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Article

The Influence of Ionic Liquids Additives on the Tribological Properties of Molybdenum Amide Complexes

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Abstract: Ionic liquid as a new lubrication additive which form adsorption film on the surface of the friction pair, reduce friction and wear, and have good anti-wear performance and high-temperature resistance. The molybdenum ammonia complex can generate MoS_2 on the friction surface and reduce the friction between friction pairs. There have been a lot of studies on the lubrication properties of molybdenum ammonia complex, or the ionic liquid additive alone. However, the corresponding research on the lubrication and wear-reduction properties of the two compounds steel need more search. Therefore, the effects of ionic liquid additives on the tribological properties of molybdenum-ammonia complexes were studied in this paper. It is found that the friction coefficient can be reduced by adding an ionic liquid additive, and the anti-wear effect of the molybdenum ammonia complex on lubricating oil can be improved. Among them, at 50°C and 20N, the mixed oil sample of "base oil + molybdenum ammonia complex + ionic liquid additive" has the best comprehensive friction performance, and the friction coefficient is 0.062, which is 0.02 lower than that of the mixed oil sample of "base oil + molybdenum ammonia complex".

Keywords: Molybdenum ammonium complex; Ionic liquid additive; Friction coefficient; Lubricating performance

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1. Introduction

The ship's primary power source is the internal combustion engine. As the marine industry continues to grow, the demands on internal combustion engines are also increasing, which include increasing demands on the engine's load, temperature, and rotational speed, all of these necessitate the use of lubricating oil. The internal combustion engine's friction lubrication conditions are rather harsh, necessitating both an improvement in the engine's structure and lubricant formula's composition. The lubricant and additive requirements are gradually raised. The addition of additives to lubricating oils has emerged as a key strategy for enhancing their anti-wear and wear-reduction properties. Scholars have focused a lot of emphasis on ionic liquid additives and molybdenum-ammonia complexes as lubricant additives in recent years due to their improved anti-wear and wear reduction performance. Ionic liquids, a novel class of lubricant additives, have superior wear-reduction capabilities and excellent temperature tolerance. They may also create an adsorption film on the surface of the friction sub-surface to lessen wear and friction. MoS_2 can be produced on the friction partner's surface by the molybdenum-ammonia complex, which also lowers friction between the friction partners. Many researchers have conducted numerous studies on molybdenum amine complexes and ionic liquid additives. Li et al. investigated the oil-soluble molybdenum amine complex additives and used a four-ball testing machine to assess the products' tribological characteristics in 150SN base oil. According to the findings, the additive in 150SN base oil exhibits specific anti-wear properties [1]. The development process of molybdenum amine complexes was described by Jiang et al. They also explained that when combined with ZDTP, molybdenum amine complexes have excellent lubricating properties and can greatly enhance lubricant performance, including anti-oxidation, anti-wear, friction reduction, and weak corrosion to metals [2].

The categorization of organic molybdenum lubricating additives based on their sulfur and phosphorus content was first presented by Jing et al. [3]. Jing examined the impact of an organic molybdenum additive package on the high-temperature micromotional and sliding wear performance of 45 steel/GCr15 bearing steel friction parts. The findings demonstrated that the organic molybdenum additive created a composite surface protective layer comprised of adsorbed phosphate and a chemical reaction film including FeS and MoS_2 on the metal surface by breakdown, adsorption, and friction chemical reaction. According to Gao et al., organic molybdenum is progressively moving toward low sulfur and phosphorus or pollution-free, sulfur and phosphorus-free [4]. Molybdenum dithiophosphate additions improved the base oil's antiwear performance by 53%, its friction reduction performance by 40%, and its extreme pressure loading capacity by more than double, according to an experimental investigation conducted by Shi et al. [5]. On the surfaces of five distinct materials, including bearing steel, aluminum alloy, and titanium alloy, Ling et al. examined the impact of non-sulfur phosphorus oil-soluble organic molybdenum (SPFMo) additives on the tribological characteristics of low viscosity lubricant (0W-20) at varying temperatures, loads, and speeds. The findings demonstrate that SPFMo can considerably enhance 0W-20's anti-friction and anti-wear properties on the surfaces of all five materials.

With the exception of titanium alloy, all four materials can lower the friction coefficient from 18% to 23% at higher temperatures, making the impact of SPFMo more noticeable [7]. Using an SRV friction and wear tester, Zou added SPFMo to 0W-20 lubricant and thoroughly examined the tribological characteristics under various load and temperature conditions. The findings demonstrated that molybdenum will be enriched during the friction process and that a friction chemical reaction will produce sulfur.-sulfur-containing composite friction-reducing sheet layer with molybdenum and oxygen-molybdenum-oxygen, achieving anti-wear and friction-reducing properties [8]. Ionic liquid additives have been shown to have good lubricating qualities in recent years, and several studies have been conducted in this area by both domestic and international researchers. In order to test the tribological properties, viscosity, and corrosion on copper sheets of two different base lubricants, Hao synthesized over ten different types of ionic liquid additives. This demonstrated that the ability of ionic liquid additives to aid lubrication in different base oils varies and that additives containing sulfur and halogen corrode more on copper sheets [9].

A new research method to study the lubrication mechanism of ionic liquid additives was provided by Yang et al., who examined the tribological properties of in-situ ionic liquid additives under mixed or fluid lubrication and tested the tribological properties of the added ionic liquid additives under various conditions using a miniature traction tester [10]. Lisha et al. designed and synthesized an ionic liquid-based organic molybdenum compound (IOMo), which was found to improve the anti-wear and wear reduction properties when compounded with ZDDP [11]. IOMo was found to improve antiwear and wear reduction properties when used in combination with ZDDP [11]. In order to create MoS_2, Rodríguez et al. used friction surfaces with metallic Mo in the presence of a lubricant containing sulfur. They discovered that MoS_2 reduced friction, whereas when the lubricant lacked sulfur, friction was high and unstable [12].

After preparing three environmentally friendly organic molybdenums with varying structures that are free of sulfur and phosphorus, Zhao et al. discovered that the uniform and dense friction film made up of molybdenum disulfide, molybdenum oxide, sulfate, phosphate, and polyphosphate had excellent antiwear and wear reduction properties [13]. Sun et al. synthesized two new amino acid-based ionic liquids (AAILs) and investigated their tribological properties as water-ethylene glycol (W-EG) lubricant additives. The derived and friction-chemically produced films of these two ionic liquids can increase the lubricating properties of the lubricants, and these two ionic liquids have good prospects for application in metallic fluids and hydraulic fluids [14]. Eight water-soluble ionic liquids were created by Zhang et al., who then examined their tribological characteristics as additions to base fluids made of water-diethylene glycol (WDG). Adsorbed films and friction films were two of the suggested lubricating techniques that successfully decreased shear stresses and, consequently, sliding friction [15]. Zhang et al. looked at how ionic liquids when added to base lubricants, affected their capacity to form films as well as their wear and friction characteristics. The findings demonstrated that ionic liquids as additions can successfully lower wear and friction when compared to base oil and base grease. Under high load circumstances, it is more evident that lubricants with ionic liquid additives have thicker films. Ionic liquids can be added to base oil to efficiently lessen its level of depletion [16]. Ionic liquids have an excellent compatibility with polyurea greases, according to research from Lanzhou Institute of Chemical Physics on the possible use of ionic liquids in greases. Excellent friction reduction and antiwear capabilities were noted at high temperatures when 1% of ionic liquids based on alkyl imidazoles were added to polyurea grease for steel/steel friction partners [17]. The tribological characteristics of greases with 10% and 20% ionic liquids added under steel/steel contact conditions were examined by Li et al. using a UMT-3 friction and wear tester. The findings demonstrated that bis(trifluorosulfonate) ionic liquids, as a conductive additive, can greatly increase the conductivity of lithium grease. Surface abrasion investigation demonstrates that the wear in the contact zone is greatly improved under reciprocating motion circumstances, and the lubricating power of lithium grease may be considerably increased by adding bis(trifluorosulfonate) ionic liquid additive. When the ionic liquid grease is exposed to an electric field for a while, its lubricating properties are further improved [18]. According to the investigation into the influence influence of ionic liquid-nano kaolin composite additives on friction reduction performance, the ionic liquid additives perform best at 90 °C, with a friction factor of roughly 0.025. When the nano-kaolin and ionic liquid additives are combined together, the friction factor of the friction vice is greatly decreased [19]. Numerous research has examined the lubricating qualities of ionic liquid additives and molybdenum-ammonia complexes separately, but the experiments of the lubricating and wear-reducing properties of the two combined still lack of further study. In order to improve the lubrication performance of the friction substitutes, it is crucial to investigate how ionic liquid additives affect the tribological properties of molybdenum-ammonia complexes.

Based on domestic and international research findings, tribological performance experiments were conducted using the HK09-type ring-block friction and wear tester The objectives were to investigate the tribological performance of ionic liquid-molybdenum-ammonia complex additives in the same load at different temperatures.

2. Materials and Methods

2.1 Material

The synthetic base oil PAO10 lubricant with a viscosity index of around 143, the viscosity at 100 °C is 10.21 mm^2/s.

Trihexyl(tetradecyl) phosphonium bis (2,4,4-trimethylpentyl)phosphinate, an ionic liquid additive, is used in this paper. Its molecular formula is $C_{48}H_{102}O_2P_2$, Its basic physical quantity is 773.27, its density is 0.895 g/mL at 20ºC, and the purity is 98%. Figure 1 displays the ionic liquid additive along with its chemical formula.

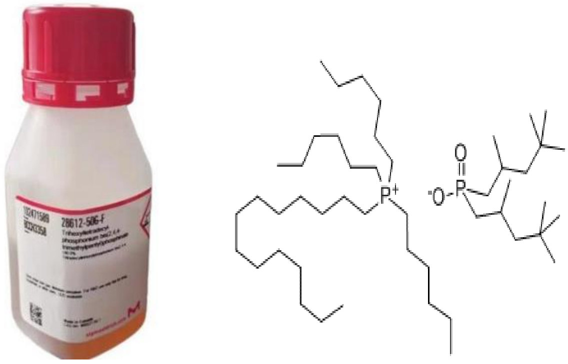

Figure 1. Ionic liquid additives and their chemical formulas

Because molybdenum-ammonia complexes don't contain substances like phosphorus and sulfur, they can be utilized as lubricants to reduce friction loss and have specific anti-wear and wear-reducing qualities that can help the environment.

The friction specimens in this experiment is made of bearing steel, which is frequently used in marine internal combustion engines, in order to replicate the actual friction environment and improve the accuracy of the experimental data. The friction surface is the circular surface of the friction ring and flat surface of block. Figure2 shows the friction block and friction ring.

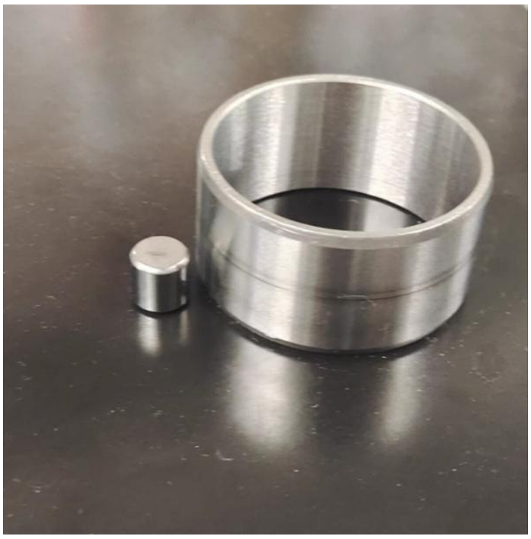

Figure 2 Friction block and friction ring

2.2 Experimental Methods

The HK09 type ring and block type friction and wear tester are used in this experiment; its essential components are as follows: The friction ring is rotated by a servo motor to create friction with the friction block. Pressure transducer: The pressure transducer measures the friction value and sends it to the computer via the data collector. Loading device: The loading and display components make up this experimental machine's device. By turning the bolt, the loading part presses the spring downward and sends the pressure signal to the display via the sensor and data line. The display part connects the loading and display parts via the data line to show the pressure and modifies the load based on the display while loading. Friction block fixed part: This component is the friction block fixed on a boom. To create friction, a revolving bolt pushes down on the friction block to make contact with the friction ring. Friction ring fixed shaft: Servo motors rotate this shaft, which has a friction ring mounted to it. The lubricating oil is heated in part by the adjustable heating oil tank, which is positioned beneath the friction ring. The data transmission portion, which is made up of a data collector and a data line, is designed to collect and transmit data at a specific frequency. The computer then uses this data to obtain the data curve needed for the experiment. Figure 3 displays a friction and wear tester of the HK09 ring block type.

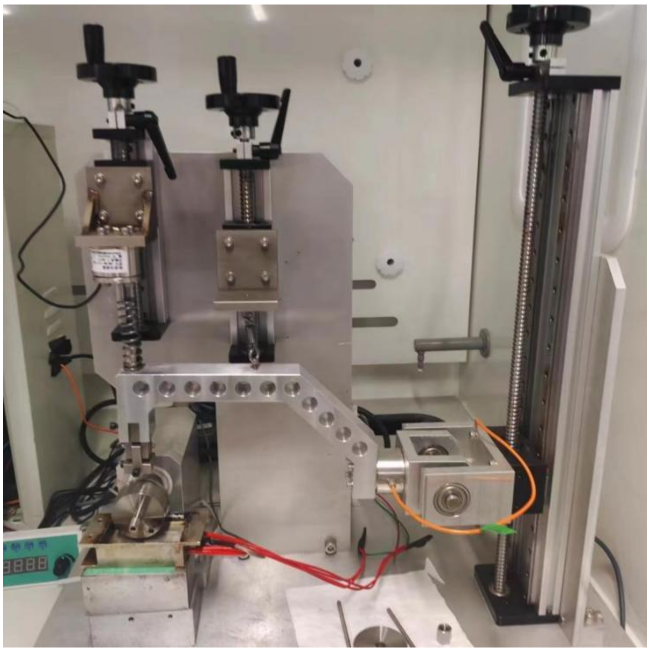

Figure 3. HK09 Ring Block Type Friction and Wear Tester

2.3 Experimental procedure and parameters

To guarantee a clean surface, the friction ring and friction block were ultrasonically cleaned for five minutes using anhydrous ethanol. The experimental oil samples were put into the oil tank. The compositions and mass fractions of the two experimental oil samples for this investigation are displayed in Table 1. The trials were carried out in four groups, each experiments were conducted for eight hours, with the experimental temperatures at 50°C, 70°C, 90°C, and 110°C, and the loads being 5N, 10N, 20N, and 40N, respectively. One group of "base oil + molybdenum-ammonia complex" and one group of "base oil + molybdenum-ammonia complex + ionic liquid" composition were evaluated under 50°C and 20N load conditions. The loading trials were conducted under 5N, 10N, 20N, and 40N. Following the test, the friction blocks were examined under an electron microscope to determine the width of the abrasion marks, the friction surface condition, and other information.

Table 1. Composition and mass fraction of experimental oil samples

Experimental oil samples	Molybdenum ammonia complex / wt%	Ionic liquid /wt%	Base oil PAO10 /wt%
Base Oil + Molybdenum Ammonia Complex	1	0	99
Base oil + molybdenum-ammonia complex + ionic liquid additive	1	1	98

3. Results

3.1 Friction reduction performance with the variation of temperature

(1) Base Oil PAO10 + Molybdenum Ammonia Complex

Figure 4 displays the friction coefficient data for the oil samples labeled "base oil + molybdenum-ammonia complex." between 50°C and 70°C, the friction decreases from high to low and then tends to be stable; between 90°C and 110°C, the friction gradually increases and then tends to be steady, although it has been routinely changing within a specific period. The last and most constant friction coefficient at the experimental temperature is 0.656 in the case of 70°C.

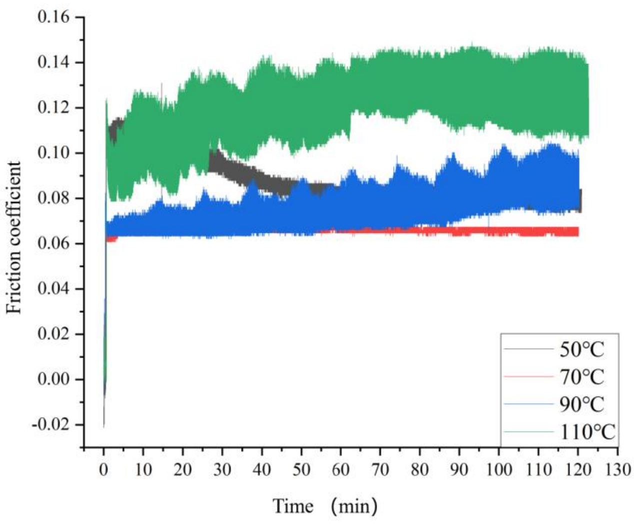

Figure 4. Friction coefficient of "base oil + molybdenum-ammonia complex" mixed oil samples at different temperatures

(2) Base oil PAO10 + molybdenum ammonia complex + ionic liquid additive

Figure 5 displays the friction coefficients of the friction tests conducted at various temperatures with an oil mixture consisting of "base oil + molybdenum-ammonia complex + ionic liquid additive" under a load of 20N. Although it can vary within a specific range, the friction coefficient generally tends to be consistent at all four temperatures.

As the temperature increases and the stability varies, the coefficient of friction continues to change. First, the friction coefficient rises between 50°C and 70°C and falls between 70°C and 90°C and 110°C. However, the data routinely varies within a specific range, where the friction coefficient at 50°C is 0.062 and at 110°C it is 0.058. Compared to the last set of studies, this group's friction coefficient change is more erratic and variable.

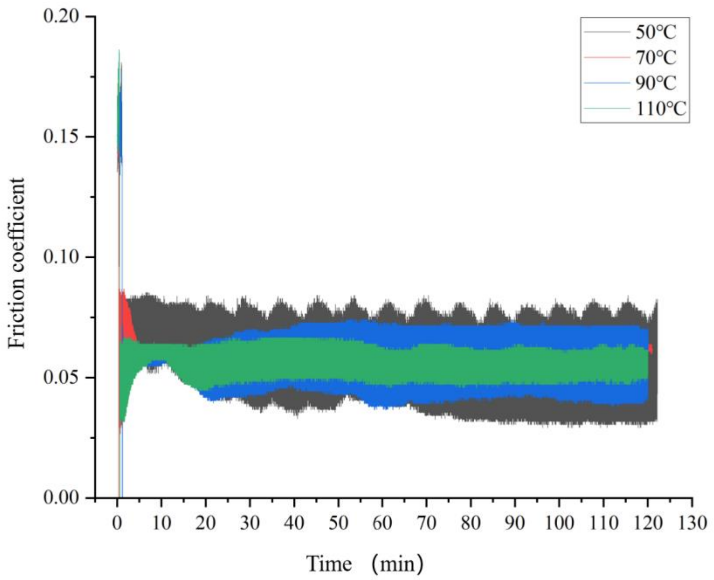

Figure 5. Friction coefficient at different temperatures of “base oil + molybdenum-ammonia complex + ionic liquid additives” mixed oil samples

Figure 6 shows the comparison of two groups of experiments at 50°C load 20N, 70°C load 20N, 90°C load 20N, and 110°C load 20N, respectively. As can be seen from the figure, the coefficient of friction is reduced after adding an ionic liquid additive, and the data tends to be stable in general, but the fluctuation after adding an ionic liquid additive is larger than that without adding.

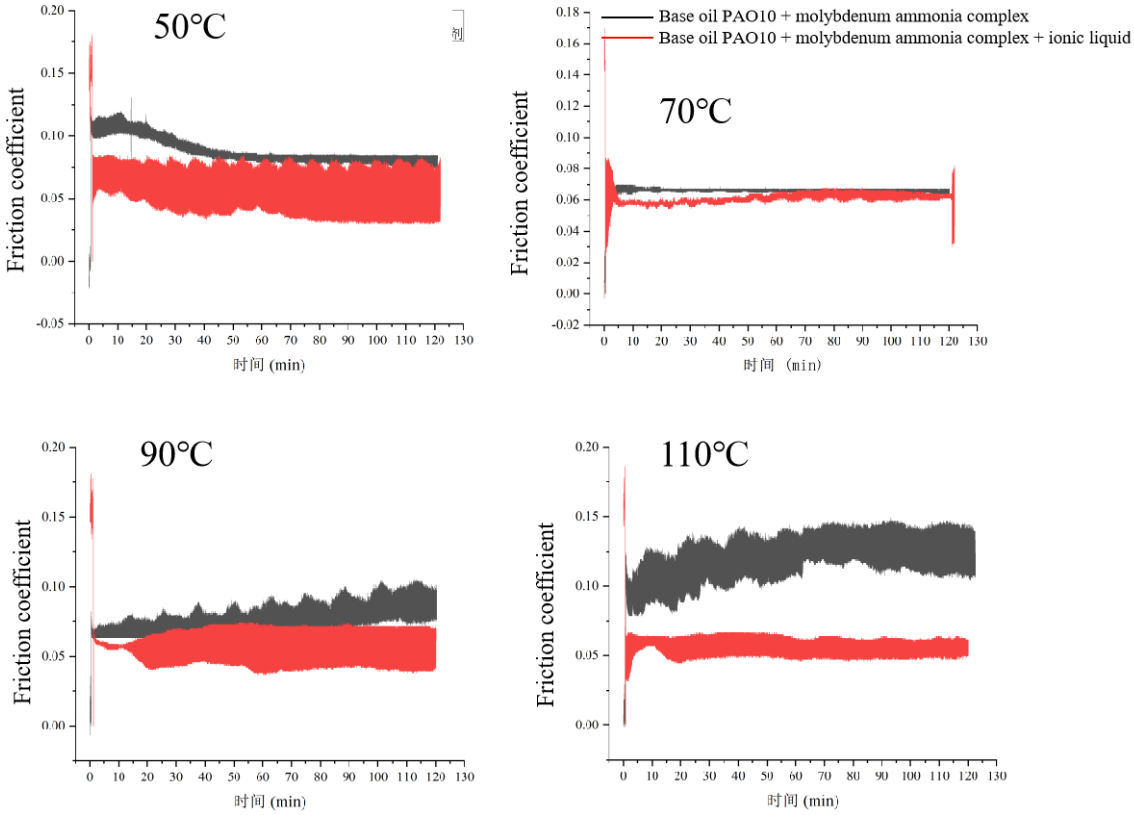

Figure 6. Comparison of friction coefficients of two oil samples at 50°C, 70°C, 90°C, 110°C

Each of these two experimental groups needs to be chosen as an appropriate temperature for the load test. The average friction coefficient is the lowest and the coefficient of friction curve is more steady in the load trials conducted with the "base oil + molybdenum-ammonia complex" mixed oil sample group at 70 °C; Given the poor oil solubility of the ionic liquid additive [20], the experimental data of the group without ionic liquid additive, and the fact that the friction coefficient and friction curve of "base oil + molybdenum-ammonia complex + ionic liquid additive" do not change regularly with the temperature and fluctuate more than those without ionic liquid additive, the temperature of this group of load experiments was chosen to be 50°C. The temperature of this loading experiment group was chosen at 50°C due to the low oil solubility of ionic liquid additives and the experimental data of the group without ionic liquid additions.

3.2 Friction reduction performance with the variation of load

(1) Base Oil PAO10 + Molybdenum Ammonia Complex

As illustrated in Figure7, the trials were conducted at 70°C with four loads of 5N, 10N, 20N, and 40N. According to data analysis, the "base oil + molybdenum ammonia complex" mixture's friction coefficient is comparatively consistent under four distinct loads; the average friction coefficient is lowest at 5N, 0.049, and highest at 20N, 0.065.

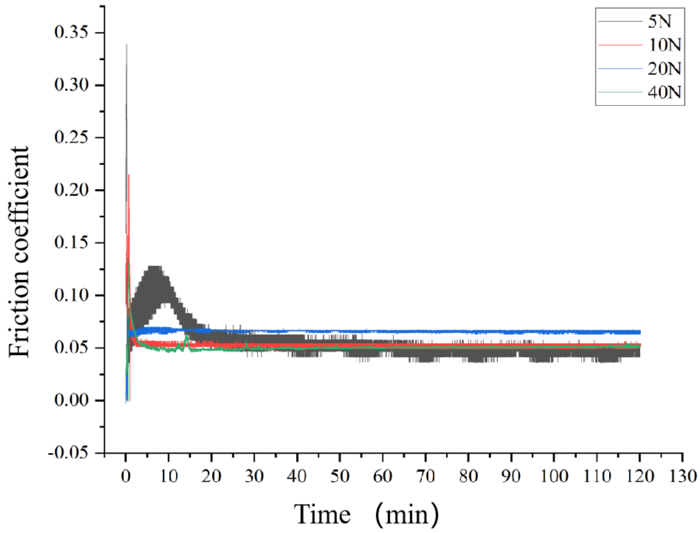

Figure7 Comparison of friction coefficients of “base oil + molybdenum-ammonia complex” blended oil samples at different loads

(2) Base oil PAO10 + molybdenum-ammonia complex + ionic liquid additive loading experiment

As illustrated in Figure8, this set of experiments was conducted at 50°C with four sets of loads of 5N, 10N, 20N, and 40N. According to data analysis, the average coefficient of friction was highest at 40 N and lowest at 50°C when the load was 20 N (0.062 and 0.089, respectively). The coefficient of friction increased from 5 N to 10 N, decreased from 10 N to 20 N, and then began to grow from 20 N to 40 N. Overall, the coefficient of friction curve was quite smooth.

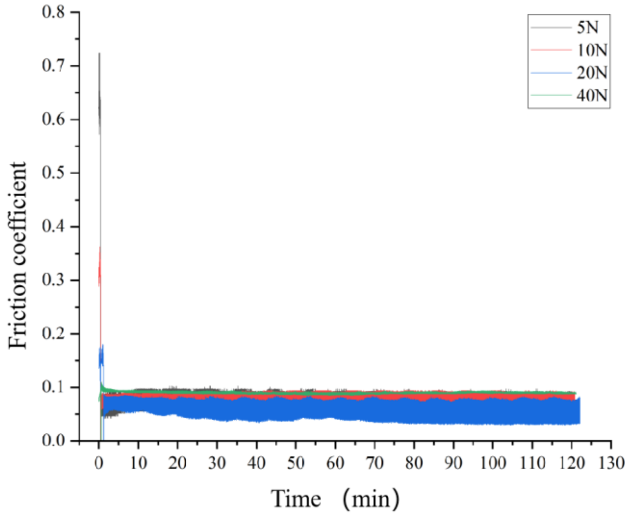

Figure 8. Comparison of friction coefficients of “base oil + molybdenum-ammonia complex + ionic liquid additives” blended oil samples at different loads

3.2 Analysis of tribological properties of molybdenum-ammonia complexes by ionic liquid additives

(1) Tribological performance tests of "base oil + molybdenum-ammonia complex" blends with and without the addition of ionic liquid additives at various temperatures yielded a range of friction coefficients. When ionic liquid additives were added at 50°C, 70°C, 90°C, and 110°C, the average coefficients of friction were compared and found to decrease.

The friction coefficient without adding ionic liquid additives at 50 ℃, and 70 ℃ are more stable, the friction coefficient curve can tend to be stable, 70 ℃, the best comprehensive friction performance, the average friction coefficient of 0.066; adding ionic liquid additives friction coefficient is not so stable compared to the time of adding ionic liquid additives, 50 ℃, the best comprehensive friction performance, the coefficient of friction of 0.062. 0.062.

(2) It is shown that the effect of load on the friction coefficient after the addition of ionic liquid additives is greater than a critical value and that the comprehensive friction performance is best when the load is 20N. The load test is conducted at 70°C without the ionic liquid additive, and the friction coefficient changes with the load first increasing and then decreasing; after the addition of the ionic liquid additive, the friction coefficient first increases with the increase of load, then decreases and then increases. Right now, the average coefficient of friction is 0.062.

3.3 Friction surface and abrasion width analysis

(1) Analysis of the experimental friction block surface by X-ray photoelectron spectroscopy(XPS) demonstrated that the mechanism of friction reduction on the friction surface was the generation of MoS_2, as shown in Figure 9.

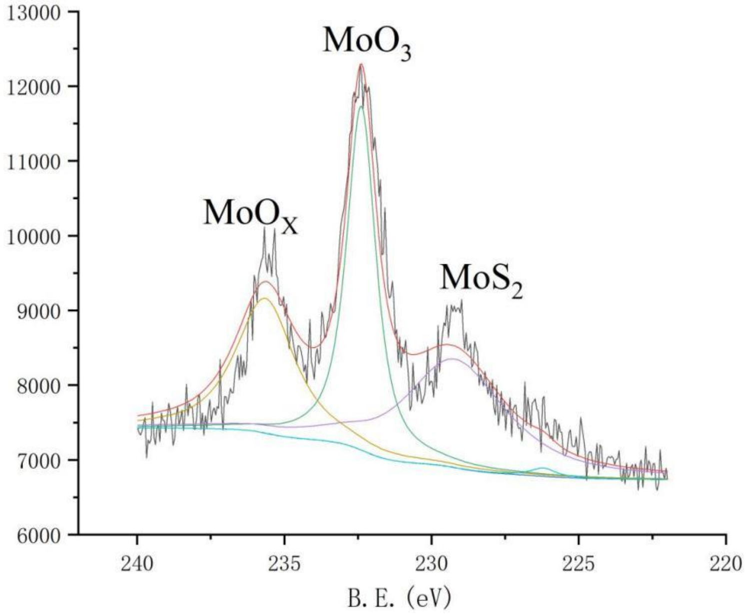

Figure 9. Friction surface analysis of XPS

(2) The abrasion width analysis reveals that, under the specified conditions, the experimental oil samples with varying formulas had varying abrasion widths. Figure10

displays the results of a microscope analysis of the surface abrasion width of the friction blocks of the "Base oil + Molybdenum ammonia complex" blend and "Base oil + Molybdenum ammonia complex + Ionic liquid additive" that were tested at various temperatures under a 20N load. According to the graph analysis, the average cumulative abrasion width of the blends "Base oil + Molybdenum-ammonia complex" and "Base oil + Molybdenum-ammonia complex + Ionic liquid additive" at various temperatures under a 20N load is 585.50μm and 509.980μm, respectively. For the mixed oil samples under a 20N load, the average cumulative abrasion breadth at various temperatures was 509.980μm. The data comparison demonstrates that the addition of ionic liquid additives reduces the breadth of the wear marks, demonstrating that the ionic liquid additives can enhance the anti-wear and wear reduction capabilities of molybdenum-ammonia complexes.

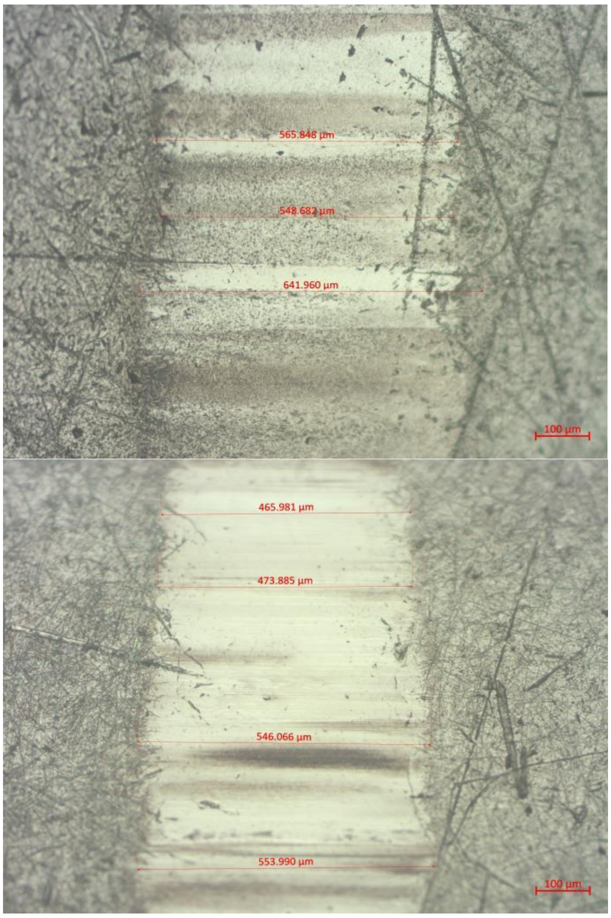

Figure10. Cumulative abrasion width at different temperatures for “base oil + molybdenum-ammonia complex” and “base oil + molybdenum-ammonia complex + ionic liquid additive” blends

Based on the experiments and analysis above, the molybdenum-ammonia complex shows synergistic lubrication effects when mixed with ionic liquid. The friction coefficients show stable value in various testing temperature in the present of ionic liquid, which is around 0.05~0.06. As for the anti-wear performance, the ionic liquid additive also reduced the wear scar width obviously. The “base oil + molybdenum-ammonia complex + ionic liquid additive” blends show potential to produce high performance lubricants, and the more detailed experiments under a wide range of temperature, loads and sliding speed is necessary for future study.

4. Conclusions

The effects of ionic liquid additives on the tribological properties of molybdenum-ammonia complexes were studied in this paper. PAO was select as lubricant base oil, Trihexyl(tetradecyl) phosphonium bis (2,4,4-trimethylpentyl)phosphinate was used as ionic liquid additive, ring and block friction and wear tester are used in this experiment, the findings have been listed here.

(1) Lubricants containing molybdenum-ammonia complexes have improved anti-wear and wear reduction qualities when ionic liquid additives are added. Molybdenum-ammonia complexes can be used to further reduce the friction loss of marine internal combustion engines.

(2) When considering the anti-wear and wear reduction performance of the molybdenum ammonia complex itself as well as the anti-wear and wear reduction performance and stability of the added ionic liquid additive, the composite performance of ionic liquid additive and molybdenum ammonia complex demonstrates that the anti-wear and wear reduction effect is best at 50 °C and a load of 20 N. Currently, "base oil + molybdenum ammonia complex + ionic liquid additive" has a friction coefficient of 0.062, which is 0.02 less than "base oil + molybdenum ammonia complex."

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