

Tribological Properties of Sulphur-Free Antiwear Additives Zinc Dialkylphosphates (ZDPs)

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ABSTRACT

The film-forming, friction, and antiwear properties of zinc dialkylphosphates (ZDPs) were investigated and compared with the corresponding zinc dialkyldithiophosphates (ZDDPs). The primary ZDPs generally show similar friction and antiwear performance to the primary ZDDPs, although some differences are seen between them in film-forming properties. For the secondary ZDP and ZDDP, there are some clear differences in their tribological properties. This indicates that the properties of the primary ZDPs and ZDDPs may be controlled predominantly by adsorbed films consisting the intact additives and/or their decomposition compounds, and that the properties of the secondary ones may be controlled by glassy reaction films consisting zinc/iron polyphosphates.

INTRODUCTION

In all industries, environmental issues are vital in the quest to achieve a sustainable world. This is, of course, true for the automotive industry, which has to improve the fuel efficiency of automobiles and also decrease the emission of hazardous gases such as nitrogen oxides, sulphur oxides, and carbon monoxides. Engine lubricants are expected to contribute to these issues, especially because improved lubricants offer a relatively low cost approach compared to development of new engines and other equipment. These environmental demands are posing three key requirements in the development of engine oils. The first is the improvement of fuel efficiency, which can be achieved by decreasing engine friction. Lowering oil viscosity and employing friction modifiers such as MoDTC and surfactant molecules could be effective in reducing the friction. However, this necessitates optimization of additive formulations since lower viscosity and the employment of friction modifiers may cause poorer antiwear performance and thus reduce engine durability. The second is the elimination of substances such as sulphur, phosphorus, and metal ions contained in engine oils because they can

damage or block the catalysts and filters of exhaust after-treatment systems [1, 2]. The last requirement is to extend the useful life of engine oil performance, which contributes to lower maintenance costs as well as less waste oil. In practice, it is quite difficult to satisfy these three environmental demands without compromising the essential performance of engine oils in terms of engine durability.

Additives known as zinc dialkyldithiophosphates (ZDDPs), which were firstly developed more than 60 years ago, are employed in most modern engine oils [3, 4]. They are very effective, multi-functional additives having both antiwear and antioxidant properties. However, ZDDPs have some negative features in terms of the environmental demands described above. They have been reported to increase friction by forming rough, glassy films on rubbing surfaces [5-7]. They also contain all of the species that are hazardous to the after-treatment systems, *i.e.* sulphur, phosphorus, and metal cations. In addition, it has been reported that ZDDPs produce sulphuric acid during their decomposition process which reduces engine oil life by consuming detergents [8]. Many studies have been carried out to find additives that are effective substitutes for ZDDPs, but very few convincing candidates have yet been identified. Recently, the use of sulphur-free analogues of ZDDPs, *i.e.* zinc dialkylphosphates (ZDPs) in engine oils has been proposed [9-11]. It has been shown that ZDPs make it possible to achieve engine lubricants with better performance such as detergency, base number retention, and catalyst compatibility, than conventional ZDDP-formulated ones by optimizing the formulation of other additives and base oils. However there is still much that is unknown concerning the mechanism by which ZDPs (and, indeed, ZDDPs) control wear. Therefore, the tribological properties of ZDPs have been studied as single component solutions by using MTM-SLIM (mini traction machine – spacer layer interferometry) and HFRR (high frequency reciprocation rig), and their behaviours have been compared with that of the corresponding ZDDPs.

EXPERIMENTAL

MTM-SLIM and HFRR (PCS Instruments) were employed to evaluate the film-forming, friction, and antiwear properties of ZDPs in this study. Figure 1 shows a schematic diagram of MTM-SLIM set-up. The MTM is a ball-on-disc type tribo-machine which can measure friction properties of lubricants under a wide range of sliding-rolling conditions by controlling sliding and rolling speeds separately. The SLIM attached to the MTM can capture interference images from the ball wear track and thus monitor the film forming of additives on its surface during tests without removing the specimens from the machine. The principle of the measurement can be found in previous papers [12-14]. The test specimens are a 19.05 mm diameter ball and a 46 mm diameter disc which are made of 52100 steel with hardness 750-770 VPN. The rubbing conditions were; temperature 70 and 100 °C, load 31 N (a maximum Hertzian contact pressure 0.93 GPa), mean speed 100 mm/s, and SRR (slide-roll ratio) 50%. HFRR is also a ball-on-disc type machine, in which the ball specimen reciprocates and the disc specimen does not move. Specimens are a 6 mm diameter ball and a 10.0 mm diameter × 3.0 mm thick disc which are also made of 52100 steel with hardnesses Rockwell hardness 'C' scale (HRC) number of 58-66 and Vickers hardness "HV30" scale number of 800 respectively. These two hardnesses were roughly same, although it is impossible to compare these two hardness values directly. The rubbing conditions were; temperature 100 °C, load 600 g (a maximum Hertzian contact pressure 1.16 GPa), frequency 50 Hz, stroke 1000 µm.

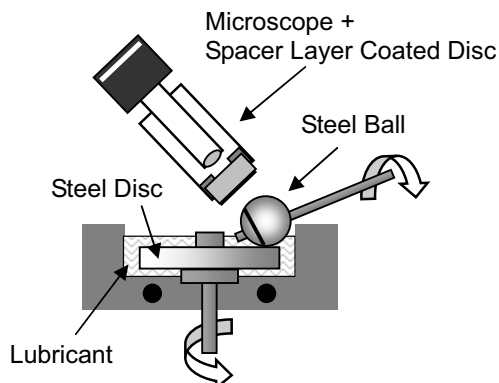


Figure 1. Schematic diagram of *in situ* spacer layer interferometry (SLIM) set-up on the MTM.

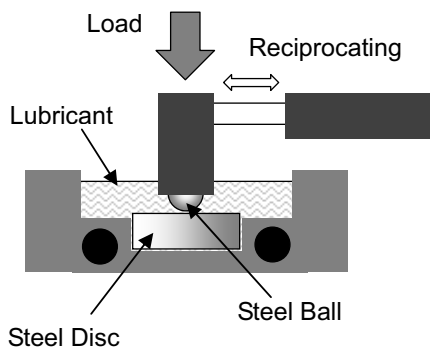


Figure 2. Schematic diagram of HFRR set-up.

Three types of ZDPs having different alkyl chains were employed in this study. **ZDP-iC8** and **ZDP-nC8** are the primary-type ZDPs having 2-ethylhexyl and n-octyl chains respectively, while **ZDP-secC6** is the secondary-type ZDP having 1,3-dimethylbutyl chains (Figure 3). The corresponding ZDDPs, **ZDDP-iC8**, **ZDDP-nC8**, and **ZDDP-secC6** were also employed to compare the properties of ZDPs and ZDDPs (Figure 4). Polyalphaolephin **PAO2** was employed as base oil in order to avoid chemical contributions from the base oil and its impurities so as to focus on the properties of the additives as much as possible. The kinematic viscosities of **PAO2** are 5.0 and 1.7 mm²/s at 40 and 100 °C respectively. In this study, simple solutions of the antiwear additives in **PAO2** without any other additives were mainly employed for the MTM-SLIM and HFRR tests. The concentration of the antiwear additives corresponded to 0.08 wt% phosphorus.

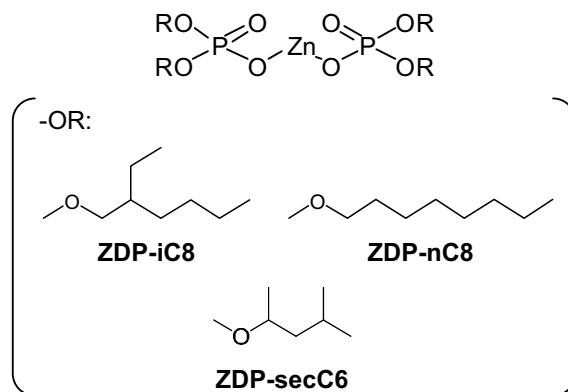


Figure 3. Chemical structures of ZDPs.

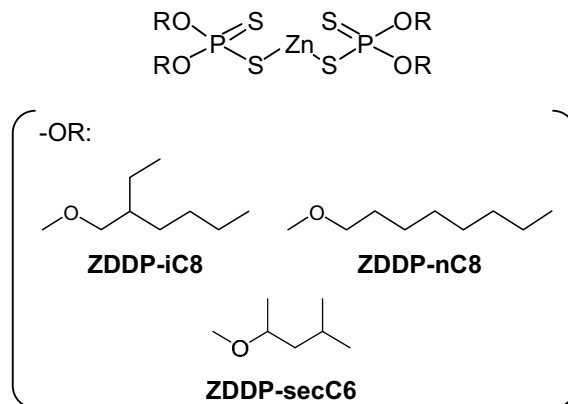


Figure 4. Chemical structures of ZDDPs.

RESULTS

The film-forming and friction properties of ZDPs, which were evaluated by MTM-SLIM, were compared with those of ZDDPs. Also, the antiwear performance of ZDPs was studied by HFRR and compared with that of ZDDPs. Wear volumes on ball and disc specimens were measured by an optical probe (WYKO NT9100).

ZDP-iC8 AND ZDDP-iC8

The tribological properties of ZDP and ZDDP having 2-ethylhexyl chains were compared as below.

Film-forming Properties

The growths of mean-film thickness during rubbing with **ZDP-iC8** and **ZDDP-iC8** at 100 °C are shown in Figure 5. It was observed that **ZDP-iC8** and **ZDDP-iC8** both form thick tribo-films by rubbing. This indicates that ZDPs may provide antiwear performance by a similar mechanism to ZDDPs. However, some differences are seen between their film-forming properties. It is clear that **ZDP-iC8** forms a tribo-film more slowly than **ZDDP-iC8** and that the film formed by **ZDP-iC8** is thinner than the film formed by **ZDDP-iC8**. This may be due to the lower reactivity of **ZDP-iC8** than **ZDDP-iC8** caused by the molecular difference between them, *i.e.* sulphur content.

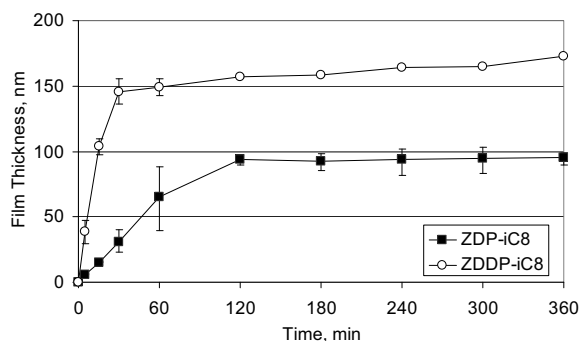


Figure 5. Growths of mean film thickness of **ZDP-iC8** and **ZDDP-iC8** at 100 °C.

Friction Properties

It has been previously reported that friction in the mixed lubrication region increases as ZDDP tribo-film grows [5-7]. This was seen for both **ZDP-iC8** and **ZDDP-iC8** in the current study [15]. Figure 6 shows the friction properties of the films formed after 6 hours rubbing with **ZDP-iC8** and **ZDDP-iC8** at 100 °C. Generally, the friction property of **ZDP-iC8** is similar to **ZDDP-iC8** over the range of mean speeds measured here which is probably in the mixed and boundary lubrication regions. There is no difference in their boundary friction, although a small difference between them is seen in the mixed lubrication region. The difference in the friction in the mixed lubrication may be caused by the difference in the thickness between the **ZDP-iC8** and **ZDDP-iC8** films.

Antiwear Performance

Figure 7 and 8 show the antiwear performances of the two additives on HFRR ball and disc respectively. For both of **ZDP-iC8** and **ZDDP-iC8**, only tiny wear scars were observed on the balls even after 4 hours rubbing. The wear volumes on discs were also quite small and much less than for **PAO2** alone (more than 2 million μm^3 after 60 minutes rubbing). These results show that both of **ZDP-iC8** and **ZDDP-iC8** have excellent antiwear performances. In addition, there is no

significant difference in the antiwear performance between **ZDP-iC8** and **ZDDP-iC8** for both ball and disc under the conditions applied in this study, although a clear difference were observed in the film-forming properties between them. It seems that the sulphur content hardly influences the antiwear performance for these additives in this condition.

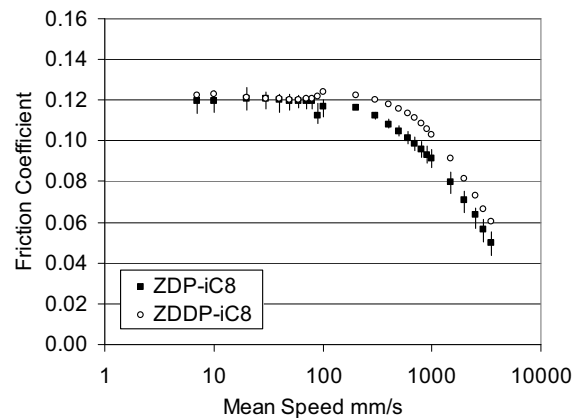


Figure 6. Friction properties of the films formed by 6 hours rubbing with **ZDP-iC8** and **ZDDP-iC8** at 100 °C.

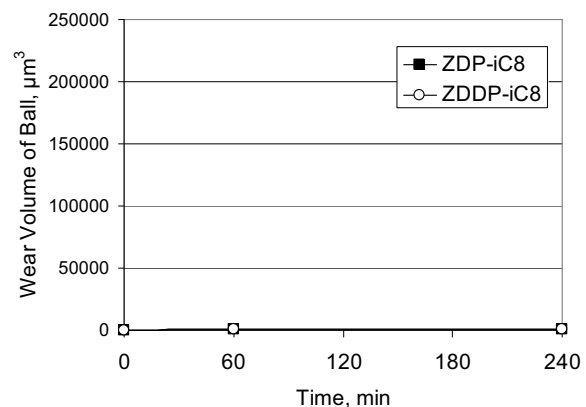


Figure 7. Growths of wear volumes of balls with rubbing time for **ZDP-iC8** and **ZDDP-iC8**.

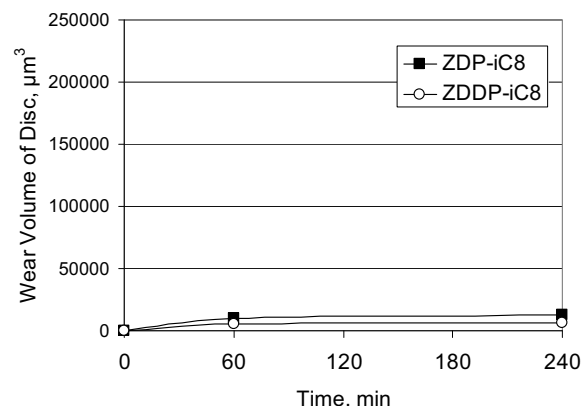


Figure 8. Growths of wear volumes of discs with rubbing time for **ZDP-iC8** and **ZDDP-iC8**.