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Compatibility Between Various Ionic Liquids and an Organic Friction Modifier as Lubricant Additives

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ABSTRACT

Tribological performance of a boundary lubrication contact is largely dominated by the friction modifier (FM) and anti-wear additive (AW) in the lubricant. While oil-soluble ionic liquids (ILs) have recently demonstrated promising AW functionality, their compatibility with FMs is little known and even less understood for non-ferrous alloys. Here we report the latest results for several selected ILs when used together with an organic FM (OFM) in lubricating a steel-bronze contact. Depending on the IL chemistry, either synergistic or antagonistic effects were observed. The three aprotic ILs ([P₈₈₈₈][DEHP], [P₆₆₆₁₄][BTMPP] and [P₆₆₆₁₄][C₁₇H₃₅COO]) seemed to degrade the OFM's lubricating performance. In contrast, the protic IL [N₈₈₈H][DEHP] exhibited a strong synergistic effect with the OFM, yielding ultra-low steady-state friction coefficient (0.02) and wear rate (<10⁻⁸ mm³/N-m), which significantly outperformed the IL or the OFM alone. Surface characterization found no chemically-reacted tribofilm on the bronze worn surface. On the other hand, a unique physically-adsorbed surface film as a result of interconnection between the IL and OFM molecules by hydrogen bonds is proposed based on chemical analysis. Such an adsorption surface film is expected to be difficult to compress vertically but easy to shear horizontally, leading to low friction and wear.

KEY WORDS:

organic friction modifier, ionic liquid, bronze, synergistic effect, friction reducing, anti-wear

INTRODUCTION

It is estimated that friction losses in automotive applications, primarily in engines and transmissions, are responsible for up to 10-15% of fuel consumption.¹ Engine lubricants are designed to lubricate the engine moving parts, reduce friction, protect against wear, and remove contaminants from the engine. Advance in lubricant technology is considered one of the most effective ways to achieve fuel economy in modern engines.² A commercial engine lubricant is composed of base oil(s) and a series of additives with different functionalities, such as anti-wear (AW), friction modifier (FM), antioxidant, detergent, dispersant, viscosity modifier, etc.³ Tribological behavior of an engine oil largely depends on the FM(s) and AW(s). In practice, FM and AW are often used together in an engine oil to balance the tribological performance under various lubrication regimes experienced by different engine components.^{4, 5} From the chemical perspective, both the FM and AW are polar molecules and interact (adsorption and/or chemical reaction) with the contact surfaces, and therefore either synergistic or antagonistic effects could occur between a set of FM and AW in terms of friction reduction and wear protection. Therefore, it is fundamentally important to understand the compatibility between FMs and AWs.⁶

Currently, there are two main types of FMs used in engine lubricants, metal-free organic FMs (OFMs) and organic-molybdenum based FMs, such as molybdenum dialkyldithiocarbamate (MoDTC). The most widely used AW is zinc dialkyldithiophosphate (ZDDP), which has been used in engine oils for more than 70 years. The compatibilities between ZDDP and various Mo-based FMs have been extensively studied. Depending on the contact surface materials and experimental conditions, either synergistic or antagonistic effects were reported.⁷⁻¹⁰ In contrast, much less is known about the interaction between ZDDP and OFMs.^{5, 11}

On the other hand, due to increasing concerns about ash/deposit generation and catalyst poisoning by ZDDP, there is strong demand to develop more effective, ashless AWs.³ Ionic liquids (ILs) possess unique physicochemical properties, as well as excellent tribological performance, and have shown significant potential for lubrication.^{12, 13} Use of ILs as lubricant additives became technically feasible after overcoming the oil-solubility barrier in 2012.¹⁴ Since

then, various oil-miscible ILs with promising anti-scuffing/anti-wear functionalities have been developed and studied.¹⁴⁻¹⁷ These ILs are ashless and possess excellent tribological properties, and thus are being considered as candidates to replace ZDDPs in engine oils.¹⁸ However, to the best of our knowledge, there is no literature in the public domain reporting the compatibility between ILs and OFMs.

Bronze alloys possess low friction and good corrosion resistance, which make them ideal materials for high strength bushings and journal bearings.¹⁹⁻²² In diesel engines, bronze alloys are commonly used in connecting rod end journal bearings that normally operate under elastohydrodynamic lubrication (EHL), but also inevitably experience boundary and mixed lubrication under certain circumstances such as running-in and start-stop periods. Most AWs and FMs were designed for ferrous alloys and their compatibility with bronze is not well understood.

This study aims to investigate the compatibility between an OFM and selected AWs, including several ILs and a secondary ZDDP, for a steel-bronze contact under boundary lubrication. While the ZDDP and most ILs seemed to compete with the OFM on the contact surface, a protic ammonium-phosphate IL exhibited a synergistic effect with the OFM leading to an ultra-low friction coefficient (~0.02) and a very low wear rate. The mechanisms are discussed based on surface characterization and chemical analysis.

MATERIALS AND EXPERIMENTAL

Materials

A synthetic base oil, poly alpha olefin (PAO 4 cSt, noted as PAO4), and an OFM were provided by Exxon Mobil Corp. While the exact molecular structure is not known, Fourier-transform infrared spectroscopy (FTIR) (see the Discussion section) and proton nuclear magnetic resonance (H NMR) (Figure S1) spectra suggest that the OFM is a mixture of partial polyesters with saturated long hydrocarbon chains and free hydroxyls. A secondary ZDDP was supplied by Lubrizol Corp. Four ILs tetraoctylphosphonium bis(2-ethylhexyl) phosphate [P₈₈₈₈][DEHP], trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate $[P_{66614}][BTMPP]$, trihexyltetradecylphosphonium stearate $[P_{66614}][C_{17}H_{35}COO]$, trioctylammonium bis(2-ethylhexyl) phosphate $[N_{888}H][DEHP]$ were synthesized in our lab. Detailed synthesis procedures for the ILs had been reported previously.¹⁴⁻¹⁷ The molecular structures of the ZDDP, ILs, and OFM (estimated based on chemical analysis) are depicted in Figure 1. Lubricant samples were made by adding 0.8 wt.% OFM alone or together with a ZDDP or an IL at the same molecular concentration (specifically, 0.8 wt.% ZDDP, 1.04 wt.% $[P_{8888}][DEHP]$, 0.99 wt.% $[P_{66614}][BTMPP]$, 0.99 wt.% $[P_{66614}][C_{17}H_{35}COO]$, or 0.87 wt.% $[N_{888}H][DEHP]$) into the PAO base oil.



Figure 1. Molecular structures of the ILs, ZDDP and OFM (estimated).

Chemical analysis

FTIR spectra of different additives were recorded in the range of 650 to 4000 cm⁻¹ using a Perkin Elmer FTIR spectrometer (Frontier LR 64912C) equipped with Universal ATR Sampling Accessory.

Proton nuclear magnetic resonance (NMR) analysis of the OFM was carried out using a Bruker MSL-400 at 400 MHz. The spectrum was obtained in CDCl₃ with reference to tetramethylsilane (TMS, 0 ppm) for ¹H, and results are presented in the Supporting Information (see Fig. S1).

Tribological Testing

Boundary lubrication tests were conducted on a Plint TE 77 tribometer under a ball-on-flat contact configuration. A bronze plate $(25.37 \times 25.37 \times 6.35 \text{ mm}^3)$ slid against an AISI 52100 bearing steel ball (10 mm diameter). The steel ball was a Grade 25 bearing ball with roughness in the range of 25-50 nm (R_a). The roughness of the bronze flat before wear testing was ~120 nm (R_q). Table 1 summarizes the composition and hardness of the test materials. Tests were carried out under a 20 N load (Hertzian contact stress at the beginning of the test was calculated to be 1.65 GPa) and an oscillation frequency of 10 Hz with a stroke of 10 mm, at 100 °C for 1000 m of sliding. The contact interface was fully submerged in the lubricant and at least two repeat tests were conducted at each condition. Friction force was captured in situ by measuring the tangential force using a piezoelectric load cell and the friction coefficient was calculated by normalizing the friction force by the normal load. After tests, contact surfaces were quantified using a Wyko NT9100 white light interferometer.

Table 1. Composition and hardness of the test material.				
Materials	Composition (%)	Vickers Microindentation Hardness (load)		
AISI 52100	C, 1.04%; Mn, 0.11%; Si, 0.25%; Cr, 1.58%; Balance-Fe	878 (500 gf)		
Bronze	Cu, 81-85 %; Pb, 6-8%; Sn, 6.3-7.5%; Zn, 2-4 %	116 (200 gf)		

The lubrication regime is determined by the λ ratio (h/σ) which represents the ratio of lubrication film thickness (h) to the composite roughness (σ) at the contact area. The central

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lubricant film thickness at the stroke midpoint (maximum velocity) was calculated to be about 8 nm using Hamrock and Dowson formula.²³ The composite roughness σ is defined as $\sqrt{R_{q,ball}^2 + R_{q,plate}^2}$ and the steel-bronze contact in this study was calculated to be more than 125 nm before the wear testing. Therefore, the λ ratio at the contact interface was far less than 1 in the entire oscillation stroke indicating boundary lubrication in the beginning of the test.

Surface Characterization

The morphology and chemical composition of the bronze plate worn surfaces after the tribological testing were examined using a Hitachi TS-4800 (Tokyo, Japan) field emission scanning electron microscope (SEM) equipped with energy-dispersive x-ray spectroscopy (EDS). EDS analysis was done at a potential of 10.0 kV over a time span of 60 s for each measurement. A scanning transmission electron microscopy (STEM) sample was prepared using a Hitachi NB-5000 dual-beam focused ion beam (FIB) system with a gallium source to extract a thin cross-section of the selected area on the wear scar. A protective tungsten layer was deposited on the tribofilm prior to the FIB process. STEM imaging and EDS elemental mapping were conducted from the cross-section to study the nanostructure and composition of the surface boundary film.

Chemical compositions of the bronze surface inside and outside the wear scar were analyzed using a Thermo Scientific K-Alpha X-ray photoelectron spectroscope (XPS). Al-Ka x-rays, focused to a 250 micron spot, were used to excite photoelectrons that were measured with a hemispherical electron energy analyzer and 128 channel detector. Composition-depth profiles were measured using an argon ion sputter gun (2 KeV Ar ions) for up to 500 seconds. XPS data were analyzed using Thermo Avantage (v.4.61).

RESULTS

Tribological Properties

The friction traces of the experimental lubricants are depicted in Figures 2 and S3, each curve

representing the average of two repeated tests. The wear volumes, worn surface roughness, and steady state friction coefficients (COF, mean value of the last 200 m sliding) are listed in Tables 2 and S1. A strong correlation was observed among the steady-state friction coefficient, wear volume, and worn surface roughness: all three values increasing or decreasing together.

Initially, the neat PAO4 base oil was used as the baseline but it showed very poor repeatability among the tests (Figure S2) because it was prone to scuffing failure and sensitive to contamination. Instead, PAO4 containing 0.8 wt.% OFM was chosen as the baseline, and as shown in Figure 2, its COF started at 0.08 and ended with a steady state value of 0.075. Interestingly, when being used alone, the OFM outperformed the ZDDP and ILs in terms of both friction coefficient (see Figures 2 and S3) and wear rate for the steel-bronze contact (see Tables 2 and S1).

When the OFM was combined with the ZDDP or an IL, the friction and wear behavior could be either improved or deteriorated, depending on the chemical compatibility, as shown in Table 2. PAO4 containing the OFM together with the ZDDP or any of the three aprotic ILs $([P_{8888}][DEHP], [P_{66614}][BTMPP], and [P_{66614}][C_{17}H_{35}COO])$ produced higher friction coefficient and poorer wear protection compared with the oil containing the OFM alone. This likely is due to their competition on the surface adsorption, which is further discussed in Section 4.

In contrast, a significantly reduced COF was achieved by adding 0.87% wt.% [N₈₈₈H][DEHP] into the fluid PAO4+0.8 wt.% OFM, leading to a steady state COF as low as 0.03, about 50 % reduction. The wear volume ($0.85 \times 10^7 \,\mu\text{m}^3$) for using the OFM+[N₈₈₈H][DEHP] combination was much lower (by 65%) than that ($2.48 \times 10^7 \,\mu\text{m}^3$) when using the OFM alone. This implied a synergistic effect between OFM and [N₈₈₈H][DEHP]. To validate it, PAO4 containing 0.87 wt.% [N₈₈₈H][DEHP] (without OFM) was tested under the same condition. The COF had an initial spike but quickly dropped below 0.1 and then fluctuated around 0.09 and the wear volume was $10.5 \times 10^7 \,\mu\text{m}^3$. Evidently, using OFM and [N₈₈₈H][DEHP] together produced significantly better lubricating performance than either alone.





Figure 2. Friction coefficient traces of lubricants containing the OFM alone, OFM+ZDDP, OFM+IL, or IL alone.

Table 2. Steady state COF and wear volume and worn surface roughness of the bronze flat

Lubricant	Steady state	Wear volume ($\times 10^7$	Scar roughness
	COF	μm^3)	(R_q, nm)
PAO4 + 0.8 wt.% OFM	0.075	2.48 ± 0.82	167
PAO4 + 0.8 wt.% OFM+0.8 wt.% ZDDP	0.086	3.65±1.00	225
PAO4+0.8 wt.% OFM+1.04 wt.%	0.127	8.39±2.00	493
[P ₈₈₈₈][DEHP]	0.137		
PAO4+0.8 wt.% OFM+0.99 wt.%	0.126	13.90±1.90	394
[P ₆₆₆₁₄][C ₁₇ H ₃₅ COO]	0.130		
PAO4+0.8 wt.% OFM+0.99 wt.%	0.114	8.26±0.20	216
[P ₆₆₆₁₄][BTMPP]	0.114		
PAO4+0.8 wt.% OFM+0.87 wt.%	0.022	0.85±0.07	81
[N ₈₈₈ H][DEHP]	0.032		
PAO4+0.8 wt.% OFM+0.87 wt.%	0.020	0. 82	87
[N ₈₈₈ H][DEHP]-10000 m	0.020		
PAO4+0.87 wt.% [N ₈₈₈ H][DEHP]	0.090	10.5±1.85	251

Elongated test of PAO4 containing both OFM and [N₈₈₈H][DEHP]

In Figure 2, it's worth noting that the oil containing both the OFM and [N₈₈₈H][DEHP]

shows a clear trend of COF decreasing along with the sliding distance, and does not seem to reach a true steady-state by the end of the 1000 m of sliding. In order to learn how low the COF may reach, an elongated test (10,000 m) was carried out and the friction trace (bold blue line) was depicted in Figure 3 with the friction traces of four repeat tests of 1000 m sliding in the insert. The similar COF curves for the four 1000 m tests show good repeatability. The COF of the elongated test gradually decreased from about 0.1 to below 0.02 in the first 3000 m of sliding, though with some fluctuation, and eventually stablized at around 0.02.

Since COF 0.02 is significantly below the conventional range of COF in boundary lubrication (0.05-0.15),²⁴ it was initially thought that the lubrication regime might have shifted from boundary to mixed lubrication during sliding as a result of more conformal contact (due to wear) and smoother contact area. The wear scars on the bronze flat and steel ball were examined to validate the hypothesis. The radius of curvature across the wear scar on the bronze flat was measured to be 5.97 mm and the worn surface roughness was 87 nm. The wear loss and roughness change on the steel ball were minimal. The central lubricant film thickness at the stroke midpoint was calculated²³ to be about 10 nm and the composite roughness was calculated to be >90 nm. Thus, the λ ratio evidently was still far less than 1, suggesting boundary lubrication even after 10,000 m of sliding. Therefore, the ultra-low COF (0.02) was attributed to an easy-to-shear surface film on the contact surface formed by the OFM+[N₈₈₈H][DEHP].

In addition, it was interesting to notice that the wear volume of the bronze plate after 10,000 m sliding test $(0.82 \times 10^7 \,\mu\text{m}^3)$ was similar to or even slightly smaller compared to that after the 1,000 m sliding test $(0.85 \times 10^7 \,\mu\text{m}^3)$. In other words, little wear occurred between 1,000 and 10,000 m of sliding. Since the contact interface was under boundary lubrication throughout the 10,000 m of sliding, the strong wear protection (wear rate: $4.1 \times 10^{-8} \,\text{mm}^3/\text{N-m}$) on the bronze surface would have to be provided by either a chemically-reacted tribofilm or a physically-adsorbed surface film or both. However, no evidence for the tribofilm was found in worn surface characterization as presented in Section 3.4. The surface film produced by the OFM+[N₈₈₈H][DEHP] is further discussed and compared with those formed by other OFM-AW

combinations in Section 4.



Figure 3. Friction traces of an elongated test (10,000 m of sliding) and several repeated standard tests (1,000 m of sliding) of PAO4+OFM+[N₈₈₈H][DEHP].

Roles of the cation and anion of [N₈₈₈H][DEHP] in the synergism with OFM

[N₈₈₈H][DEHP] is a protic IL, produced by transferring a proton from the Brønsted acid HDEHP to the Brønsted base N888. This creates proton-donor and acceptor sites, which may be used to build up a hydrogen-bonding network.²⁵ Ideally for protic ILs, the proton transfer is complete from the acid to the base, however, in reality, this is unlikely, resulting in a transition equilibrium between the neutral species and ions.²⁶ In order to understand the interactions between the OFM with the IL anion or cation alone, OFM plus 0.415 wt.% HDEHP or 0.455 wt.% N888 (same molecular concentration as OFM+[N₈₈₈H][DEHP]) were added to PAO4, respectively, and the blends were tested for 1000 m of sliding. As compared in Figure 4, PAO4+OFM+HDEHP produced a similar friction behavior (gradually decreasing and dropped below 0.035 by end of the test) and wear volume with PAO4+OFM+[N₈₈₈H][DEHP]. In contrast, the COF of PAO4+OFM+N888 decreased in a slower pace and seemed to stabilize at a higher level (0.06) than that of PAO4+OFM+[N₈₈₈H][DEHP] (0.035) but still lower than that of PAO4+OFM alone (0.08). The wear volume in lubrication of PAO4+OFM+N888 was similar to PAO4+OFM+[N₈₈₈H][DEHP], significantly lower than that of PAO4+OFM alone. Results

suggest that both the cation and anion of $[N_{888}H]$ [DEHP] have synergism with the OFM in lubricating the steel-bronze contact and the anion-OFM interactions is primarily responsible for the ultra-low friction.



Figure 4. Friction and wear results of PAO4 containing OFM, OFM+[N₈₈₈H][DEHP], OFM+N888, and OFM+HDEHP.

Worn surface characterization

The surface morphologies of worn surfaces of the bronze plates are presented in Figure 5. As shown in Figure 5a, PAO4+OFM generated a relatively smooth surface with mild plastic deformation and only Cu and a small amount of O were detected on the worn surface. The addition of ZDDP resulted in a higher wear rate but did not significantly change the worn surface morphology. Only a small amount of S and O were found on the wear scar without detectable Zn or P, as shown in Figure 5b, which is distinct from ZDDP-lubricated ferrous alloy worn surfaces that often contain abundant signature elements including Zn, P, and S.²⁷ The EDS spectrum implies that no significant tribochemical reactions took place between ZDDP and the bronze surface. The small amount of S may be ascribed to the strong chelating effect between sulfur and copper.

Similarly, to ZDDP, $[P_{8888}]$ [DEHP] also had a detrimental effect on tribological performance when added to PAO4+OFM. The SEM images in Figure 5c clearly show long grooves, small craters, and material smear, which implied that the contact area experienced a combination of

abrasive wear, adhesive wear, and plastic deformation. The rough appearance is in line with the increased surface roughness shown in Table 2. The absence of P, signature element of the IL, in the EDS spectrum indicates no IL-induced tribofilm on the worn surface.

For the PAO4+OFM+[N₈₈₈H][DEHP], a much more narrow wear scar was detected in both short (1000 m) and long (10,000 m) tests, as shown in Figure 5d and 5e, respectively. Both worn surfaces appeared uniform and smooth with little sign of adhesion or plastic deformation, which correspond well to the low wear and roughness reported in Table 2. While this fluid exhibited superior friction and wear behavior, no IL or OFM-induced tribofilm was detected on the worn surface as lack of P, N, or C peak in the EDS spectrum.



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Figure 5. SEM images and EDS spectra of the bronze worn surfaces tested in PAO4+OFM for 1000 m (a); PAO4+OFM+ZDDP for 1000 m (b); PAO4+OFM+[P₈₈₈₈][DEHP] for 1000 m (c); PAO4+OFM+[N₈₈₈H][DEHP] for 1000 m (d); PAO4+OFM+[N₈₈₈H][DEHP] for 10,000 m (e).

Cross-sectional STEM imaging and EDS elemental mapping were conducted on the bronze worn surface lubricated by PAO4+OFM+[N₈₈₈H][DEHP] after the elongated test, as presented in Figure 6. There is clearly a subsurface plastic deformation zone (about 2.5 μ m thick) with a refined grain structure, as a result of repeated normal contact and shear (1 million times for the 10,000 m of sliding). The EDS elemental maps showed no N, P, or O in the near surface zone, suggesting no tribofilm formed by the IL or OFM on the bronze surface. This agrees with the top surface SEM/EDS examination described above.



Figure 6. Cross-sectional TEM images and EDS elemental maps of the bronze worn surface lubricated by PAO4+OFM+ $[N_{888}H]$ [DEHP] after the elongated sliding test (10,000 m). A tungsten layer was deposited onto the worn surface before the FIB process to protect the surface from damage.

XPS was employed to further analyze the chemical composition of the bronze surface lubricated by PAO4 containing both OFM and $[N_{888}H][DEHP]$ after the elongated (10 km sliding) tribological test. Figure 7 shows the composition-depth profile on the wear track (on track) compared with that outside the wear track (off track). Both of the detected areas contain

significant amount of C and O which is probably due to adsorption of the OFM and/or $[N_{888}H][DEHP]$. The similar P concentrations on the wear track (3.7 %) and outside of wear track (3.6 %) as well as the easy removal of the P (P signal was essentially gone by a few nm sputtering) suggested that the P on bronze surface was due to physical adsorption rather than chemical adsorption, agreeing with the EDS and STEM results above.



Figure 7. XPS composition-depth profile on the wear track (a, a' zoomed in) and outside area (b, b' zoomed in) of the bronze surface lubricated by PAO4+OFM+[N₈₈₈H][DEHP] after the elongated sliding test (10,000 m).

DISCUSSION

The classic working mechanism for OFMs is that their amphiphilic molecules self-assemble on a metal surface either by physical adsorption or chemical reaction to form vertically oriented, close-packed layers while their hydrocarbon chains extend into the base fluid and associate with

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one another and the base oil by intermolecular forces to form a low-friction surface film.^{3, 4} The film thickness and effectiveness in friction control not only depend on the OFM molecular structure, which determines the interactions with the metal surface as well as the intermolecular van der Waals forces for self-assembly, but also are influenced by external factors such as interaction with other additives in the lubricant, surface alloy composition, contact pressure, shear rate, and temperature.³ Based on the above theory, the tribological behavior of the experimental lubricants in this study is discussed below.

PAO4 additized with the OFM alone showed an intermediate level of COF and wear volume for the steel-bronze contact. The polar portion of the OFM molecule (see Figure 1) may attach onto the steel and bronze surfaces by hydrogen bonding and its hydrocarbon tail extends into the base oil, perpendicular to the metal surface. van der Waals forces and hydrogen bonds help the OFM molecules to align themselves such that they form multi-molecular clusters that are parallel to one another. Therefore, the OFM intermolecular bonding and the interactions with the metal surface are the dominating factors influencing the tribological performance. As shown by the FTIR spectrum of the OFM in Figure 8, the wide peak around 3420 cm⁻¹ of hydroxyl absorption peak confirms strong intermolecular hydrogen bonding among OFM molecules.

For the mixture of OFM and $[P_{8888}]$ [DEHP], FTIR analysis showed the hydroxyl peak shifts from 3420 cm⁻¹ to 3220 cm⁻¹, implying a strong intermolecular hydrogen bond formed between OFM and $[P_{8888}]$ [DEHP], which is expected to interfere with the self-assembly of OFM molecules in the surface film formation. What's more, competition in surface adsorption between $[P_{8888}]$ [DEHP] and OFM is inevitable. As a result, the integrity of the OFM surface film is rather low or even no adsorption-based surface film is formed. On the other hand, $[P_{8888}]$ [DEHP] evidently couldn't form a typical anti-wear tribofilm on the bronze surface via tribochemical reactions as it usually does on a steel or cast iron surface.^{15, 18} Consequently, neither OFM nor $[P_{8888}]$ [DEHP] could work effectively to provide proper protection for the bronze surface.

The FTIR spectra of OFM+ $[P_{66614}][C_{17}H_{35}COO]$ and OFM+ $[P_{66614}][BTMPP]$ showed a red-shift of the hydroxyl peak similar to OFM+ $[P_{8888}][DEHP]$, which can be used to explain the



similarly deteriorated tribological behavior when they were used together with the OFM.

Figure 8. FTIR spectra of OFM, OFM+ZDDP, and OFM+IL (analysis on the neat additives without diluted in the PAO base oil).

The combination of ZDDP and OFM didn't show a shift of the hydroxyl absorption peak, which means ZDDP has negligible effect on the OFM film self-assembly. However, the sulfur atoms in the ZDDP molecule have a strong chelating effect with copper causing a competition with OFM in adsorption onto the bronze surface. This explains why the addition of ZDDP into PAO4+OFM did not help on wear protection but rather slightly degraded the friction behavior.

The mixture of the OFM and $[N_{888}H]$ [DEHP] showed a smaller red-shift compared with the mixtures of OFM with other three ILs. Since the protic $[N_{888}H]$ [DEHP] contains a significant amount of N888 and HDEHP neutral molecules in a transition equilibrium with N888H⁺ and DEHP⁻ ions, the interactions of N888 and HDEHP with OFM are considered separately here. As shown in Figure 8, no sign of red-shift was observed for either the N888 or HDEHP when mixed with the OFM, which suggests that the hydrogen bonds between the N888 or HDEHP and the OFM molecules are in a similar energy level to that among the OFM molecules themselves. We believe that these newly formed intermolecular hydrogen bonds between the OFM and the N888 or HDEHP are a key factor influencing the tribological performance.

First, the new OFM-N888 or OFM-HDEHP hydrogen bonds may not destroy the

integrity of the OFM-assembled surface film due to the similar energy level.

- Second, the OFM-N888 or OFM-HDEHP hydrogen bonds could enhance the affinity between the OFM molecules and the metal surface. The OFM-N888 or OFM-HDEHP complex has a higher polar/nonpolar ratio and possesses more polar fronts than the OFM to promote more interactions with the metal surface.
- Last, the OFM-N888 or OFM-HDEHP hydrogen bonds could enhance the intermolecular forces inside the OFM self-assembly film. It is well recognized that van der Waals forces are mainly responsible for the formation of self-assembly film of an OFM.³ The additional hydrogen bonds may lead to formation of a denser, more closely packed layer-structured surface film. Such a film is difficult to compress in the vertical direction but easy to shear, which is responsible for the outstanding friction reducing and wear protecting behavior.

It is worth noting that the N888 and OFM-HDEHP from [N₈₈₈H][DEHP] do not function in the same way in interacting with OFM. Both the N888 and OFM-HDEHP are able to enhance the affinity between the OFM and the metal surface through formation of additional hydrogen bonds to provide wear protection, as illustrated in Figure 9. Their impact on the friction behavior however was different. The -POOH functional group in HDEHP could help OFM form a strong intermolecular network in the bulk fluid by connecting adjacent OFM molecules through donating and accepting protons simultaneously, which is believed to be crucial for achieving the ultra-low COF in the oil containing OFM+HDEHP. In contrast, due to the absence of N-H bond, N888 can only act as a proton acceptor and is incapable of connecting adjunct OFM molecules. Therefore, the intermolecular hydrogen bond between N888 and OFM is much weaker than that between HDEHP and OFM, and, as a result, the friction reduction by N888+OFM was less significant than that by HDEHP+OFM. While HDEHP seemed as effective as [N₈₈₈H][DEHP] in friction reduction when used together with the OFM, HDEHP is not recommended in practice due to its high chemical reactivity posing a corrosion risk.



Figure 9. Schematic diagram of tribological mechanism of combination of OFM and [N₈₈₈H][DEHP]

CONCLUSIONS

In this work, the compatibility between an OFM and selected AWs (including a secondary ZDDP and four different oil-soluble ILs) for a steel-bronze contact in boundary lubrication was investigated. The main findings are summarized as follows:

1) The addition of ZDDP slightly degraded the tribological performance of the OFM. ZDDP may physically adsorb onto the bronze surface by the strong chelating effect between its sulfur atoms and the copper atoms, which inevitably is in competition with the OFM surface adsorption impairing the integrity of the OFM surface film.

2) Depending on the IL chemistry, either synergistic or antagonistic effect was observed when used together with the OFM.

3) The OFM seemed to not work well with the three aprotic ILs ($[P_{8888}][DEHP]$,

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 $[P_{66614}][BTMPP]$ and $[P_{66614}][C_{17}H_{35}COO]$), resulting in increased friction and wear. Strong intermolecular hydrogen bond and competitive adsorption between OFM and the aprotic ILs are believed to interfere with the self-assembly of the OFM molecules, causing deterioration in the surface film properties.

4) In contrast, the protic IL [N₈₈₈H][DEHP] showed a strong synergistic effect with the OFM, yielding an ultra-low steady-state friction coefficient (0.02) and wear rate ($<10^{-8}$ mm³/N-m), significantly outperforming the OFM or the IL alone. Surface characterization of the bronze worn surface found no chemically-reacted tribofilm and thus the superior tribological performance is hypothetically attributed to a physically-adsorbed surface film constructed by the OFM and [N₈₈₈H][DEHP] combination. FTIR analysis suggested that the N888 and HDEHP molecules in the IL may form intermolecular hydrogen bonds with the OFM molecules at a similar energy level as that among the OFM surface film, they do not impair the film integrity but instead enhance the attraction with metal surface by their higher polarity and strength the interactions among the OFM molecules by the stronger hydrogen bonds. As a result, the surface film becomes more difficult to compress vertically but easier to shear horizontally, leading to low friction and low wear.

Supporting Information

Proton NMR spectrum of the OFM, Friction traces of repeat tests of the PAO4 base oil, Friction traces of PAO4 containing ZDDP or selected ILs, Summary of friction and wear results of PAO4 containing ZDDP or selected ILs.

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