³ reporting synergism for MoDTC+ZDDP did not use any dispersant/detergent and the one ²⁴ that used dispersant/detergent did not disclose the chemistry. In this study, the PIBSI dispersant might be responsible for the inferior performance for the MoDTC+ZDDP combination. While there is no report for the interaction between PIBSI and MoDTC, PIBSI and MoDDP (similar structure with MoDTC) have been found to form a complex structure by the electron pairs of the nitrogen of PIBSI and the Mo of MoDDP 50,51. This may explain how PIBSI suspends/disperses MoDTC in oil. In the meantime, PIBSI was also reported to interact/react with ZDDP ^{47,49} and the interaction/reaction largely depends on the chemical structures of both PIBSI and ZDDP. When PIBSI has stronger interaction/reaction with ZDDP than MoDTC in fluid, there would be two negative effects: (i) less ZDDP available leading to weaker wear protection and (ii) less PIBSI available to suspend/disperse MoDTC in oil causing agglomeration/precipitation of MoDTC and consequently deteriorated friction behavior.

It is clear that the impact on friction and wear behavior by adding an IL to PAO4+PIBSI+MoDTC strongly depends on the IL's chemical structure. When either $[P_{8888}][DEHP]$ or $[P_{66614}][BTMPP]$ was used, similar to that with ZDDP, increased COF, 0.11 and 0.10, and wear volume, 16.3 and 9.1 x10⁷ µm³, respectively, were observed, as summarized in Table 1. Interestingly, $[P_{8888}][DEHP]$ appeared to have the

best wear protection by itself in the base oil $(5.1 \times 10^7 \,\mu\text{m}^3)$, see Table S1), deteriorated in presence of the PIBSI $(7.8 \times 10^7 \,\mu\text{m}^3)$, see Table S1), and further worsened when used together with both PIBSI and MoDTC $(16.3 \times 10^7 \,\mu\text{m}^3)$, see Table 1). Such antagonistic effects are discussed in Section 4.1.

In contrast, PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] produced the lowest COF (~0.05) and lowest wear volume $(2.7 \times 10^7 \,\mu\text{m}^3)$ among all the tested lubricants, as shown in Table 1. Compared with the mean COFs, 0.11 and 0.12, and wear volumes, 9.0 and 8.0 ×10⁷ μ m³, for using [N₈₈₈H][DEHP] alone and together with PIBSI in the base oil (see Table S1 and Figure S1), there seems to be a synergistic effect among [N₈₈₈H][DEHP], MoDTC, and PIBSI. It is worth mentioning that two out of three COF curves of MoDTC+[N₈₈₈H][DEHP] appeared to have a high-friction bump (~0.09), which is further investigated in Section 3.2 and then discussed in Section 4.1.





Figure 2. Friction curves of 2-3 repeat tests and representative SEM image and EDS spectrum of a worn cast iron surface tested in: (a) PAO4+PIBSI, (b) PAO4+PIBSI+MoDTC, (c)
PAO4+PIBSI+MoDTC+ZDDP, (d) PAO4+PIBSI+MoDTC+[P₈₈₈₈][DEHP], (e)
PAO4+PIBSI+MoDTC+[P₆₆₆₁₄][BTMPP], and (f) PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] (for each lubricant, SEM image and EDS spectrum corresponding to the wear scar with the black friction curve).

SEM and EDS were employed to examine the worn surface morphology and elemental composition for the cast iron flats. Results are presented in the middle and right columns of Figure 2. The cast iron coupon surface before wear testing had a low roughness of about 0.08 µm and its SEM image and EDS spectrum are shown in Figure S3a in Supporting Information. SEM image of the worn cast iron surface tested in the PAO4+PIBSI showed wide and deep grooves indicating significant abrasive wear plus plastic deformation (Figure 2a), which resulted in a high roughness of 1.10 µm. The addition of MoDTC to PAO4+PIBSI evidently made the grooves narrower (Figure 2b) and shallower and the wear scar roughness dropped to 0.42 µm. A lower magnification image in Figure S3b shows the difference between inside and outside of wear scar. The worn surfaces produced in the fluids containing PIBSI+MoDTC together with [P₈₈₈₈][DEHP] or [P₆₆₆₁₄][BTMPP] had similar features of abrasive wear and plastic deformation (Figures. 2c-2e) and both produced rather high roughness of 0.74 and 1.28 µm, respectively. In contrast, the surface lubricated by the PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] appeared to be rather flat and smooth with little surface damage, implying mild polishing wear (see Figure 2f). The worn surface was so smooth that even the original cast iron grain structure can clearly be seen and there is little difference between inside and outside the wear scar, as shown in Figure S3c. Generally, the worn surface morphology agrees with the friction and wear behavior presented above.

In EDS chemical analysis, Fe, Si, and O were the dominant elements of the worn surface produced by PAO4+PIBSI (Fig. 2a). Noteworthy, the oxygen content is the highest among all the tested samples corresponding to the most severe surface damage. A significant S/Mo peak can be observed on the worn surface lubricated by the PAO4+PIBSI+MoDTC, which might indicate formation of MoS₂ on the contact area responsible for the good friction reducing and anti-wear performance as suggested in the literature. ⁹⁻ ¹² (Due to the closer characteristic X-ray energies between S and Mo, their EDS signals tend to overlap each other.) All signature elements of ZDDP, Zn, P, and S, are present on the worn surface tested in PAO4+PIBSI+MoDTC+ZDDP, but the origin of sulfur is unclear because both ZDDP and MoDTC contain sulfur. When an aprotic phosphorus-containing IL, [P₈₈₈₈][DEHP] or [P₆₆₆₁₄][BTMPP], was added to PAO4+PIBSI+MoDTC, a small P peak appeared while the S/Mo signal was weakened on the worn surface.

This implied that both the IL and MoDTC participated in the tribofilm formation, but the involvement of MoDTC was restrained, probably due to the competition with the IL for surface adsorption. For the worn surface tested in PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP], the S/Mo peak disappeared while a small P peak was detected, suggesting a thin tribofilm produced primarily by the protic IL.

3.2. Different friction stages for PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP]

As shown in Figure 2f, although PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] generally exhibited relatively low COF (0.04-0.05), two out of the three repeat tests experienced an unignorable friction transition to a higher level (0.07-0.10): one had a friction bump for about 250 m sliding (blue) and another jumped to the higher friction level at the end of the test (red). In order to understand the cause and impact of the highfriction stage, additional three repeat tests were conducted. The friction behavior, wear scar morphology, and worn surface chemistry of the six repeat tests are displayed in Figure 3 in a reversed order of the occurrence of friction transition: the high-friction stage did not occur during the 1,000 m sliding in Run 1 and Run 2, initiated right before the end of Run 3, appeared after 850 m sliding and reached the plateau in Run 4, started from 650 m sliding and almost fell back the low-friction level by the end of Run 5, and completed its course between 150 and 400 m sliding in Run 6.

Correlated to the different friction behavior, there is considerable difference with respect to the worn surface morphology among these six tests. Maintaining the friction at a low and stable manner throughout the testing course, Runs 1 and 2 showed signs of mild polishing wear. EDS detected a small amount of P and O but no Mo/S, which suggests that the IL possibly reacted with the iron surface to form a thin tribofilm but MoDTC was not involved. In contrast, at the end of Run 3, the test was at onset of transition to a higher friction level, when Mo and/or S peak(s) started to appear. Runs 4-6 experienced high friction and ended in the middle, at the tail, and well after the high-friction stage, respectively. Similar to that of Run 3, the worn surfaces of Runs 4-6 also contained Mo and/or S. While a higher roughness was expected for the midgles did not support so. On the other hand, higher roughness was observed on the Run 6 surface when the friction already dropped back to the lower level. This indicates that the surface adsorption film along

with the chemically-reacted tribofilm had more impact than the roughness on the friction behavior in boundary lubrication.

Results imply that (i) MoDTC might have contributed to the initial low-friction stage before the highfriction bump via physical adsorption, but did not participate in the tribofilm formation; (ii) The up-hill friction transition might be a result of a failed MoDTC adsorption film and the high-friction bump likely triggered tribochemical reactions between MoDTC and the contact surface to introduce Mo/S compounds into the tribofilm; and (iii) The Mo/S compounds could hypothetically enhance the tribofilm to allow reestablish a MoDTC adsorption film on top, eventually leading to the friction transitioning back down. The formation and evolution of the surface adsorption film and tribofilm, as a result of combined contribution from the IL and MoDTC, and their correlations to the friction behavior are further discussed in Section 4.2.





Figure 3. Friction behavior, wear scar morphology, and worn surface chemistry of the total six repeat tests of PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP].

3.3. Elongated tests

То investigate sustainability of promising friction behavior of the the PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP], and further understand the evolution of the tribofilm composition, elongated tests with a sliding distance of 10,000 m ($10 \times$ of the standard 1,000 m) were conducted. As shown in Figure 4, the COF of PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] experienced two consecutive bumps at 100-450 m sliding (see a zoomed-in plot in Figure S4 in Supporting Information) in the early stage of the test and quickly dropped to and stabilized at around 0.04 for the rest of the course (>9,500 m sliding). Without the IL, PAO4+PIBSI+MoDTC produced a consistently higher COF and ended around 0.07, as compared in Fig. 4. In addition, introduction of $[N_{888}H]$ [DEHP] also reduced the wear volume moderately, as shown in Table 1.

The worn surface lubricated by PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] appeared relatively smooth (R_a : 0.15 µm, see Table 1) with clear signs of tribofilm (dark color patches) after 10,000 m sliding. Both P and Mo/S signals were detected by EDS suggesting a tribofilm with significant contributions from both the IL and MoDTC. In contrast, the wear scar tested in PAO4+PIBSI+MoDTC was much rougher (R_a : 1.05 µm, see Table 1) with a higher content of Mo/S compounds.





Figure 4. Elongated tests (10,000 m sliding). (a) Friction behavior, (b) Worn surface morphology and composition.

3.4. Tribofilm characterization by XPS

To further understand the tribochemical reactions at the contact interface lubricated by $PAO4+PIBSI+MoDTC+[N_{888}H][DEHP]$, XPS was employed to characterize the worn cast iron surfaces of four representative repeat short tests of 1,000 m sliding (Runs 1, 3, 4, 6) and the long test of 10,000 m sliding. The composition-depth profiles and core level spectra are shown in Figures 5 and 6, respectively. Results indicate that the tribofilm composition changed significantly at different friction stages.

On the worn surface generated in Run 1, the XPS data show significant amount of oxygen (up to 60 at.%) and phosphorus (up to 12 at.%) but little Mo or S (<1 at.% each), as shown in Figure 5, which is in line with the EDS results above. It confirmed that the tribofilm in the low-friction stage without or before a high-friction bump was primarily formed by $[N_{888}H]$ [DEHP]. After 50 nm sputtering, all oxygen and phosphorus were removed, suggesting that the tribofilm thickness was up to 50 nm, much thinner than those produced in Runs 3, 4, and 6 with a high-friction stage, as compared in Figure 5.

Compared with that of Run 1, there were much less phosphorus (up to 3-4 at.%) but a lot more sulfur (up to 4-5 at.%) and slightly more molybdenum (up to 1 at.%) on the worn surfaces of Runs 3 and 4 (see Figure 5), implying increased involvement of MoDTC but reduced contribution from the IL in the tribofilm formation. The signals of O and S did not fully fade off even after 250 nm sputtering, indicating a much thicker tribofilm formed in these two cases that ended at high-friction.

Run 6 and the elongated test experienced a high-friction bump but ended at low-friction. The composition-depth profiles in Figure 5 suggest that their tribofilms are relatively thick (>200 nm) and have

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high contents of phosphorus (up to 12 at.%), molybdenum (up to 3-4 at.%), and sulfur (up to 3-5 at.%), which indicates that both MoDTC and $[N_{888}H][DEHP]$ played important roles in growing the tribofilm during the low-friction sliding post the high-friction stage.



Figure 5. Comparison of XPS composition-depth profiles of O, P, Mo, and S of the tribofilms formed in four regular (1,000 m) runs and an elongated test (10,000 m) of PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] and a regular run of PAO4+PIBSI+MoDTC+[P₈₈₈₈][DEHP] (labeled as MoDTC+[P₈₈₈₈][DEHP]).

XPS core level spectra of key elements are shown in Figure 6, which provide insights of the tribofilm's compositional transition for PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP]. Note: For each element, the core level spectra's peak amplitudes were adjusted to be roughly proportional to the element's peak concentrations in the composition-depth profiles shown in Figure 5. This allows us to learn not only what compounds exist in a tribofilm but also the relative amounts compared with the tribofilms in other runs.

In the low-friction Run 1, the tribofilm appears to be dominated by iron phosphate(s) with small amounts of Mo oxides (primarily MoO₃) and sulfate. Both Fe³⁺ and Fe²⁺ were detected. Non-existence of sulfide suggests that the low-friction agent MoS₂, if produced during the sliding, would rather be physically adsorbed on the metal surface than enclosed in the tribofilm. Physically adsorbed surface film is easily washed off by the post-test sonication cleaning.

For Run 3 or 4 that ended at a high-friction stage, the tribofilm seems to contain less iron phosphate(s) (lower P-O peak in the P 2p chart) and significantly increased amounts of metal oxide(s) (much higher O-metal peak in the O 1s chart) and sulfide(s) (much higher sulfide peak in the S 2p chart), which are likely Fe₂O₃, MoO₃, and FeS₂ because little Mo⁴⁺ was detected. It was noticed that the Fe³⁺/Fe²⁺ ratio became a lot higher, indicating stronger oxidation, probably a result of the high friction.

After passing the high-friction bump, Run 6 produced a tribofilm, similar to that by Run 1, with a high ratio of phosphate(s)/oxide(s), as suggested by the O 1s and P 2p charts, and Fe²⁺ regained some ground, as shown in the Fe 2p3/2 chart. On the other hand, Mo⁴⁺ compounds were developed likely including both MoO₂ and MoS₂, which might be related to the regained low-friction. The tribofilm composition of the elongated run shares good similarities with that of Run 6, but has a few notable differences: the amount of MoO₂ and MoS₂ decreased but the amount of FeS₂ increased.







Figure 6. XPS core level spectra revealing the tribofilm composition evolution during the three-stage tribochemical process in lubrication of PAO+PIBSI+MoDTC+[N₈₈₈H][DEHP]. The XPS core level spectra of the tribofilm formed by PAO4+PIBSI+MoDTC+[P₈₈₈₈][DEHP] is also included for comparison.

For comparison, Figures 5 and 6 also include the XPS analysis data for the worn surface tested in PAO4+PIBSI+MoDTC+[P₈₈₈₈][DEHP], which had antagonistic friction and wear performance (see Table 1 and Figure 2d). High oxygen (>50 at.%) but low molybdenum (<0.5 at.%), sulfur (<2 at.%), and phosphorous (<2 at.%) were detected on the rubbing surface. This suggests that the tribofilm formed in PAO4+PIBSI+MoDTC+[P₈₈₈₈][DEHP] is likely composed of primarily iron oxides with small amount of iron phosphates and sulfides, which evidently failed to provide effective wear protection.

3.5. Tribofilm characterization by STEM

The tribofilm formed by PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] during the elongated test was further examined from the cross section using STEM and EDS, as shown in Figure 7. The tribofilm section shown

in the STEM image is about 150-200 nm thick, which agrees with what the XPS -composition-depth profiles indicated (Figure 5). Elemental maps show Mo, S, P and O in the tribofilm, which is consistent with the above EDS and XPS results, and again suggest that both MoDTC and $[N_{888}H][DEHP]$ played important roles in growing the tribofilm in the elongated run. The tribofilm can be divided into two layers: an amorphous top layer (100-150 nm) and a composite interlayer (~50 nm) that is composed of nanocrystals (<10 nm) in an amorphous matrix. Compared with that formed by $[N_{888}H][DEHP]$ alone ³⁰, while both tribofilms have a two-layer structure, the nanostructures and compositions are quite different. The $[N_{888}H][DEHP]$ -produced tribofilm was reported with a top layer primarily composed of iron phosphates and oxides with lots of nanocrystals embedded in the amorphous matrix and an amorphous interlayer predominantly consisting of iron oxides. ³⁰



Figure 7. Cross-sectional STEM images and EDS elemental maps of the tribofilm on the cast iron flat lubricated by PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] after long sliding test (10,000 m).

4. DISCUSSIONS

4.1. Compatibility among PIBSI, MoDTC, and ILs

Without the PIBSI, the 0.8 wt.% MoDTC could not fully stay afloat in the PAO4 base oil and some brownish precipitates were observed, as shown in Figure S5 in Supporting Information. The EDS elemental maps in Figure S6a in Supporting Information suggest that the precipitates contain Mo, S, O, and C, indicating MoDTC particles. PAO4+PIBSI+MoDTC experienced a friction transition and then had a relatively low and stable COF. Such a type of friction transition has been reported as a sign of formation of a tribofilm containing layer-structured MoS₂. ¹ To further understand the interactions among the PIBSI, MoDTC, and ILs, FTIR was used to analyze PIBSI+MoDTC, PIBSI+IL, MoDTC+IL, and PIBSI+MoDTC+IL mixtures (neat additives, not in oil). The FTIR spectra are compared in Figures 8 and S7 (see Supporting Information). For PIBSI, the peaks around 1705 and 1770 cm⁻¹ can be assigned to the symmetric and asymmetric stretching vibrations of carbonyl groups in cyclic imides, respectively. The double peaks around 1380 cm⁻¹ likely are deformation bands of tert-butyl and the peaks around 920 and 950 cm⁻¹ represent the skeleton vibration of gem-dimethyl ⁵². When mixed with MoDTC, the signature peaks of PIBSI were slightly weakened without distortion or shift, because the concentration of PIBSI within the probe volume decreased.

Blending either $[P_{8888}]$ [DEHP] or $[P_{66614}]$ [BTMPP] into the PAO+PIBSI+MoDTC had detrimental impact on the lubricating behavior (see Figure 2 and Table 1). PAO4+PIBSI+MoDTC+[P_{8888}][DEHP] appeared cloudy and PAO4+PIBSI+MoDTC+[P_{66614}][BTMPP] showed brownish precipitates after 3-day of storage (without wear testing), as shown in Figure S5. Precipitates from both fluids (collected by centrifuging for PAO4+PIBSI+MoDTC+[P_{8888}][DEHP]) are composed of Mo, S, O, and C, indicating MoDTC particles, as suggested by EDS elemental maps in Figures S6b and S6c. One possibility is that PIBSI might preferably bond to and/or react with the IL to leave MoDTC lack of suspension.

This has been confirmed by the FTIR analysis. As shown in Figures 8 and S7a, the absorption intensities of the PIBSI's signature peaks around 920, 950, 1380, 1705, and 1770 cm⁻¹ all are significantly reduced for both PIBSI+[P₈₈₈₈][DEHP] and PIBSI+MoDTC+[P₈₈₈₈][DEHP] (additive blends, no oil) in a similar manner. The less absorption around 1705 and 1770 cm⁻¹ are likely associated with the interactions between

PIBSI's carbonyl and IL's cation $[P_{8888}]^+$. $[P_{8888}]^+$ is a strong electron acceptor and thus is attracted by the electron rich functional group such as C=O of PIBSI to form a complex. This could be accompanied by the lone pair on O moving closer to $[P_{8888}]^+$ resulting in a weakened absorption of C=O. ^{53,54} In addition, the interaction between $[P_{8888}]^+$ and C=O seems to also affect the PIBSI's isobutyl group due to the steric hindrance effect, as indicated by the absorption peak weakening and distortion in fingerprint region, specifically, 1380 cm⁻¹, 920-950 cm⁻¹. FTIR results clearly indicate that PIBSI would preferably interact/react with $[P_{8888}]$ [DEHP] in PAO4+PIBSI+MoDTC+ $[P_{8888}]$ [DEHP], which would cause (i) PIBSI not to provide adequate suspension/dispersion for MoDTC and (ii) $[P_{8888}]$ [DEHP] to be partially consumed or even depleted. While it takes hours to observe MoDTC precipitating out in room temperature storage, such a process is expected to accelerate at the contact interface upon the thermal and mechanical stresses during the 100 °C wear test. Consequently, the lubricant lost the friction reducing (due to MoDTC precipitation) and wear protection (due to IL consumption/depletion by reacting with PIBSI) functionalities.

In contrast, PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] appeared clear upon blending, stayed clear after 3day storage (see Figure S5), and still is clear as of today after more than one year on the shelf. This implies that the PIBSI dispersant had no overwhelming preference to bond and/or react with [N₈₈₈H][DEHP] over MoDTC (i.e., still enough PIBSI available to suspend MoDTC). FTIR spectra of the PIBSI+[N₈₈₈H][DEHP] and PIBSI+MoDTC+[N₈₈₈H][DEHP] additive mixtures (see Figures 8 and S7a) support the hypothesis: the PIBSI's signature peaks slightly decreased, likely due to dilution. The hydrogen bond between [N₈₈₈H]⁺ and [DEHP]⁻ is believed to hinder the interactions between the IL and PIBSI. Therefore, all three additives were able to maintain their functionalities: (i) PIBSI suspending/dispersing MoDTC, (ii) [N₈₈₈H][DEHP] reacting with metal surface to provide wear protection, and (iii) MoDTC adsorbing onto the surface for friction reduction. On the other hand, the protic [N₈₈₈H][DEHP] exists in equilibrium between cation-anion couples and separated neutral molecules (N₈₈₈ and HDEHP) ³⁹. Both N₈₈₈ and HDEHP are classic metal extracting agents and can be used to extract Mo ⁵⁵. Therefore, N₈₈₈ and HDEHP could possibly interact with MoDTC to form some complexes. This might be responsible for the improved MoDTC suspension in PAO4 when [N₈₈₈H][DEHP] was added in the absence of PIBSI, as shown in Figure S5. The superior friction and

wear behavior of PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP] (see Figure 2 and Table 1) are further discussed below in Section 4.2.



Figure 8. FTIR spectra of PIBSI and its mixture with MoDTC and selected ILs (neat additives, no oil).

4.2. Understanding the low-high-low friction behavior of PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP]

Based on the friction behavior and worn surface morphology and composition of $PAO4+PIBSI+MoDTC+[N_{888}H][DEHP]$ in Figure 3, a three-stage tribochemical process is proposed to explain how the $[N_{888}H][DEHP]$ and MoDTC synergistically worked together, as illustrated in Figure 9.

During the initial period (Stage 1), [DEHP]⁻ adsorbs and chemically reacts with steel surface to generate a thin protective tribofilm (<50 nm, according to the XPS composition-depth profiles of Run 1 in Figure 5), primarily composed of iron phosphates and oxides (as suggested by the XPS core level spectra of Run 1 in Figure 6). Meanwhile, MoDTC and newly formed N888-MoDTC and/or HDEHP-MoDTC complexes (as discussed in Section 4.1) would physically adsorb onto the surface to perform as friction reducing agents,

leading to a low COF (0.04-0.05). At a certain point, due to change of the external conditions (e.g., vibration, wear debris abrasion/adhesion, etc.), such a thin tribofilm was broken causing metal-metal contact leading to a high-friction stage (Stage 2). The higher thermomechanical stresses forced MoDTC to decompose and participate in the tribochemical tribofilm formation process. As a result, and a thicker tribofilm (>150 nm, according to the XPS composition-depth profiles of Runs 3-6 in Figure 5) was grown with contributions from both the [DEHP]⁻ and MoDTC (as suggested by the XPS core level spectra of Runs 3, 4, and 6 in Figure 6). After the thick tribofilm stabilized, MoDTC and newly formed N888-MoDTC and/or HDEHP-MoDTC complexes started to establish a new friction-reducing adsorption layer on top to reduce the COF back down to the lower level (~0.04), which is the Stage 3 with demonstrated long-term stability (see Figure 4).

Such a three-stage process eventually builds a chemically-reacted, wear-protective tribofilm with contributions from both [DEHP]⁻ and MoDTC and a physically-adsorbed, friction-reducing film on top by MoDTC and newly formed N888-MoDTC and/or HDEHP-MoDTC complexes. This is very different from the mechanism for the synergism between this IL and an OFM reported earlier ³⁹, which did not form any tribofilm but solely relied on an adsorption film of a network of IL-OFM molecules.



Figure 9. Schematic of the three-stage tribochemical process explain how [N₈₈₈H][DEHP] and MoDTC work together to eventually establish a chemically-reacted, wear-protective tribofilm and a physically-adsorbed, friction-reducing film on top.

5. CONCLUSIONS

In this study, compatibilities among three selected ILs, a MoDTC friction modifier, and a PIBSI dispersant were investigated for lubricating a steel-cast iron contact in boundary lubrication. Both synergistic and antagonistic effects were observed depending on the ILs' chemistry. Adding MoDTC alone into PAO4+PIBSI seemed to effectively reduce friction and wear. Introducing ZDDP to PAO4+PIBSI+MoDTC however showed detrimental impact. More significant antagonism was found when an aprotic IL ([P₈₈₈₈][DEHP] or [P₆₆₆₁₄][BTMPP]) was blended in PAO4+PIBSI+MoDTC: precipitates in the oil and inferior lubricating performance. FTIR analysis indicated that PIBSI would preferably interact/react with the aprotic IL to lose its ability to suspend MoDTC and to partially consume or even deplete the IL. In contrast, no notable interaction/reaction was observed between PIBSI and the protic [N₈₈₈H][DEHP], likely hindered by the strong H-bonding between the IL's cation and anion. Superior

friction reducing and wear protection with ultra-low stead-state boundary lubrication COF (~0.04) were observed for PAO4+PIBSI+MoDTC+[N₈₈₈H][DEHP]. A three-stage tribochemical process is proposed to explain how [N₈₈₈H][DEHP] and MoDTC work together to establish a chemically-reacted, wear-protective tribofilm with contributions from both additives and a physically-adsorbed, friction-reducing film on top by MoDTC and/or IL-MoDTC complexes. Results from this study are not limited to engine lubrication, but rather provide fundamental insights of the compatibilities among three common lubricant components, anti-wear, friction modifier, and dispersant, which are involved in many other lubricant systems as well and therefore are expect to have broad impact on lubricant research and development.

ASSOCIATED CONTENT

Supporting information

The Supporting Information is available free of charge on the ACS Publications website

Friction and wear results of additional tribological tests; Alloy compositions of testing materials; Flash temperature at the beginning of the sliding test for each lubricant; Wear depth profiles and additional SEM and EDS results of selected worn cast iron surfaces; Photos of selected fluids after ultrasonication and storage; EDS elemental maps of the precipitates from selected fluids; and Additional FTIR spectra of mixtures of neat additives

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