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DESIGN AND SYNERGISTIC INTERACTION OF ETHERAMINE-BASED ASH-FREE ORGANIC FRICTION MODIFIERS WITH ZDDP

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Abstract: *Engine oil is crucial for optimal internal combustion engine performance. With tightening global emissions regulations, low-viscosity engine oil development has become a key trend, aiming to reduce viscosity while maintaining or enhancing engine protection and improving fuel economy. However, low-viscosity lubricants face challenges in boundary lubrication, where friction and wear are more pronounced. Lubrication additives, particularly friction modifiers and anti-wear agents like zinc dialkyl dithiophosphate (ZDDP), are essential in addressing these issues. Although ZDDP effectively prevents wear, it can increase friction coefficients, potentially reducing fuel efficiency. Building on prior work on sulfur-free organic friction modifiers, this study explores the synergistic effects and mechanisms of alkylated end-amine polyether derivatives (SA) combined with ZDDP in low-viscosity engine oil. Tribological test results demonstrated that combining SA with ZDDP significantly lowered friction coefficients and wear condition. Mechanistic studies suggest that polar nitrogenous compounds in organic FMs preferentially adsorb onto friction surfaces, delaying ZDDP film formation. Simultaneously, nitrogen atoms form coordination bonds with electron-deficient sites on ZDDP films, enhancing adsorption and further reducing friction. This dynamic interaction between organic FMs and ZDDP underpins their synergistic lubrication performance. The research offers a vital theoretical foundation and practical guidance for developing high-performance, environmentally friendly low-viscosity engine oils.*

Keywords: *Organic friction modifier, Low-viscosity lubricants, Synergistic effects, Anti-wear performance, Lubricant mechanism*

1. INTRODUCTION

Engine oil is crucial for maintaining the performance of internal combustion engines [1-3]. With increasingly stringent global emissions regulations, low-viscosity engine oil technology has emerged as a significant trend [4]. This trend demands that lubricants reduce viscosity while maintaining or enhancing engine protection and improving fuel economy. To meet these requirements, it is essential to optimize the hydrodynamic properties of the lubricating oil to minimize dynamic shear, agitation, and friction pumping losses [5]. However, this optimization introduces new challenges, particularly in boundary lubrication areas where friction and wear are prevalent, and the risk of direct metal-to-metal contact becomes more pronounced. Consequently, lubrication additives play a critical role in formulations, helping to counteract insufficient lubrication caused by reduced viscosity [6-8].

Engine oils typically contain a variety of additives designed to enhance fuel economy, efficiency, and extend the lifespan of engine components. Among these, friction modifiers and anti-wear agents are particularly important when the lubrication film thickness is less than the average roughness of the contact surfaces [9]. Friction modifiers improve lubrication and energy efficiency by adjusting the friction characteristics at the contact interface. Both organic and inorganic friction modifiers are widely used in engine oil formulations to enhance performance in boundary and mixed lubrication regimes [10-12]. Additionally, zinc dialkyl dithiophosphate (ZDDP), the most common anti-wear additive in engine oils, forms a protective film at the contact interface by decomposing, preventing direct contact between rough surfaces [13]. Despite growing environmental concerns and the need to find phosphorus-free alternatives to ZDDP, progress in developing such alternatives without compromising tribological performance has been slow. As a result, ZDDP remains a key component in most engine oil formulations.

Although ZDDP's anti-wear film is highly effective, it can also increase the coefficient of friction, thereby reducing fuel economy [14-16]. To address this issue, ZDDP can be combined with appropriate friction modifiers to reduce the friction coefficient in boundary lubrication conditions. While some friction modifiers synergize well with ZDDP to enhance anti-friction effects, others may produce antagonistic effects [17]. Research has shown that certain friction modifiers, particularly primary amine compounds, can significantly degrade or even completely destroy the ZDDP friction film while effectively reducing boundary friction [18]. Therefore, understanding the interaction between friction modifiers and ZDDP during the friction process and uncovering their compounding mechanisms is of great importance for the development of advanced lubricant formulations.

In previous studies, we developed a series of sulfur-free organic friction modifiers [19]. Our findings revealed that alkylated end-amine polyether derivatives demonstrated outstanding anti-friction and anti-wear performance as additives in low-viscosity lubricating oils. To further evaluate their suitability for low-viscosity engine oils, we selected polyalphaolefin (PAO) and synthetic ester as base oils, both of which are widely used in engine oil formulations. This study investigates the synergistic effects and underlying mechanisms of an alkylated terminal amine polyether derivative (SA) in combination with the anti-wear agent ZDDP. The wear surface components were examined using energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS). The synergistic effects were discussed, and the underlying mechanisms were explored. The research offers a significant theoretical foundation and practical insights for the development of high-performance, environmentally friendly low-viscosity engine oils.

2. TRIBOLOGICAL EVALUATION

The tribological properties were evaluated on a Bruker UMT tribolab friction tester. The composition and physical properties of base oil are shown in Table 1.

For the UMT reciprocation friction tests, the ball (diameter of 8 mm, AISI 52100 steel) slides reciprocally at a stroke of 10 mm with a frequency of 4 Hz against the lower steel plate (AISI 304). A normal force of 3 N was loaded on the ball. Each friction test was performed at least twice to ensure the repeatability.

Table 1 Composition and viscosity of base oil

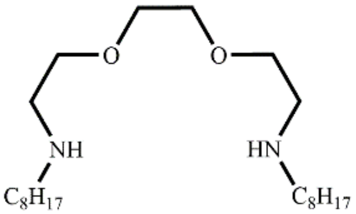
Composition (v/v)	Kinematic viscosity@40 ℃（mm^2/s）	Kinematic viscosity@100 ℃（mm^2/s）	Viscosity Index
PAO8/3970（8/2）	42.131	7.007	126

3. RESULTS AND DISCUSSION

3.1 Investigation of the Synergistic Effects of the Organic Friction Modifier SA with ZDDP

Comparison of Anti-Friction Properties of the Composite Systems

In this paper, the synergistic anti-friction properties of compound SA and ZDDP were investigated using UMT point-on-flat reciprocating friction experiments. The molecular structure of SA was shown in Fig. 1.



SA

Figure 1. The molecular structure of SA

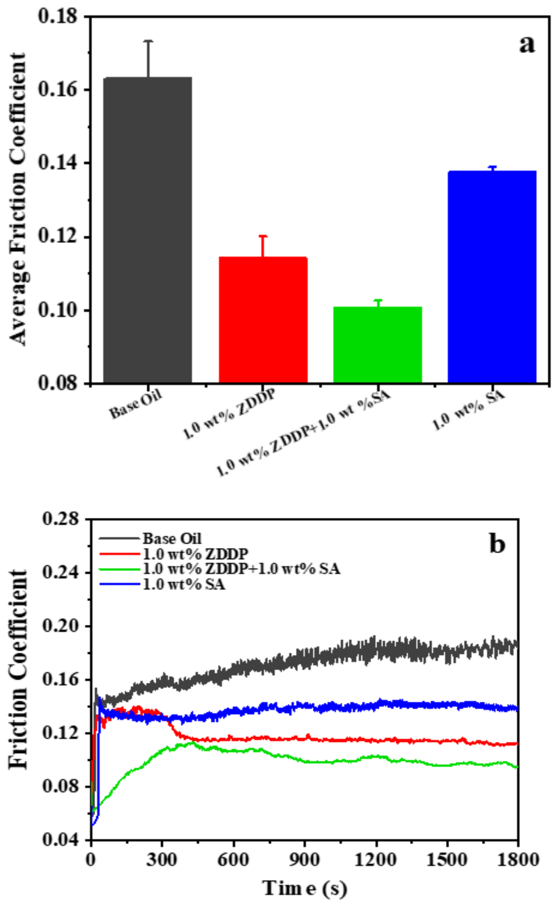


Figure 2. Comparison of average friction coefficient (a) and friction coefficient curve (b) of different types of organic friction modifier combined with ZDDP

ZDDP and SA were each added to the base oil at a concentration of 1.0 wt%, and the average friction coefficient and friction coefficient curves of the resulting oils were compared, as shown in Fig. 2.

The results indicate that the friction coefficient of the oil containing both friction modifier SA and ZDDP is significantly lower than that of the oil with ZDDP alone. As shown in the friction coefficient curve in Fig. 2, the oil mixture of SA and ZDDP consistently exhibits a lower friction coefficient without an obvious run-in period.

Comparison of Anti-Wear Properties between Friction Modifier and ZDDP

The surface morphology of the steel plate after the friction experiment was examined using a white light interferometer, and the wear width and depth were measured, as shown in Fig. 3. For the oil containing only ZDDP, the wear width and average depth were 0.281 mm and 2.665 µm, respectively. Upon combining SA with ZDDP, the wear width and depth were reduced by 41.6% and 74.9%, respectively. These results demonstrate that the combination of SA and ZDDP exhibits significant synergistic anti-friction and anti-wear effects.

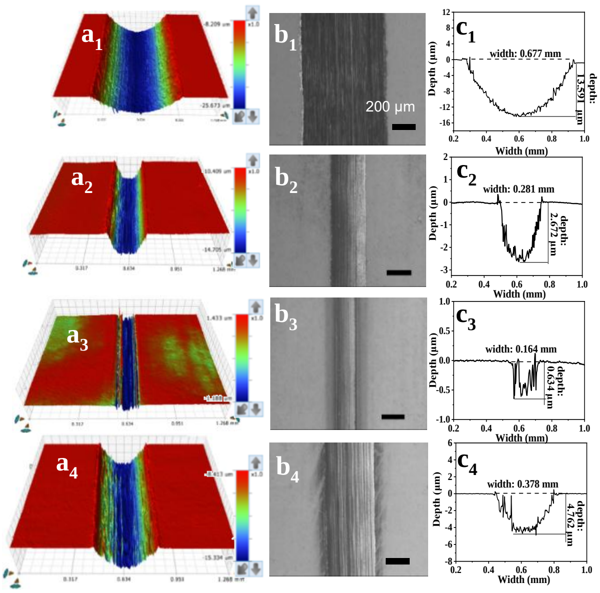


Figure 3. Three-dimensional morphology, micrographs, width and depth of wear marks on the surface of the experimental steel ball after the combination of SA and ZDDP (a_1/b_1/c_1: base oil; a_2/b_2/c_2: 1 wt% ZDDP; a_3/b_3/c_3: 1 wt% ZDDP + 1 wt% SA; a_4/b_4/c_4: 1 wt% SA)

3.2 Investigation of the Synergistic Mechanism between Friction Modifier and ZDDP

EDS analysis of worn surfaces

To investigate the synergistic mechanism between the organic friction modifier and ZDDP, EDS analysis was conducted on the surface of the steel plate after the compounding experiment with SA and ZDDP. Fig. 4 presents the surface morphology and elemental analysis results of the steel ball following the UMT point-on-flat friction test at room temperature. The results show that after the friction experiment, black deposits of varying degrees were observed at the edges of the wear marks. EDS analysis of these deposits revealed that the steel plate lubricated with oil containing only ZDDP exhibited the presence of Fe, C, O, and P elements. In contrast, the steel plate lubricated with the oil mixture of SA and ZDDP primarily contained Fe, C, and O elements, with no significant signals for P or S elements.

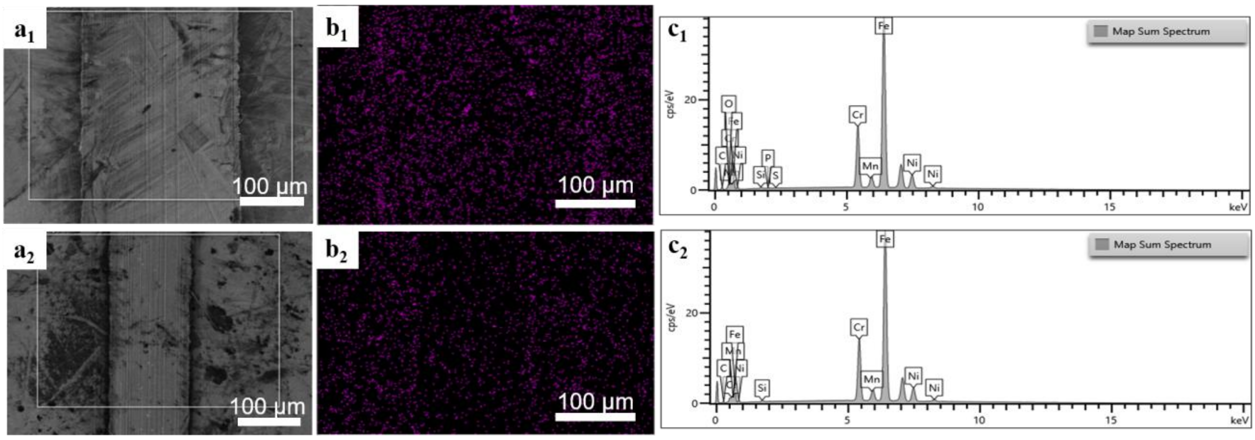


Figure 4. Surface morphology of wear marks after UMT point-surface friction experiment, EDS-mapping of C element and energy spectrum results ($a_1/b_1/c_1$: 1.0 wt% ZDDP, $a_2/b_2/c_2$: 1.0 wt% ZDDP + 1.0 wt% SA)

XPS analysis of worn surfaces

XPS was employed to analyze the valence states of elements on the worn surface. Fig. 5 presents the XPS spectra of Zn2p, C1s, O1s, N1s, P2p, and S2p. In the Zn2p spectrum, two symmetric peaks are observed at 1022.0 eV and 1044.7 eV, corresponding to Zn2p 3/2 and Zn2p 1/2, respectively, indicating the presence of Zn^{2+}. The presence of Zn^{2+} (indicated by Zn2p peaks) and ZnO (indicated by the O1s peak at 530 eV) suggests the formation of a zinc-based protective film on the worn surface, which is crucial for reducing wear and friction.The C1s spectrum shows peaks at 283 eV and 285 eV, representing sp^3 and sp^2 hybridized carbon, respectively. The O1s spectrum features a peak at 530 eV attributed to ZnO, while the peak at 532 eV originates from non-bridging oxygen and other oxygen-containing groups in the polythiophosphorus chain, such as sulfate, carbonate, or hydroxide. The N1s spectrum exhibits a peak at 400 eV corresponding to C-N/N-H bonds. The P2p signal is derived from phosphorus in the phosphate chain within the friction film.The binding energy difference between Zn3s and P2p3/2 can indicate the phosphate chain length, as reported in previous studies [20]. A larger difference suggests a shorter chain length. Since the binding energy difference between Zn3s and P2p3/2 is essentially the same for the friction films formed by the two oils, it is inferred that the phosphate chain lengths are similar. The difference in the peak intensity of P2p3/2 in the two systems indicates that the chemical state of phosphorus is different, which may be related to the action of additives. The S2p spectrum shows a peak at 164.4 eV corresponding to the C-S bond, while peaks near 168.4 eV likely correspond to sulfur oxides [21], indicating the presence of oxidized sulfur species. Both systems have characteristic peaks of $-SO_2$ and S-C, but the intensity and location of the peaks are different, reflecting the

differences in the chemical environment and existence form of sulfur in different systems.
The similar phosphate chain lengths (indicated by the consistent binding energy differences between Zn2p and P2p3/2) suggest that the combination of SA and ZDDP does not significantly change the chain length but rather enhances the overall effectiveness of the film through complementary mechanisms. ZDDP provides a robust phosphate-based film, while SA improves the film's stability and reduces friction through its organic components, leading to enhanced tribological performance.

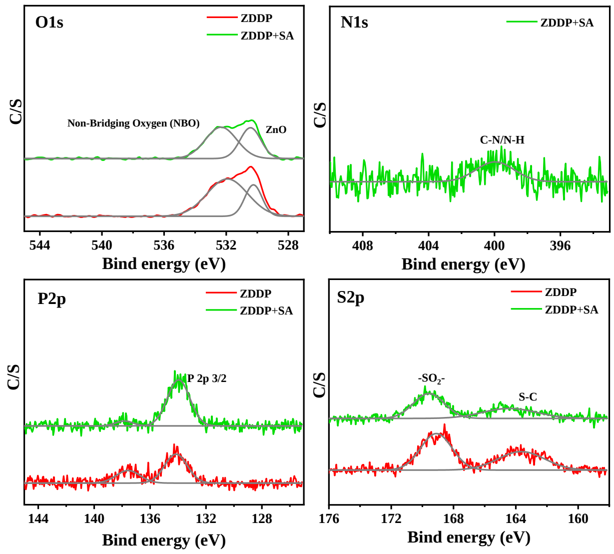


Figure 5. XPS spectrum of worn surface after UMT point-surface friction test

4. CONCLUSION

In this paper, we investigated the synergistic effects of the synthetic organic friction modifier SA with ZDDP and preliminarily explored their synergistic mechanism through the analysis of wear surfaces. The following conclusions can be drawn:

(1) Friction experiments demonstrated that SA significantly enhanced the tribological performance when combined with ZDDP, indicating a strong synergistic effect between the two additives.

(2) EDS and XPS analyses of the steel plate surfaces after experiments revealed the presence of zinc and iron oxides, phosphates, and sulfur oxides on the friction surfaces. These results suggest that nitrogen-containing friction modifiers (such as SA) were effectively adsorbed onto the friction surfaces. During the experiments, SA molecules and ZDDP competed for adsorption sites on the surface. The more polar nitrogen-containing compounds in SA were preferentially adsorbed, thereby delaying the formation of the ZDDP anti-wear protective film.

(3) Overall, the combination of SA and ZDDP exhibited significant synergistic anti-friction and anti-wear effects, attributed to the competitive adsorption and coordination interactions between SA and ZDDP on the friction surface.

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