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The lubrication effectiveness of dialkylpentasulfide in synthetic ester and its emulsion

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ABSTRACT

The application of dialkylpentasulfide (DPS) in synthetic ester (pentaerythritol tetraoleate known as PETO ester) and its emulsion is studied in this paper. PETO ester blended with DPS shows good antiwear, friction reducing and extreme pressure performance, while PETO emulsion doped with DPS exhibits only excellent extreme pressure properties. The above difference originates from the tribofilm formed on the worn surface by tribochemical reaction. SEM-EDS and XANES are applied to determine the relationship between tribochemical products and lubrication effectiveness. The tribofilm is composed of $FeSO_4$, FeS, FeS_2 and $FeSO_3$. DPS in PETO ester and PETO emulsion undergoes tribochemical reaction dominated by sulfidation and thermal oxidation respectively, resulting in distinct tribological properties. This provides an essential explanation for the improvement of tribological properties of DPS in PETO ester and emulsion, and also indicates that sulfur is not fitted as antiwear, friction-reducing additive in water based system.

1. Introduction

Vegetable oil is composed of saturated or unsaturated fatty acids and glycerol, leading to its separated regions of polar and non-polar groups in one molecule [1]. So it is amphiphilic and could be used as both hydrodynamic and boundary lubricant [2]. Vegetable oil exhibits remarkable higher flash point, high lubricity, high viscosity index, and low evaporative loss over mineral oil [3]. The triglyceride structure leads to inherent instability of vegetable oil, such as poor oxidative and thermal stability, which could be ascribed to structural "-CH group" on triglyceride parts. But it can be effectively improved by chemical modification with pentaerythrotol (PE) or trimethylolpropane (TMP) [4–6]. Researchers focus on their physical properties such as viscosity index, viscosity, cold point, pour point, and oxidation stability [7]. Investigation into tribological and tribochemical properties of trimethylolpropane trioleate (TMPTO) and PETO ester is rather few. Compared with mineral oil or refined vegetable oil, PETO ester and TMPTO contain more polar groups and free acid, leading to the distinction of tribochemcial process and the variation of chemical composition on the tribofilm, resulting in an unexpected tribological properties [8].

Dialkylpentasulfide (DPS) is widely used as an extreme pressure additive in mineral oil and emulsion for ferrous metal cutting and forming process [9]. Sulfur in DPS can quickly react with nascent surface to avoid the seizure of asperities under high contact load [10,11]. However, DPS in mineral oil is not environment-friendly [12]. Thus we aims to find reasonable strategy to replace conventional combinations of DPS and mineral oil: firstly, superseding mineral oil with biodegradable vegetable-derived oil; secondly, elucidating tribological properties and tribofilm-forming mechanism of DPS in PETO ester and other environment-friendly lubricants; thirdly, exploring reasonable methods to reduce or replace additives with high S content.

Water-based emulsion is an alternative to oil-based lubricants for its remarkable refrigerating, cleaning and low cost [13]. Emulsion used in metalworking fluid requires strong anti-seizure properties [14]. And water plays a significant role in accelerating wear in practical application [15]. Additives can decompose in water and generate acid and sludge which are deteriorated to tribological properties [8,16]. Water can delay the formation of tribofilm and reduce the strength of tribofilm [17]. Previous investigations put emphasis on water decreasing polyphosphates chain length [18,19]. Sulfur is also an integral part of lubricant additive. However, there are few investigation about the role of water in tribochemical process with sulfur as the additive.

In the present study, the differences in the tribological properties of PETO ester and its emulsion were presented with the same additive.

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PETO was chosen as a base oil and DPS was used as an additive in PETO ester and PETO emulsion. Tribological evaluation of lubricants was conducted on a four-ball tester. SEM-EDS was carried out to examine the morphology and chemical composition on the worn surface. K-edge XANES was used to investigate the surface composition of tribofilm formed by PETO ester and its emulsion. Finally, a plausible tribochemical mechanism was proposed.

2. Materials and experimental details

2.1. Materials

A commercial synthetic ester, pentaerythritol tetraoleate (PETO ester, acquired from KLK OLEO, Malaysia) was used as the base oil. Table 1 exhibited the physical characteristics of PETO ester. Dialkylpentasulfide (DPS) was supplied by STARRYCHEM. Its molecular structure and typical properties were outlined in Fig. 1 and Table 2. Polyethylene glycol 600 monooleate (PEG600MO) used for emulsifing PETO ester was purchased from Haian Petrochemical Plant. The steel balls (φ12.7 mm, HRC 59–61) were made of GCr15 (chemical composition: 0.95–1.05 wt % C; 0.15–0.35 wt % Si; 0.20–0.40 wt % Mn; 0.027 wt % P; 0.020 wt % S; 1.30–1.65 wt % Cr; 0.30 wt % Ni; 0.25 wt % Cu).

2.2. Lubricant sample preparation

PETO was used to prepare blends with DPS at various concentrations under a magnetic stirrer at room temperature (25 °C) for 5 min (denoted as PETO ester). Emulsion was prepared by mixing 0.95 wt% previous prepared DPS-containing PETO lubricant, 0.05 wt% of PEG600MO (surfactant) together, then adding water (29.0 wt%) gradually and stirring (800 r/min) for 30 min (denoted as PETO emulsion).

2.3. Tribological evaluation

Tribological test was conducted using a MS-10J four-ball tester, Xia' men tenkey automation Co. Ltd, China. Wear scar diameters (WSDs) were measured by using an optical microscope with a resolution of 0.01 mm and the coefficient of friction (COF) was recorded automatically as indicated by the screen. The lubricant samples were tested for extreme pressure performance on four-ball tester as GB12583-98, similar to ASTMD-2783.

2.4. Preparation of tribofilm and thermal film

Tribofilm was obtained by washing the upper ball ultrasonically with acetone and drying with tissue paper. In order to prepare thermal films, steel balls were dipped in a glass beaker containing lubricant samples which were preheated up to 150 °C for PETO ester (60 °C for PETO emulsion) in the furnace [8]. All types of steel balls were heated for 6 h.

Table 1
The physical characteristic of PETO ester.

Parameters	Index
Extrinsic feature	Yellow and transparency liquid
Density (20 °C, g/cm^3)	0.92
Viscosity index	208
Kinematic viscosity (mm^2/s)	
40 °C	65
100 °C	13
Open flash point (°C)	310
Pour point (°C)	−27
Saponification value (mg KOH/g)	185
Iodine value (g/100 g)	84
Acid value (mg KOH/g)	<2
Hydroxyl value (mg KOH/g)	7

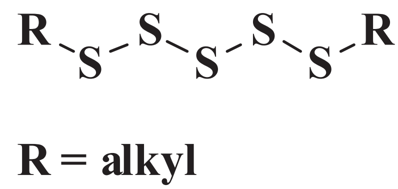

Fig. 1. The molecular structure of dialkylpentasulfide (DPS).

2.5. Analysis of the worn surface morphology and the element distribution

The morphology and active element content of worn surface were performed on a Nova Nano SEM 450 FEI Scanning Electron Microscope (SEM) coupled with Kevex energy dispersive spectroscopy (EDS).

2.6. Size distribution of the emulsion

The size distribution of emulsion particles was determined by Nano particle size and Zeta potential analyzer (ZS90) provided by Malvern Instruments Ltd, UK. Each test was repeated for three times.

2.7. XANES analysis

P K-edge X-ray absorption near edge structure (XANES) spectra of the samples were conducted on the beamline 4B7A at Beijing Synchrotron Radiation Facility (BSRF) [20]. X-ray beam was monochromatized using a fixed-exit double-crystal Si (111) monochromator with 0.30 eV resolution. Sample spectra were recorded in fluorescence yield (FY) mode using for bulk information or total electron yield (TEY) mode for near surface information. All of spectra were recorded from 2460 to 2490eV with a step size of 1.0eV on the region of 2460–2475 eV, 0.50 eV in pre-edge region of 2140–2149 eV, 0.20 eV in near edge region of 2149–2160 eV and 0.50 eV in the post edge region of 2160–2200 eV.

3. Results and discussion

3.1. Tribological performance

The relationship between WSD and different concentration of DPS in PETO emulsion and PETO ester is shown in Fig. 2. The addition of DPS can significantly improve the antiwear performance of PETO ester at all concentrations. WSD decreases rapidly with the increase of additive concentration, and then the decreasing trend slows down and finally remains stable. WSD reduces 68.04% in DPS-containing PETO ester at the optimum concentration (1.5 wt%). This may due to that the decomposition of DPS can form dense lubricating film on the surface of friction pairs to improve the wear resistance of PETO ester. The thickness and density of the lubricating film grow with the increase of additive concentration, then the antiwear performance further enhances [21,22]. When the addition amount exceeds the optimal concentration, the excessive additive could not adsorb on the surface of friction pairs. Therefore, the antiwear performance cannot be further improved

Table 2
Typical properties of dialkylpentasulfide (DPS).

Parameters	Index
Extrinsic feature	Yellow and transparency liquid
Density (20 °C, g/cm^3)	1.047
Kinematic viscosity 40 °C (mm^2/s)	48.5
Open flash point (°C)	150
Pour point (°C)	−35
Total sulfur content (wt %)	40
Active sulfur content (wt %)	38
Odor	Low smell
Chrominance	2