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A New Extreme Pressure Additive Containing Phosphorus and Nitrogen (PN) to Improve Gear Oil Tribological Properties

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Keywords：PN additive; extreme pressure; friction reduction; formation process of film

ABSTRACT

In this paper, a new benzotriazole phosphite ammonium salt derivative extreme pressure additive called PN was synthesized. Four-ball and optimal schwinggung reibungund verschleiss (SRV) testing machine were used to test the high temperature and extreme pressure performance of PN additive, and comparisons were made with the commonly used additives including Zinc Dialkyl Dithiophosphates (ZDDP) and Di-n-butyl phosphite (T304). The results show that the coefficient of friction (COF) and wear amount of the PN additive in the four-ball experiment were much smaller than that of the ZDDP and T304 additives. The COF of the PN additive in the RSV experiment changed slightly with temperature, and it had better high temperature extreme pressure performance in friction reduction than the traditional ZDDP and T304 additives. When the temperature was 120ºC, the COF of PN was about 30% lower than that of traditional additives. Thermogravimetric analysis showed that the failure temperature of PN additives was within 180-200ºC, and the thermal stability was better than that of ZDDP and T304. After the four-ball test, a scanning electron microscope (SEM) was used to observe the morphology of wear spots on the ball surface. It was found that the wear spots containing PN additive had slight adhesive wear, while those containing ZDDP and T304 showed serious adhesion and ploughing wear, and the surface appeared peeling and tearing. XPS was used to detect the chemical composition of friction surface containing PN additive, and thus the formation process of film on frictional surface was analyzed.

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INTRODUCTION

At present, lubricant chemistry, especially additive technology, is a very complex field. This is because lubrication engineering is based on empirical methods which is demand-centered (Xue et al., 1994). Therefore, the preparation principle and anti-friction mechanism of lubricant additives become very important (Minami et al., 2005; Li, 2006). According to the function, the additives mainly include anti-oxidant, anti-wear agent, extreme pressure additive, dispersant, anti-corrosive and anti-rust agent (Xu et al., 2004; Zhao et al., 2014; Singh et al., 2012; Zhang, 1991), etc. Chlorinated additives such as chlorinated waxes, olefins and esters are very effective extreme pressure additives despite various prescribed restrictions (Asadauskas et al., 2010; Petrushina et al., 2000). Sulfur-based extreme pressure additives include sulfide fats, hydrocarbons, heterocyclic compounds and derivatives (Rastogi et al., 2013; Spikes, 1974). They may also contain nitrogen and phosphorus groups (Fang et al., 2002; Aliev, 2012; Qiao et al., 2002). These additives are usually used in boundary or mixed lubrication to promote lubrication and reduce wear by friction chemical reaction between active substances such as sulfur, phosphorus, chlorine and metal surface (Nakayama, 2006; Minfray et al., 2008).

Various additives and their anti-friction and anti-wear mechanisms have been studied for a long time. S. J. Asadauskas et al. (2009) found the effects of chlorinated paraffin and zinc di-ethylhexyl dithio phosphate on the boundry lubrication of plant base oils performed better than mineral base oils. Elin Larsson et al. (2018) and Duzcukoglu H et al. (2010) investigated the anti-friction and fuel saving potential of a boric acid based additive by simulating the reciprocating model test of fuel additive and engine oil dual lubrication and found the friction energy loss is reduced by 76%. Bora Lee et al. (2019) and Sophie Loehlé et al. (2018) established the adsorption model of boundary lubrication and observed the molecular dissociation of sliding iron interface under pressure in real time, so as to understand the formation mechanism of iron phosphide. Nian et al. (2016) calculated and screened the compatibility, shear film formation and energy dissipation of trimethol phosphate and tris (2-octyldodecyl) phosphoric acid, based on 1,3,4-tris (2-octyldodecyl) cyclopentane as base oil. However, in recent years, the research on additives mainly focuses on the friction reduction of friction components to reduce energy consumption, and there are few researches about the effect of additives on friction reduction and anti-wear under extreme pressure conditions. The most well-known organophosphorus additive is zinc dialkyl dithiophosphate (ZDDP), which is widely used in gear oils and hydraulic oils as an anti-wear and anti-friction agent. Its mechanism is to form a glass like phosphate film between the friction interfaces of iron-based materials, so as to reduce friction and wear (Nicholls, 2005; Spikes, 2004; Martin, 2001). Dibutyl Phosphite (T304) is also a commonly used anti-wear agent in gear oils. It can form phosphite films on the metal surface through tribo-chemical reactions to reduce the wear of the metal friction interface (Li, 2015; Zhang, 2005).

This paper reported an additive named PN which was synthesized from dibutyl phosphite(T304), petroleum ether and Mannich base containing benzotriazole. Compared with traditional additives, PN had good high temperature stability and could improve lubrication effect under extreme pressure conditions. After chemical synthesis, PN was characterized by IR and elemental analysis, and its thermal stability was investigated by thermal analyzer. The tribological properties of PN was compared with the traditional additives ZDDP and T304, and the friction coefficient and wear under different concentrations and loads were obtained by four-ball-tester. Their high temperature tribological properties were tested by RSV test machine, and the temperature of the tested additives were measured by inserting three thermocouples into the gear oil for friction test, and the temperature changes were monitored in real time.

EXPERIMENTAL DETAILS

Materials and specimen preparation

Chemical reaction equation of additive PN synthesis is shown in Fig. 1(a). Added benzotriazole, dodecylamine and formaldehyde solution with a molar ratio of 1:1:1 to the reactor, while adding petroleum ether at the same time as a solvent, then stirred and mixed evenly. Heated up the reactor to 80 ~ 90ºC and removed water by gas stripping. After reacting for 7 ~ 8 hours, the solvent was removed by vacuum distillation, and Mannich base containing benzotriazole could be obtained. And then dibutyl phosphite (T304) and petroleum ether were added into the reaction vessel, stirred and mixed evenly, then heated to 80-100ºC. Mannich base containing benzotriazole was added into the reactor within 1-2 hours with a molar ratio of 1:1, and then continued to react for 3 hours to obtain a benzotriazole phosphite ammonium salt derivative additive, which was called PN. T304 was a commonly used anti-wear agent, its phosphoric acid group had excellent anti-wear performance, and Mannich base had strong oxidation resistance. This combination would improve the extreme pressure working ability of gear oil.

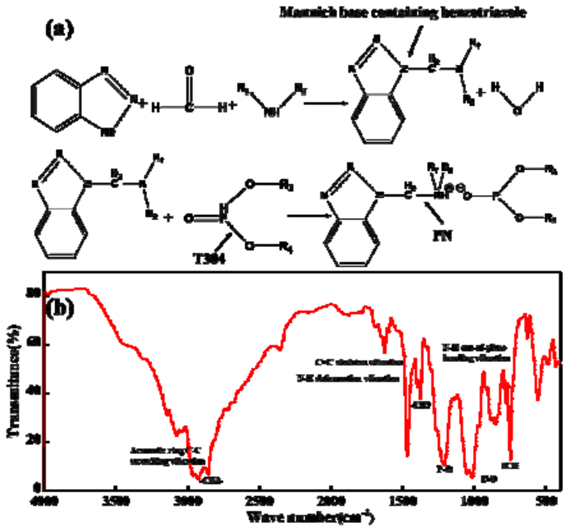

Fig.1. Synthesized PN additive structure(a) and its infrared spectrum(b); Where R_1, R_2, R_3, R_4 represent H, $C_{12}H_{25}$, C_4H_9, C_4H_9, respectively

The obtained product was characterized by infrared spectroscopy and elemental analysis. The product was analyzed by Anatar-360 Fourier Transform Infrared Spectrometer (Shimadzu Co. Ltd, Japan). The KBr coating film was used in the test. From Fig. 1, there was aromatic ring unsaturated hydrocarbon stretching vibration at wave number 3072 cm^{-1} and aromatic ring skeleton stretching vibration at wave numbers 1619 and 1465 cm^{-1}, which indicated the presence of benzene ring in the product. The peak at wave number 1373 cm^{-1} was the stretching vibration peak of aryl carbon and nitrogen, and wave number 1621 cm^{-1} was the deformation vibration peak of nitrogen and hydrogen. The peaks with wave numbers at 1218 cm^{-1} and 1002 cm^{-1} showed that the compound contained phosphorus oxygen bond, indicating that the product contained phosphoric acid group. Element analysis was performed for the reaction product, in which element P was measured by titration method, and element N was measured by C, H, N analyzer method (SH/T0656, Petrochemical industry standard of the people's Republic of China). The experimental value and theoretical value of element content are almost the same (Table1). Combined with the functional group analysis in Fig. 1(b), it can be concluded that the product is additive PN.

Table1. P and N elements contents

Element	P	N
Theoretical (%)	6.07	10.97
Experimental (%)	5.84	10.36

Thermal stability test

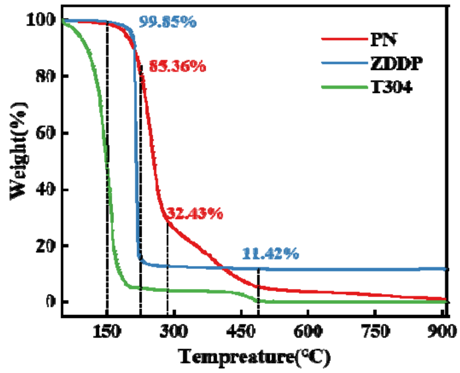

Fig.2 Thermal stability of ZDDP, T304 and PN additives

The high-temperature thermal stability of lubricating oil additives is of great significance. Under a nitrogen atmosphere, the thermal analysis of ZDDP, T304 and PN additives was done with using the TA-9900 thermal analyzer (TA Instruments Co., American). As shown in Fig.2, at 150 ºC, PN and ZDDP had almost no weight loss, and the remaining weight was above 99%, while T304 only had a remaining weight of about 48.35%. When the temperature was between 180 and 200ºC, ZDDP would experience rapid weight loss, and the final remaining weight would stabilize at about 11.4%, while the remaining weight of PN is 85.36% at 200ºC. After being higher than 200 degrees, PN weight began to lose rapidly. This showed that the synthetic PE additive had a relatively high failure temperature and could exhibit good extreme pressure and anti-wear performance at higher temperatures.

Tribology tests

The base oil used in tribology tests was MVI-500 and its main physical and chemical properties was listed in Table 2. AISI-52100 steel balls (with a diameter of 12.7 mm, hardness of 60 HRC, and surface roughness Ra 0.025 μm) were used in four ball experiments. The upper sample used in SRV testing machine was a cylinder with size of Φ15 mm×22 mm and material of 100Cr6, and the lower sample is a disc with size of Φ60 mm×5 mm and material of AISI-52100. The hardness and roughness of the two samples are 62 HRC and Ra 0.05 μm respectively. The tests were repeated three times for each group and the data was averaged.

The friction and wear tests of additives were carried out on the MS-10J four ball friction and wear tester (Xiamen Tianji Automation Co., Ltd., China). The friction coefficient (COF) and temperature data in the friction process were recorded automatically by computer. The experiments were done with the speed of 1200 rpm and duration of 60 min. The load range was from 98 N to 687 N and the initial temperature was 26.5ºC. The method of measuring the wear spot diameter was to measure the wear spot diameter of three lower test balls with a reading microscope (with an accuracy of 0.01mm) and took the average value. The error of wear spot diameter in two tests should not exceed 5%. The COF change trend of three additives in the temperature range of 50-120ºC was tested by SRV test machine (Optimal Machinery Co., Ltd., China).

Table 2. Main physical and chemical data of MIV-500 base oil

Items	Measurements
Kinematic viscosity/mm^2.s^{-1} (40 ºC)	106
Viscosity index	62
Flash point / ºC	232
Pour point / ºC	-9

RESULTS AND DISCUSSION

Friction and wear behaviors

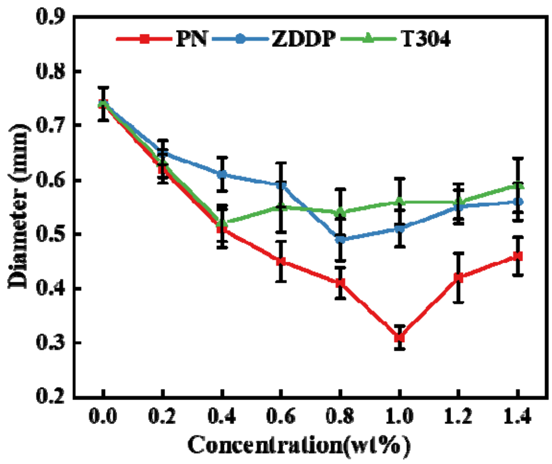

Fig.3 The relationship curve between the wear diameter of the balls and the concentration of the additive in the four-ball experiments

The relationship between the concentration of different additives in lubricating oil and wear under extreme pressure conditions was tested by four ball friction and wear tester. The amount of wear was expressed by the wear diameter of the ball and the experimental results were shown in Fig.3. The wear spots diameter of lubricating oil with different additives first decreases and then increases with the increase of the concentration. When the concentration was 0.4wt%, the minimum wear spot of oil containing T304 additive was 520 μm, and when the concentration was 0.8wt%, the minimum wear spot of ZDDP was 490 μm. The wear loss of the lubricating oil with PN additive was relatively small, and it reached the minimum value of 310 μm when the concentration was 1wt%.

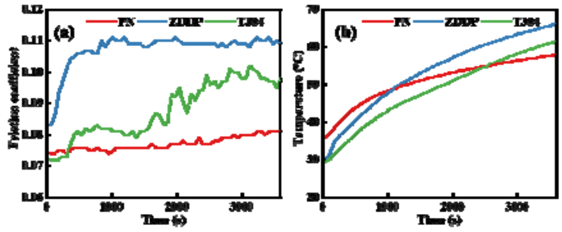

Fig. 4 Time dependent curves of COF and temperature of lubricants with different additives

Fig. 4(a) and fig. 4(b) represented the time-dependent curves of COF and temperature of different additives, respectively. The experimental load was 392 N, and the speed is 1200 r/min. The concentration of these three additives was 1wt%. It could be seen from Fig. 4 that the COF of ZDDP was stable above 0.1, and it had the largest COF. The COF of T304 rose with time and fluctuated greatly. The COF of additive PN was the lowest among the three additives, and after quickly reaching stability, it always remained at about 0.75. After 3600 s four ball test, the temperature of lubricating oil with ZDDP additive was the highest, reaching 66ºC, and the temperature with T304 additive was 61ºC. The experimental temperature of lubricating oil with additive PN was the lowest, which was 58ºC. This showed that under low-load and high-speed conditions, the synthetic PN additive had a better anti-friction effect than the commonly used ZDDP and T304 additives. Lower temperatures also meant lower oxidation rates and longer service life of gear oils. So, during the using process, it would increase the transmission efficiency of the gear set and extend the service life of gear oil.

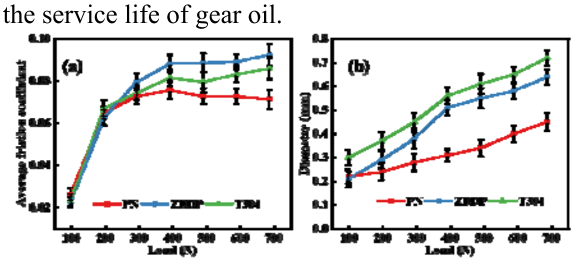

Fig.5 (a)The average COF of additive lubricants under different loads; (b) the balls wear diameter of additive lubricants under different loads

Fig. 5 showed the changing curve of COF and wear amount in the four-ball experiment of lubricating oil with different additives under different loads. The experimental conditions were as follows: rotating speed is 1200 r/min; running time is 3600s; the additive concentration was 1wt%. In Fig. 5(a), the average COF rose sharply with the load from 98 N to 392 N. When the load was greater than 392 N, the COF of lubricating oil containing ZDDP and T304 slowly rose and the COF of lubricating oil containing PN additives had a slow downward trend. Overall, the COF of lubricating oil containing PN additives was the smallest, and it changed relatively smoothly as the load increased. Fig. F(b) showed change of wear spot diameter with load. It was clearly that the wear spots increased with the load, and the wear loss of the lubricating oil containing PN additive was smaller than that of the other two additives. The higher the load was, the greater the difference between the wear scar of the PN additive and the other two additives were. Therefore, it could be said that PN additive would exert excellent anti-friction and anti-wear performance under extreme pressure conditions.

SRV testing

Table 3. The RSV tests experimental conditions

Items	parameter
Frequency /Hz	50
Amplitude /mm	1.5
load /N	400
Time /min	40
temperature / ºC	50-120
Heating rate / ºC /5min	10

To study the effect of experimental temperature on the tribological properties of PN additives in MVI-500 base oil, the SRV testing machine was used to test the oil with 1wt% ZDDP, T304 and PN additives, respectively. The contact mode of friction pair was line contact movement mode. The experimental conditions were shown as Table 3 and the results were shown as Fig. 6. It could be seen from the curve of COF changing with temperature in the figure that the lubricating oil containing PN additive showed excellent anti-friction performance at high temperature. As the temperature increased, the COF of lubricants containing ZDDP and T304 additives increased significantly, while the COF of lubricants containing PN additives decreased first, then slowly increased, and the minimum COF was 0.066 at 70 and 80ºC. At the high temperature of 120 ºC, the COF of PN additive was 0.073, while ZDDP and T304 were 0.104 and 0.112, respectively. The COF of PN additive at high temperature was 30% lower than traditional additives. Therefore, PN additive could effectively improve the antifriction performance of lubricants and the transmission efficiency of gears and other transmission components under high temperature conditions.

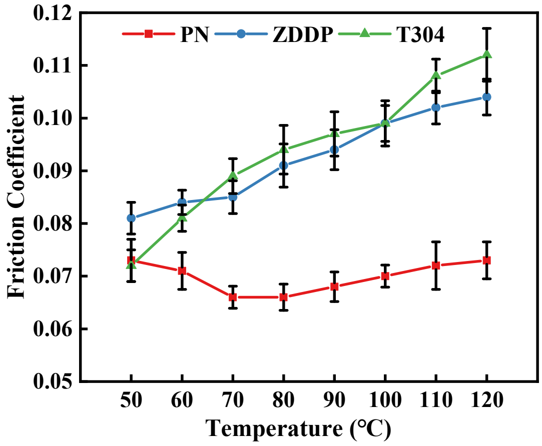

Fig.6 COF of oil with additives at different temperatures

SEM and EDS analysis

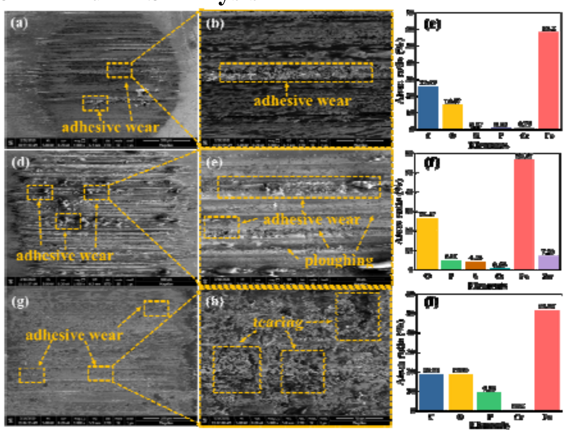

Fig. 7 SEM images and EDS analysis of the surface of the ball wear spot (where a, b and c are the figures of wear spot with PN additive; d, e and f are the figures of wear spot with ZDDP additive; g, h and i are the figures of wear spot with T304 additives)

Under the condition of 392 N load, after 3600 s four ball test, the friction interface of steel balls was seriously worn. And the SEM images of worn surface with different additives and the EDS analysis of worn surface were shown in Fig. 7. When the lubricant with PN additive was used for lubricating, the wear surface showed high temperature adhesion marks, and there was slight abrasive wear on the surface (Fig. 7a, b). After the extreme pressure test, the friction interface lubricated with ZDDP additive showed severe adhesive wear, and a large number of hard oxidized and high-temperature recast particles appeared, resulting in deep furrow at the friction interface (Fig. 7d, e). On the surface of the wear spot, the elements of P, S and Zn were detected by EDS. This was because ZDDP took place thermal decomposition reaction to generate phosphate during friction, which was chemically adsorbed to the friction interface to reduce friction and wear resistance, and the S in ZDDP reacted with Fe to form FeS, which had a certain anti-wear effect. The worn surface lubricated with T304 additive showed adhesive wear and there was shear tearing on the surface under high load condition (Fig. 7g, h). The ketone structure of phosphite ester and Fe formed a complex compound, which produced a friction reaction film attached to the friction interface, thus improving the performance of gear oil under extreme pressure. So, there was much P in the EDS graph (Fig. 7i). While the content of P and S elements on the wear spot containing PN additive was very low, which could be speculated that the anti-friction and anti-wear mechanism of PN additive on the surface of iron-based metal was mostly related to Mannich base containing benzotriazole.

XPS analysis

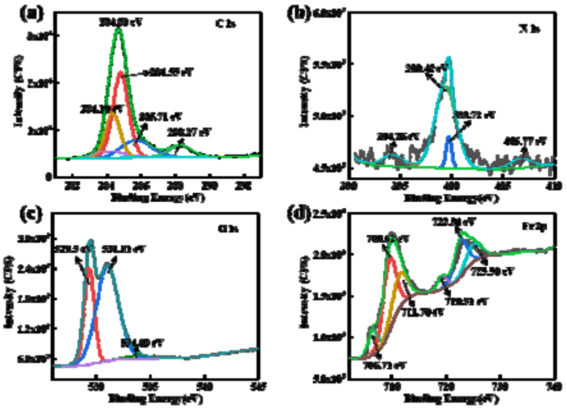

Fig. 8 XPS analysis of surface wear area with PN additive lubrication

XPS elements analysis of wear area under PN additive lubrication was done with an X-ray photoelectron spectroscopy (Thermo Fisher ESCALAB Xi+, Thermo Fisher Technology Co., Ltd., America). Fig. 8 the figure of XPS analysis of surface wear area with PN additive lubrication. The curve-fitted C 1s region was shown in Fig. 8(a). The maximum peak of the spectrum was at 284.80 eV, corresponding to the main graphite peak. The two peaks 284.55 eV and 284.10 eV were mainly caused by benzene ring, and there were peak at 285.71 eV and 288.27 eV indicating that it contained $(CH_2)_n$ and carbon-nitrogen single bonds (Roodenko, 2007; Fan, 2009). Fig. 8(b) was the N 1s region curve fitted. The two peaks 399.42 eV and 399.72 eV indicated the presence of triazole (Wipperman, 1991). Combined with the composition of additive PN, it could be speculated that the friction surface contained derivatives of mannich base containing benzotriazole. Fig. 8(c) and (d) were the fitted curves of O 1s and Fe 2p, respectively. The 531.01 eV and 534.03 eV were the peaks of Oxygen hydrogen bond and oxygen phosphorus bond, and the peak of 529.5 eV indicated that there were FeO or Fe_2O_3 (Grosvenor, 2004). The peak of Fe 2p meant that there were divalent Fe and trivalent Fe. Therefore, it could be concluded that the worn surface contained FeO, Fe_2O_3, FeOOH (Li, 2011) and a small amount of $FePO_4$ (Wang, 2003).

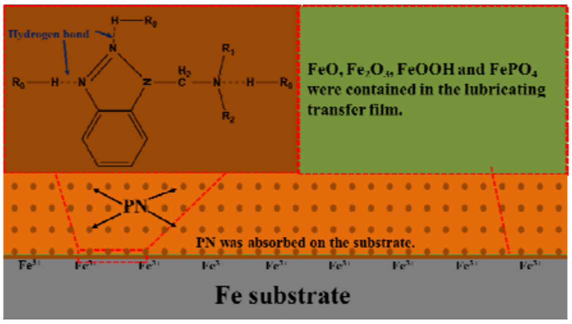

Fig. 9 Schematic diagram of friction film on substrate surface, where R_0 represent derivative of Mannich base containing benzotriazole

As it was shown in Fig. 9, additive PN contained triazole ring, and it had good affinity with metal and could quickly adhere to the metal surface during the friction process. Then PN was decomposed into phosphoric acid group and derivative of Mannich base containing benzotriazole by tribochemical reaction. The nitrogen atoms in triazole ring had lone pair electrons, which would make them form a dense chemical protective film on the metal surface, preventing the metal ions into oil and weakening its catalytic oxidation effect on oil. Therefore, PN additives could exert excellent anti-friction properties at high temperatures (Fig. 6). In addition, XPS analysis showed that there were FeO, Fe_2O_3, FeOOH and a small amount of $FePO_4$ on the worn surface. These Fe compound could form a transfer film layer to reduce friction and wear.

CONCLUSIONS

In this paper, a new extreme pressure additive called PN was synthesized, and its molecular structure and chemical composition were characterized. Tribological experiments were carried out under different temperatures and different loads. Compared with the traditional ZDDP and T304 additives, PN showed excellent anti-friction and anti-wear performance. According to the results of tribological tests, the optimal concentration of PN additive was 1wt%. The average COF was reduced by up to about 0.04, and the diameter of ball wear spots was reduced by up to about 300 μm. Moreover, PN had excellent anti-oxidation at high temperature, and with PN additive the average COF remained unchanged when working temperature up to 120°C. XPS analysis of the friction surface showed that PN was decomposed into phosphoric acid group and derivative of Mannich base containing benzotriazole due to tribochemical reaction, and these products were able to form a dense chemical protective film on the metal surface to exert excellent anti-friction and anti-wear properties at high temperatures.

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新型磷、氮（PN）極壓添加劑改善齒輪油的摩擦學性能的研究

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摘 要

本文合成了一種新的苯並三唑亞磷酸銨鹽衍生物極壓添加劑 PN。採用四球和高頻振動往復線性摩擦磨損（SRV）試驗機對 PN 添加劑的高溫和極壓性能進行測試，並與常用的添加劑二烷基二硫代磷酸鋅（ZDDP）和二正丁基亞磷酸鹽（T304）進行了對比。結果表明，PN 添加劑在四球實驗中的摩擦系數（COF）和磨損量遠小於 ZDDP 和 T304 添加劑。RSV 實驗中 PN 添加劑的 COF 隨溫度變化不大，在減摩方面的高溫極壓性能優於傳統的 ZDDP 和 T304 添加劑。當溫度為 120℃ 時，PN 的 COF 比傳統添加劑低約 30%。熱重分析表明，PN 添加劑的失效溫度在 180-200℃ 之間，熱穩定性優於 ZDDP 和 T304。四球測試後，用掃描電子顯微鏡（SEM）觀察球表面磨損點的形貌。發現含有 PN 添加劑的磨損點有輕微的粘著磨損，而含有 ZDDP 和 T304 的磨損點出現嚴重的粘著和犁磨磨損，表面出現剝離和撕裂。採用 XPS 檢測含有 PN 添加劑的摩擦表面的化學成分，分析了摩擦表面膜的形成過程。