Engine Oil Degradation Induced by Biodiesel: Effect of Methyl Oleate on the Performance of Zinc Dialkylidithiophosphate

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ABSTRACT: In the present work, the oxidation stability of blends of methyl oleate, zinc dialkylidithiophosphate (ZDDP), and a high viscosity index mineral base oil was determined by the method of a rotating pressure vessel, while the antiwear abilities were evaluated on a four-ball friction tester. Thereafter, the thermal decomposition characteristics and oxidation products of the oxidized blends were analyzed by a thermogravimetric analyzer and a gas chromatograph coupled to a mass spectrometer, respectively. The results showed that the antioxidation ability of ZDDP was substantially improved by methyl oleate, while the antiwear capacity is markedly impaired by methyl oleate. Furthermore, the thermal decomposition characteristics and oxidation products of ZDDP-containing oils were altered by methyl oleate. The present study evidently convinced that chemical interactions between ZDDP and methyl oleate had occurred, which were attributed to the increased antioxidation ability and decreased antiwear capacity of ZDDP in oils contaminated with methyl oleate.

1. INTRODUCTION

Engine oils are very important lubricants. They are blends of mineral or synthetic base oils and varieties of additives such as detergents, dispersants, and oxidation inhibitors. Zinc dialkylidithiophosphates (ZDDPs) are excellent multifunctional additives and have been extensively used in engine oils as antiwear agents, antioxidants, and corrosion inhibitors for over 60 years. Although in recent years, the total elimination of ZDDPs or only extremely low levels of ZDDPs in engine oils has been expected, due to increased automotive emissions caused by phosphorous- and sulfur-poisoned catalytic converters, no acceptable antiwear additives to replace ZDDPs are currently available, and the research concerning ZDDPs remains one of the most interested topics in the tribological field.1−4

Biodiesel is a competent, environmentally friendly substitute for conventional petrodiesel. It comes from renewable vegetable oils or animal fats and consists mainly of unsaturated and saturated fatty acid methyl esters (FAME) such as methyl oleate, methyl linoleate, methyl linolenate, and methyl stearate. In the past few decades, a vast amount of studies on the production and performances of biodiesel has been performed and reported.5−8

As we know, during the operation of an engine, a small amount of incompletely combusted fuel will scrap into the engine oil sump by oil seepage flow or gas entrainment. Therefore, engine oils are regularly exposed to fuel dilution, which adversely affects their quality and thus performances. It has been known that due to its relatively higher viscosity and reactivity, biodiesel is more prone to accumulate in engine crankcase and is more harmful to engine oil quality than conventional petrodiesels.9−10 The effects of biodiesel on engine oil degradation have as such become special concerns during operation of a biodiesel-driven engine. In previous years, although some investigations have been done to understand the negative impacts of biodiesel on engine oil deterioration,11−16 the nature of engine oil degradation caused by biodiesel is still not fully clear.

Conventionally, engine oil degradation under engine operation conditions is accompanied by very complicated chemical reactions such as oxidation and polymerization. Thus, from chemical points of view, engine oil degradation induced by biodiesel can naturally be ascribed to the chemical characteristics of FAMEs and their interactions with engine oil components, viz. additives and base oils. The present investigation focused on the performance characteristics of ZDDP in a mineral base oil under the influence of methyl oleate, which is an abundant FAME in most biodiesels. Antioxidation ability and antiwear capacity of ZDDP in oils blended with methyl oleate were evaluated, and thereafter the thermal decomposition characteristics and the chemical compositions of the oxidized oils containing ZDDP and methyl oleate were analyzed, in an attempt to understand the effectiveness of ZDDP in biodiesel-fueled engine oils.

2. EXPERIMENTAL SECTION

2.1. Materials. In this work, methyl oleate (purity ≥99%) was obtained from Xiya Chemicals Co. Ltd. China. The ZDDP used was zinc dioctyl dithiophosphate purchased from Tianhe...
Petrochemicals Co. Ltd. China, while \( n \)-hexadecane (purity ≥99.5%) was provided by Kemioiu Chemical agents Co. Ltd. China. Additionally, a mineral base oil of HVI 350 (kinematic viscosity = 68.57 mm\(^2\) s\(^{-1}\), 40 °C; viscosity index = 98; flash point = 221 °C; pour point = -6 °C) was provided by Sinopec, China. Prior to experimentations, a series of blends of different mass percentages of methyl oleate (abbreviated as MO), ZDDP, HVI 350 (abbreviated as HVI), or \( n \)-hexadecane (abbreviated as C\(_{16}\)) were prepared, which were herein named MO/ZDDP/HVI or MO/ZDDP/C\(_{16}\) blends, respectively. Namely, MO/ZDDP/HVI refers to the blends of different contents of MO, ZDDP, and HVI, while MO/ZDDP/C\(_{16}\) refers to the blends of MO, ZDDP, and C\(_{16}\). Taking MO (20%)/ZDDP (2%)/HVI (78%) for example, it indicates that it is a blend of 20% MO, 2% ZDDP, and 78% HVI.

2.2. Oxidation Stability Test. The oxidation stabilities of 12 MO/ZDDP/HVI blends with various contents of MO and ZDDP were evaluated by being rotating pressure vessel method following the Chinese standard SH/T0193, which well corresponds to ASTM D2272 in the determination of oxidation stability of lubricating oils. The oxidation induction periods of MO/ZDDP/HVI blends were determined. Longer induction period indicates better oxidation stability of a sample.

2.3. Wear Test. In this work, antiewear performances of a series of fresh and oxidized MO/ZDDP/HVI blends with a constant content of ZDDP of 2% but various contents of MO were evaluated on a MMW-1P universal four-ball friction tester. The four-ball friction tester consists of a rotating ball that slides on three stationary balls located in an oil cup under selected loads. The balls used in the wear test were GCr15 bearing steel balls (diameter 12.7 mm, hardness 59–61 HRC, and surface roughness \( R_a \) 0.040 \( \mu \)m). The wear tests were performed under the loads of 392 N at the rotary speed of 1200 rpm for 30 min. The wear scar diameters (WSDs) of the worn surfaces of the steel balls, which well characterize the antiewear behavior of a lubricant, were determined after each test run. Lower WSD demonstrates better antiewear performance of a lubricant. The oxidation experimentations of MO/ZDDP/HVI blends were performed in a glass reactor at a constant temperature of 150 °C under an air atmosphere (flow rate of 300 mL min\(^{-1}\)) for 6 h.

2.4. Thermogravimetric Analysis (TGA). To understand the interactions between ZDDP and MO, and thus the effects of MO on the performances of ZDDP, thermal decomposition characteristics of two oxidized blends of MO/ZDDP/HVI, viz. MO (0%)/ZDDP (2%)/HVI (98%) and MO (20%)/ZDDP (2%)/HVI (78%), were evaluated using a SDT-Q600 thermogravimetric analyzer (TGA) from TA Instruments. Typically, about 10 mg of samples, in an alumina pan, were heated at a rate of 10 °C/min from room temperature to 600 °C under a nitrogen atmosphere (flow rate of 50 mL/min.). The oxidation of the MO/ZDDP/HVI blends was performed following the procedures of oxidation experimentations as described in 2.3.

2.5. Gas Chromatography/Mass Spectrometry (GC/MS) Analysis. Since mineral base oils are very complex blends of hydrocarbons of different sizes and structures, characterization of chemical compositions of oxidation products of MO/ZDDP/HVI can be highly difficult. Thus, to simplify GC/MS analysis, \( n \)-hexadecane instead of HVI was used as a surrogate for mineral base oil. In this work, two MO/ZDDP/C\(_{16}\) blends, viz. MO (0%)/ZDDP (2%)/C\(_{16}\) (98%) and MO (20%)/ZDDP (2%)/C\(_{16}\) (78%), were used. Prior to analysis, the MO/ZDDP/C\(_{16}\) blends were subjected to thermal oxidation following the procedures of oxidation experimentations as described in Section 2.3. After oxidation, the chemical compositions of the oxidized samples were characterized on a gas chromatograph coupled to a mass spectrometer. The GC/MS analysis was performed following the procedures as reported previously by the authors.\(^{17}\) In short, chromatographic separation was conducted on a quartz capillary column with helium as the carrier gas. The GC oven programmed temperature was set at an initial temperature of 160 °C for 3 min and ramped at a rate of 10 °C min\(^{-1}\) to 240 °C for 2 min and then at 5 °C min\(^{-1}\) to 300 °C where it was held for 10 min. Mass spectrometry analyses were carried out in the EI mode.

3. RESULTS AND DISCUSSION

3.1. Effect of MO on the Antioxidation Ability of ZDDP. Oxidation stability is one of the most important characteristics of engine oils. Shown in Figure 1 are the oxidation induction periods for various MO/ZDDP/HVI blends.

In Figure 1, a significant increase in induction periods for oils with ZDDP is observable. However, a drastic decrease in induction periods for oils with increasing concentrations of MO is also obvious. These confirmed that ZDDP is a powerful oxidation inhibitor but adversely MO is an intense oxidation enhancer for mineral oils. The excellent antioxidation ability of ZDDP has been well known. The readily oxidizing ability of unsaturated FAMEs due to their inherent high chemical reactivity has also been widely accepted.\(^{18}\) Furthermore, by comparing the results of blends with different contents of MO, it can also be found that in the case of 0% MO, the induction periods of blends with ZDDP are approximately two times higher than that without ZDDP. However, in the case of 5% MO, 10% MO, or 20% MO, the induction periods of blends with ZDDP are even three times higher than that without ZDDP. This indicated that although the addition of MO markedly impaired the oxidation resistance of oils, the ability of ZDDP in resisting the oxidation of oils was substantially improved by MO. The enhanced antioxidative ability of ZDDP can naturally be attributed to the interactions between ZDDP and MO, on the mechanism of which intensive investigation is still required. In addition, the positive effect of MO on the...
antioxidative ability of ZDDP demonstrated that ZDDP had worked properly and efficiently as an oxidation inhibitor in oils with MO.

3.2. Effect of MO on the Antiwear Ability of ZDDP. Figure 2 shows the wear scar diameters of the worn surfaces lubricated with fresh and oxidized MO/ZDDP/HVI blends containing 2% of ZDDP but different percentages of MO. To help in understanding the antiwear characteristics of ZDDP and MO in a blend, WSDs for fresh and oxidized neat HVI 350 mineral oil were also tested and are shown in Figure 2.

It is clear from Figure 2 that the variations of WSDs for fresh and oxidized MO/ZDDP/HVI blends with contents of MO are markedly different. This indicated that MO had participated in the tribological processes but that its effects on the antiwear ability of ZDDP were different before and after oxidation of a blend. Before oxidation, a low concentration of MO, namely, 5.0%, helped in improving the antiwear ability of ZDDP, which might primarily be attributed to the fortified boundary lubrication film strength thanks to the co-adsorption of polar MO molecules on the friction surfaces. Adversely, at higher MO concentrations such as 10 and 20%, the antiwear ability of ZDDP decreased with increasing percentages of MO, as might probably be related on one hand to the competitive adsorption between ZDDP and MO on the friction surfaces and thus reduced boundary film strength, and on the other hand to the decreased oil viscosity resulting from high percentages of MO in a blend. However, after oxidation of MO/ZDDP/HVI blends, the antiwear ability of ZDDP, although slightly improved in the blend without MO in comparison to that before oxidation, was impaired obviously by various and increasing contents of MO characterized by a substantial increase in WSDs. From the chemical and tribological points of view, the observable rise of WSDs for oxidized MO-containing blends was undoubtedly correlated with the interactions, including tribo interactions, between MO and ZDDP to form very complicated chemicals, which contributed to the deteriorated antiwear performance of ZDDP.

3.3. Thermal Decomposition Characteristics. Figure 3 shows the TGA curves, the percentage of mass loss versus temperature, for two oxidized blends of MO (0%)/ZDDP (2%)/HVI (98%) and MO (20%)/ZDDP (2%)/HVI (78%). It can be observed from Figure 3 that the thermal decomposition characteristics of the oxidized blends are markedly different. Typically, the blend of MO (0%)/ZDDP (2%)/HVI (98%) thermally decomposed and volatilized by two steps, first at the temperature of 267 °C and second at about 378 °C. A rapid and significant matter loss of 77.8% was detected in the first step, which can be attributed to the evaporation of light oxidation products and low molecular hydrocarbons of HVI 350 mineral oil. However, the TGA curve of the MO (20%)/ZDDP (2%)/HVI (78%) blend shifted to a lower temperature range, in comparison to that of MO (0%)/ZDDP (2%)/HVI (98%). This indicated that thermal decomposition characteristics of ZDDP-containing oils had been changed by MO. The TGA profile for the MO (20%)/ZDDP (2%)/HVI (78%) blend can be divided into three decomposition phases or three decomposition steps. In the first phase that extends up to 326 °C, light oxidation products or hydrocarbons decomposed initially at about 223 °C and then volatilized evidently upon increasing temperatures, with a substantial percentage of matter loss of 48.6%. In the second phase, from 326 to 361 °C, heavier oxidation products decomposed and rapidly evaporated, producing a sharp loss of mass of 39.2%. In the third phase, after 380 °C, a small amount of mass loss is observable, which corresponded to the cracking of high molecular oxidation products, leaving behind traces of nonvolatile residues, possibly arising from the metallic zinc of ZDDP. The TGA results demonstrated that different varieties and amounts of chemicals had been produced during oxidation of the blends of MO (0%)/ZDDP (2%)/HVI (98%) and MO (20%)/ZDDP (2%)/HVI (78%). It is thus reasonable to speculate that very complex chemical interactions between ZDDP and MO, direct or indirect, are likely to have occurred during oxidation of the blends.

3.4. Compositions of Oxidation Products. Displayed in Figure 4 are total ion chromatograms (TICs) of GC/MS analysis for two MO/ZDDP/C_{16} blends that had been thermally oxidized at a constant temperature of 150 °C for 6 h, respectively. The identified major oxidation products are also given in Tables 1 and 2.

By comparing the GC/MS results of oxidized MO/ZDDP/C_{16} blends shown in Figure 4 and Tables 1, 2 with those of oxidized MO/C_{16} blend, which have been previously analyzed and reported by the authors, it can be observed clearly that a relatively few varieties of oxygenated degradation products had been generated for blends containing ZDDP. In fact, in our previous GC/MS analysis of the oxidized MO/C_{16} blend, many varieties of oxy-compounds of alcohols, ketones, acids, and esters were detected, typically characterized by formation of 4-hexadecanediol (retention time 14.959 min; relative
content 12.906%), 1,2-dodecanediol (retention time 15.132 min; relative content 11.023%), methyl palmitate (retention time 16.461 min; relative content 10.962%), 1-pentyl decanol (retention time 15.239 min; relative content 6.560%), and methyl stearate (retention time 18.321 min; relative content 4.363%). Thus, the GC/MS results, in combination with the oxidation stability results as shown in Figure 1, definitely convinced on one hand that MO is inclined to induce the oxidation of oils and on the other hand that ZDDP is excellent in inhibiting the oxidation of mineral oils. Furthermore, it is noteworthy from Figure 4 that for the oxidized MO (0%)/ZDDP (2%)/C16 (98%) blend, a sulfur-containing compound of dioctyl disulfide (17.893 min in Figure 4a) was detected, which is an excellent wear reducer and was thereby an important attribute for improved antiwear ability as shown in Figure 3. Moreover, for the oxidized MO (20%)/ZDDP (2%)/C16 (78%) blend, chemical species containing sulfur and phosphorus such as diocetyl sulfoxide (15.405 min in Figure 4b) and di(2-ethylhexyl) methyl phosphate (20.105 min in Figure 4b) were produced, which are also good antiewear agents and had partially compensated the loss of antiwear capacity caused by oxidation, although the antiwear abilities of the oxidized MO-containing blends were slightly poorer than those of fresh ones as also shown in Figure 3. Formation of sulfur and phosphorus-containing chemicals indicated that ZDDP had taken part in the oxidation reactions and had been partially depleted in the oxidation process. Finally, based on the results of GC/MS analysis, as well as the results of oxidation stability evaluation, TGA analysis, and wear tests, it can be firmly concluded that chemical interactions of MO with ZDDP had occurred during oxidation of MO (20%)/ZDDP (2%)/C16 (78%) blends, obviously characterized by formation of dioctyl disulfide in the oxidized MO (0%)/ZDDP (2%)/C16 (98%) blend, which might come from thermal decomposition of ZDDP, but diocetyl sulfoxide and di(2-ethylhexyl) methyl phosphate in the oxidized MO (20%)/ZDDP (2%)/C16 (78%) blend, which were definitely derived from reactions of ZDDP with MO. Thus, from the results of the present study, it is reasonable to infer that the mechanism of interactions between MO and ZDDP under elevated temperatures is closely related to the inherent nature of high chemical activity of MO to induce its intensive reactions with ZDDP as well as with thermal decomposition products of ZDDP. Noticeable chemical interactions between biodiesel and ZDDP have been previously reported by Fang et al.,19 who observed that degradation products of biodiesel could interact with oil additives including ZDDP, with an associated result of reduced oil performances. They also revealed that biodiesel dilution in lubricating oil could result in production of complexes between oxidized biodiesel components and ZDDP.

### Table 1. Predominant Products for the MO (0%)/ZDDP (2%)/C16 (98%) Blend

| no. | retention time (min) | relative content (%) | attribution            |
|-----|---------------------|---------------------|-----------------------|
| 1   | 13.067              | 92.657              | hexadecane            |
| 2   | 13.721              | 0.235               | heptadecane           |
| 3   | 14.415              | 0.501               | octadecane            |
| 4   | 15.496              | 1.113               | tetramethyl lauryl alcohol |
| 5   | 17.893              | 1.836               | dioctyl disulfide     |
| 6   | 18.267              | 0.328               | octyl dodecanoic acid |

### Table 2. Predominant Products for the MO (20%)/ZDDP (2%)/C16 (78%) Blend

| no. | retention time (min) | relative content (%) | attribution            |
|-----|---------------------|---------------------|-----------------------|
| 1   | 10.421              | 0.833               | tetradecane           |
| 2   | 10.890              | 1.504               | methyl 9-oxononoanoate |
| 3   | 13.055              | 58.627              | hexadecane            |
| 4   | 14.013              | 0.506               | methyl laurate        |
| 5   | 14.428              | 0.218               | methyl tridecanoate   |
| 6   | 15.185              | 0.885               | methyl (E)-hexadec-9-enoate |
| 7   | 15.246              | 1.638               | 2-pentadecanol        |
| 8   | 15.405              | 0.974               | dioctyl sulfoxide     |
| 9   | 16.463              | 18.937              | methyl hexadecanoate  |
| 10  | 18.069              | 10.735              | methyl oleate         |
| 11  | 19.924              | 0.765               | methyl elaidate       |
| 12  | 20.105              | 1.753               | di(2-ethylhexyl) methyl phosphate |

4. CONCLUSIONS

The current study has demonstrated that MO substantially improved the antioxidation ability but markedly impaired the antiwear capacity of ZDDP. Furthermore, the present investigation also indicated that thermal decomposition and oxidation characteristics of ZDDP-containing oils were altered by MO. Thus, based on the present results, it can be concluded that the effectiveness of ZDDP as an oxidation inhibitor was fortified but as a wear reducer was hampered by MO in mineral oils and that chemical interactions between ZDDP and MO were noticeable, which were attributed to the increased antioxidation ability and decreased antiwear capacity of...
ZDDP. Naturally, it can also be inferred from the present results that the compatibility of ZDDP with other FAMEs such as methyl linoleate and methyl linolenate is also likely to occur and needs specific attention, to fight against quality degradation of engine oil caused by biodiesel and to develop novel biodiesel engine oil formulations.

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**Notes**

The authors declare no competing financial interest.

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