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The preparation and tribological properties of surface modified zinc borate ultrafine powder as a lubricant additive in liquid paraffin

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ABSTRACT

This paper investigates the effects of surface modification of zinc borate ultrafine powders (ZB UFPs) on their tribological properties as lubricant additives in liquid paraffin (LP). ZB UFPs were successfully modified by hexadecyltrimethoxysilane (HDTMOS) and oleic acid (OA). It is evident that HDTMOS modified zinc borate ultrafine powder (HDTMOS-ZB UFP) delivered a small conglomerate size, good stability in the organic solvent and sound anti-wear property. It has been observed that a continuous and tenacious tribo-film on the worn surface generated from HDTMOS modified ZB UFP as a lubricant additive in LP plays an important role in the outstanding anti-wear property. It is suggested that HDTMOS modified ZB UFP as a lubricant additive in LP has a great potential.

1. Introduction

Metal borates as an important group of engineering additives have always been the focus of extensive researches [1–4]. Zinc borate, in particular, has been widely employed as an additive in a broad range of industrial products due to its flame resistant, smoke suppressive character as well as its interesting optical properties [5–7]. The utilisation of zinc borate nanoparticles as an inorganic lubricant additive has also raised much attention over recent years owing to their outstanding tribological properties and good environmental friendly feature compared with the traditional organic lubricant additives that contain P, S and Cl elements [8–10]. There was a report regarding zinc borate nanoparticles in liquid paraffin with assistance of dispersing agent sorbitol monostearate where an up to 50% reduction of friction coefficient and a 10% drop of wear scar diameter were observed [8]. However, without a direct evidence of testing zinc borate additive alone in the base oil, the true property of zinc borate particles in liquid paraffin cannot be identified and an actual level of contribution from either zinc borate nanoparticles or dispersing agent (sorbitol monostearate) to such improved tribological properties is still not clear. In fact, it has also been reported that without dispersing agent zinc borate powder did not demonstrate noticeable friction reduction behaviour [9]. All the zinc borate particles studied in the past as a lubricant additive are in the size of nanometre although a majority of the available commercial zinc borate powders are submicron particles. Compared with nanoparticles, submicron size particles have relatively low cost and simple preparation process which has guaranteed their domination in industrial application although submicron size particles are more thermodynamically unstable in liquid media.

The stable dispersion of solid lubricant additive in base oil has always been a great challenge, and the intrinsic poor stability of solid additives in polymers and a lubricant system has considerably restrained from their applications. Modification of particle surfaces using suitable modification agents is one of the widely applied approaches to improve the dispersibility of solid additive particles in lubricant base oil. Surface modified Al_2O_3 [11], SiO_2 [12,13], Fe_3O_4 [14], MoS_2 [15,16], ZnO [17], and LaF_3 [18,19] have all been synthesised successfully, and the improved tribological performances achieved by using these surface modified additives in lubricant base oils have also been reported. In the case of the surface modification of zinc borate particles, oleic acid is the most commonly used modification agent [9]. However the information on the surface modification of zinc borate particles using alternative agents is very limited.

In this study, zinc borate ultrafine powder functionalised with oleic acid (OA) and hexadecyltrimethoxysilane (HDTMOS) coupling agent was synthesised. Anti-wear properties of liquid paraffin with original and modified zinc borate ultrafine powders were investigated and compared using a Pin-on-disc tribotester. Conglomerate size and stability of the original and modified samples in hexane were studied with zeta-potential. The morphology and mechanical properties of worn surface were studied using atomic force microscopy (AFM), scanning electron microscopy (SEM) and nano-indentation facilities.

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The elemental analysis on the worn surfaces was also conducted with energy-dispersive X-ray spectroscopy (EDS). A significant wear reduction was achieved when the HDTMOS modified zinc borate ultrafine powder was used as the lubricant additive in liquid paraffin. A continuous and tenacious tribo-film generated on the wear scar was observed and considered to be the reason for the enhanced anti-wear performance.

2. Materials and experimental apparatus

2.1. Materials

Analytically pure liquid paraffin (LP) (Kerax Ltd., UK) was employed as lubricant base oil, which has a flash point of 220 °C, a viscosity of 24 mPa s at 40 °C and 4.8 mPa s at 100 °C. Oleic acid (OA) (Sigma-Aldrich, Inc.) and Hexadecyltrimethoxysilane (HDTMOS) (Gelest, Inc.) were used as surface modification agents and lubricant additives. Commercial zinc borate ultrafine powder (ZB UFPs) with 99.5% purity and the particle size of 500–800 nm (Shandong Jiqing Chemical Co.,Ltd., China) were employed (Molecular Formula:2ZnO $\cdot$ $3B_2O_3$ $3.5H_2O$). Fig. 1 shows a typical particle size and shape of the employed ZB UFPs.

2.2. Surface modification of zinc borate ultrafine powder

The OA modified zinc borate ultrafine powder (OA-ZB UFPs) and HDTMOS modified zinc borate ultrafine powder (HDTMOS-ZB UFPs) were synthesised in this study. ZB UFPs of 2.78 g were firstly dispersed in 40 mL mixed solution of ethanol and water (volume ratio 1:1) using a high shear homogeniser at a rotary speed of 15 K rpm for 10 min. A suitable amount of modifier (either OA or HDTMOS) dissolved in 10 mL of absolute alcohol was then added into the first dispersion. Subsequently, the mixture was heated to 70 °C and maintained at this temperature with vigorous stirring for 4 h. Then, the suspension was centrifuged at a speed of 8000 rpm for 10 min and the white precipitate was collected. The obtained precipitate was rinsed with distilled water and ethanol alternately and centrifuged repeatedly in order to remove the excessive modifier. Finally the thoroughly washed precipitate was dried in a vacuum oven at 40 °C for 6 h and the modified ZB UFPs were obtained.

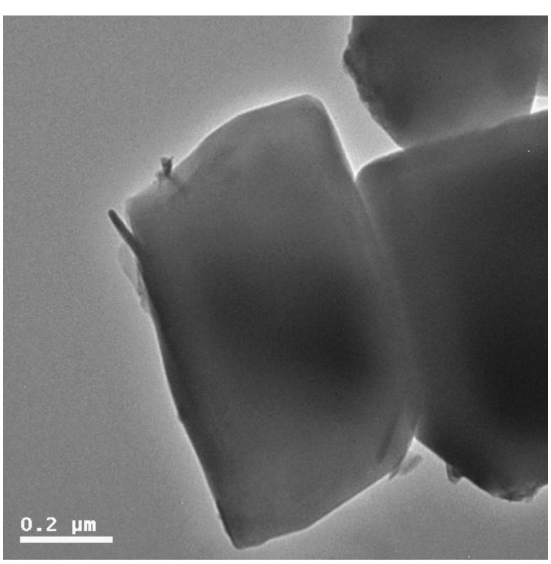

Fig. 1. Typical particle size and shape of the employed ZB UFPs under TEM.

2.3. Characterisation of surface modified zinc borate ultrafine powder

Infrared spectroscopy measurements were conducted using a Perkin-Elmer Spectrum 100 FTIR Spectrometer. Samples were prepared as powder-pressed KBr pellets. The spectra were collected in the wave range from 600 to 4000 cm^{-1} with a resolution of 4 cm^{-1} in a transmission mode.

Thermo gravimetric analysis (TGA) was carried out with a SETARAM TG-DSC 1600 instrument. For each test, approximately 10 mg sample placed in an aluminium crucible was tested with a heating rate of 5 °C/min from 80 to 500 °C in atmosphere.

2.4. Wear tests

The tribological properties of all lubricant samples were evaluated using a POD 2 Pin-on-disc tester (Teer Coatings Ltd.). All the tests were carried out with a 10 N load and a sliding speed of 50 mm/s for a testing period of 60 min and under the experimental environment that has ambient temperature of 22 °C and humidity of 45%. A bearing ball of 5 mm diameter used as the pin in a test was made of AISI52100 chrome steel with HRC of 59–61. The disc was made of the identical material, with 27 mm diameter and 3 mm thickness. Prior to each test, the discs were grounded and polished to a mirror finish and a uniform surface roughness *Ra* of 15 nm was achieved. Before each test, both the pins (bearing balls) and the discs were cleaned with toluene in an ultrasonic water bath for 5 min to eliminate any potential grease on the surface, and then a further cleaning with acetone was carried out for 5 min. In this study, a uniform concentration of 0.5% in weight fraction was applied for all friction and wear tests when the additive powders were employed. Some surfactants have excellent tribological properties when they were used as lubricant additives [20–22]. To eliminate the effects of applying surfactants on the anti-wear results of surface modified particles, OA and HDTMOS were combined with LP separately and tested on pin-on-disc rig as well. When either OA or HDTMOS was added into LP alone as an additive, the concentration of additive is 0.1% in weight. All additives (either particles or modifiers) were dispersed in LP with an ultrahigh shear homogeniser at the speed of 20 k rpm for 20 min. The lubricants prepared in this study are presented in Table 1.

2.5. Characterisation of the worn surfaces

Wear scars on the pins used in the pin-on-disc tests were observed using optical microscopy and scanning electron microscopy (SEM). Wear scar diameter of each pin was measured to the accuracy of 1 μm. The topography of the wear scar surface was studied with atomic force microscopy (AFM). Energy dispersive X-ray spectroscopy (EDS) were conducted to examine the chemical

Table 1
The lubricants prepared for the tests.

Sample code	Constituent
LP	Liquid paraffin
LP+OA	Liquid paraffin with 0.1 wt% oleic acid
LP+HDTMOS	Liquid paraffin with 0.1 wt% hexadecyltrimethoxysilane
LP+ZB UFPs	Liquid paraffin with 0.5 wt% original zinc borate ultrafine powders
LP+OA-ZB UFPs	Liquid paraffin with 0.5 wt% oleic acid modified zinc borate ultrafine powders
LP+HDTMOS-ZB UFPs	Liquid paraffin with 0.5 wt% hexadecyltrimethoxysilane modified zinc borate ultrafine powders