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Oxidation performance of oils containing ZnDTC, ZnDDP and their mixture after oxidation test by PDSC

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Abstract

Pressurized differential scanning calorimetry (PDSC) and FT–IR were employed to evaluate the anti-oxidation properties of ZnDTC, ZnDDP and their mixture in lubricating oil. PDSC data were quite different between oils containing the same additive at different concentrations and among oils containing a single additive and the mixture.

Keywords: Lubricants; ZnDTC; ZnDDP; Oxidation; PDSC; FT–IR

1. Introduction

Oxidation stability is one of the most important indexes for modern engine oils, particularly for ever prolonged oil change intervals. Oxidation also will have a significant impact on other properties of lubricants such as anti-wear performance [1]. Therefore, if zinc dialkyl dithiophosphate (ZnDDP) can be protected from oxidation by the use of alternative antioxidants, the overall anti-wear performance of the lubricant may be improved.

ZnDDP is a common and main antioxidant for lubricants [2–4]. However, it poisons emission catalysts, so modern engine oil specifications above API SG level have resulted in controlled reduction of phosphorous content. Thus, some alternative additives must be introduced to engine oils. Zinc dithiocarbamate (ZnDTC) is a preferable choice to compensate anti-oxidation property, and improve anti-wear performance of engine oils.

Several methods have been developed to evaluate oxidation of a lubricant. Thermal analytical methods are important and effective [5–9]. Improvements in thermal analysis methods and technology are a prime example of the changes in the industry that allow rapid assessment of base stocks and additives while reducing the number of expensive full-scale tests. Pressurized differential scanning calorimetry (PDSC) data exhibit a good correlation with thin-film oxygen uptake test and has been used to screen lubricants for ASTM IIID and IIIE automotive tests [9–11].

In this paper, PDSC and FT–IR were used to evaluate oxidation of oils containing ZnDDP or ZnDTC and their mixture.

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Table 1
Properties of the base oil

Properties	Yubase-6 (API Group III)
Viscosity at 40 °C (cSt)	37.65
Viscosity index	130
Flash point (°C)	234
Pour point (°C)	−15
CCS viscosity at −20 °C (cP)	1230
CCS viscosity at −25 °C (cP)	2220
Noack volatility (wt.%)	7.8
Total acid no. (mg KOH g^{-1})	<0.03
Sulfur (ppm)	<3
Nitrogen (ppm)	<3
Paraffins (wt.%)	55.5
Naphthenes (wt.%)	43.7
Aromatics (wt.%)	0.8

2. Experimental

2.1. Oils

Yubase-6, a mineral-based oil with a very high viscosity index, was used as the base oil in this study (see Table 1). Zinc diamyl dithiocarbamate (ZnDTC) and a primary C5 zinc dialkyl dithiophosphate (ZnDDP) were obtained from the RT Vanderbilt and Infinium Companies, respectively. The elemental contents of the additives are listed in Table 2. Elemental sulfur and nitrogen contents of the base oil and additives were determined with a Vario EL elemental analyzer. Zinc and phosphorus were determined by ICP. Physicochemical properties were determined by ASTM methods.

2.2. Oxidation test

The rotary bomb oxidation test (RBOT) was used to measure the oxidation stability of lubricating oils (ASTM D 2272, [12]). In all tests, the sample was placed in a rotary bomb in a heated bath (150 °C) in the presence of water and a copper catalyst coil, which was then charged with oxygen at a pressure of 629 kPa. Oxidation stability was expressed as the time required to achieve a specified pressure drop of 175 kPa.

The Indiana Stirring Oxidation Test (ISOT) were conducted according to KS M 2021-1987 [13] at 180 °C, with iron and copper plates as catalysts, and a testing time of 24 h. After testing, viscosity at 40 °C and total acid number (TAN) of the tested oil samples were determined. These tested oils were then used for PDSC analysis.

Table 2
Element composition of the additives

Elements	Zn (%)	S (%)	N (%)	P (%)
ZnDTC	4.16	15.08	4.873	–
ZnDDP	8.9	16.2	–	7.9

2.3. FT–IR

Oxidation products in the tested oil samples were determined with an FT–IR spectrometer in the region of 500–4000 cm^{-1} with a KBr cell having a thickness of 0.11 mm.

2.4. PDSC

A TA Instruments DSC 2910 pressurized differential scanning calorimetry (PDSC) was used under the conditions: aluminum pan, a heating rate of 10 °C min^{-1}, an isothermal temperature of 190 °C, sample mass in the range of 3–6 mg, and an air pressure of 150 psi.

3. Results and discussion

3.1. Oxidation test

The results of the RBOT tests are shown in Table 3. The two additives improve anti-oxidation performance in the mineral oil, but ZnDTC was much better than ZnDDP. The anti-oxidation behavior of the oils containing ZnDTC alone increased with increasing concentration, but the anti-oxidation behavior of the oils containing ZnDDP alone did not change. The mixture exhibited better anti-oxidation performance than either ZnDTC or ZnDDP used alone.

The physicochemical properties of the oils after the ISOT test (Table 3) indicate that viscosities slightly increased for cases containing additives and sharply increased for the base oil after the test. Before the test, the oils containing only ZnDTC and the base oil had very low TANs, while the oils containing only ZnDDP had very high TANs which increased with

Table 3
Physicochemical properties and RBOT results of the oils

Oil samples	ISOT				RBOT (min)
	Viscosity (cSt) at 40 °C		TAN (mg KOH g^{-1})		
	Before test	After test	Before test	After test	
Base oil	37.65	42.27	<0.01	1.41	45
0.5% ZnDTC	–	37.84	<0.01	0.11	245
1.0% ZnDTC	–	37.91	<0.01	0.24	335
0.5% ZnDDP	–	37.83	0.73	0.06	170
1.0% ZnDDP	–	37.63	1.49	0.09	160
0.5% ZnDTC + 0.5% ZnDDP	–	38.52	0.73	0.60	670

concentrations of the additive in the oils. After the test, the TANs slightly increased for the cases containing only ZnDTC but sharply increased for the base oil. Conversely, the TANs significantly decreased in oils containing ZnDDP alone. With mixtures, the change in TAN after the test was much smaller than that of oils containing ZnDDP alone and is also quite different from that of the oils containing ZnDTC alone.

FT–IR spectra are shown in Figs. 1–3. The base oil was readily oxidized during the tests. The main oxidation products were carboxylates and ether-containing species based on the absorption peaks at 1721.3 and 1779.2 cm^{-1} due to C=O and at around 3458.1 cm^{-1} due to –OH stretching vibration [14]. Obvious oxidation products were not found by FT–IR in additive-containing oils.

The characteristic absorptions of ZnDDP at 1007.3 cm^{-1} due to P–O–C vibrations and at around 656 cm^{-1} due to P=S vibrations [14,15] were reduced in the case of ZnDDP after the oxidation test. In the mixture, the P–O–C absorptions nearly disappeared after the test; showing the additive ZnDDP was depleted during the test.

In the FT–IR spectra of the oils containing ZnDTC alone, the weak absorptions at about 972 and 1092 cm^{-1} are due to C=S asymmetric stretching vibrations and C–N vibrations, respectively. Absorptions at 1211 cm^{-1} are probably due to C–N and C=S [14]. After testing, these absorptions still existed but with relatively weak intensities. ZnDTC was thus still maintained in the tested oils. The increasing intensities of absorptions at 1242 cm^{-1} after the test were probably due to C–O–C [14], which could be a primary oxidation product formed during the test.

In Fig. 3, the intensity of P–O–C absorption after the test was still strong compared with the unused

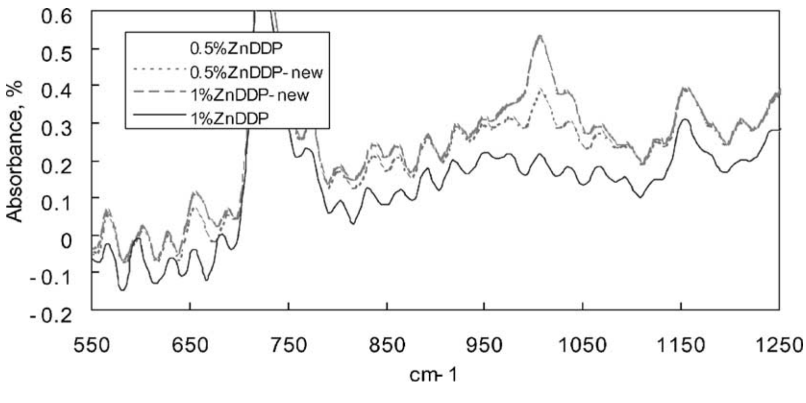

Fig. 1. FT–IR spectra of the oils containing ZnDDP alone before and after the oxidation test.

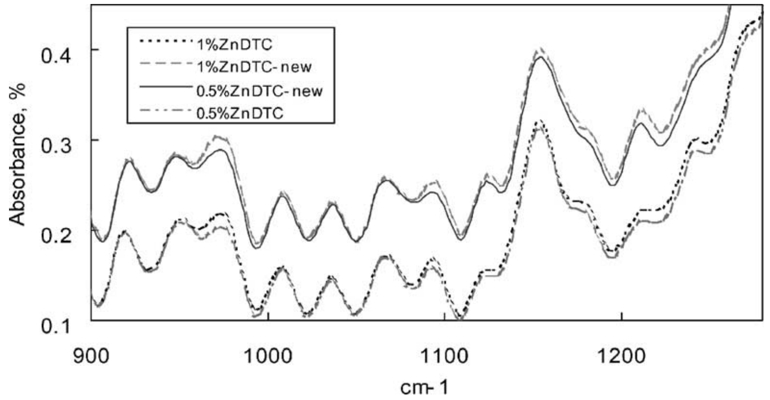

Fig. 2. FT–IR spectra of the oils containing ZnDTC alone before and after the oxidation test.

mixture. Thus, FT–IR shows that there were still a large amount of ZnDDP and/or its primarily decomposed intermediates in the tested combination. This indicates that ZnDDP can survive much longer after being mixed with ZnDTC during oxidation than ZnDDP used alone.

3.2. PDSC analysis

PDSC data are shown in Figs. 4–8. Figs. 4–7 indicate that the concentrations of the two additives used alone influenced the shapes of PDSC thermograms and onset and maximum temperatures. The onset temperature was obtained from extrapolating the tangent drawn on the steepest slope of the reaction exotherm [16,17]. T_{max} defined as the time at which a maximum exothermal peak appears, can also be used to evaluate oxidation condition of a sample [8]. Figs. 4 and 5 show the onset temperatures (T_o) at 18.28 and 24 min and the maximum temperatures (T_{max}) at 23.02 and 27.16 min for 0.5% ZnDTC and 1% ZnDTC, respectively.

Figs. 6 and 7 indicate that oil containing 0.5% ZnDDP shows T_o at 15.68 min and T_{max} at 17.85 min with a right shoulder peak; 1% ZnDDP has T_o at 16.51 min and T_{max} at 21.05 min with a left shoulder peak.

Fig. 8 shows that the mixture exhibited three exothermal peaks with an onset temperature at 17.26 min and a maximum temperature at 37.93 min.

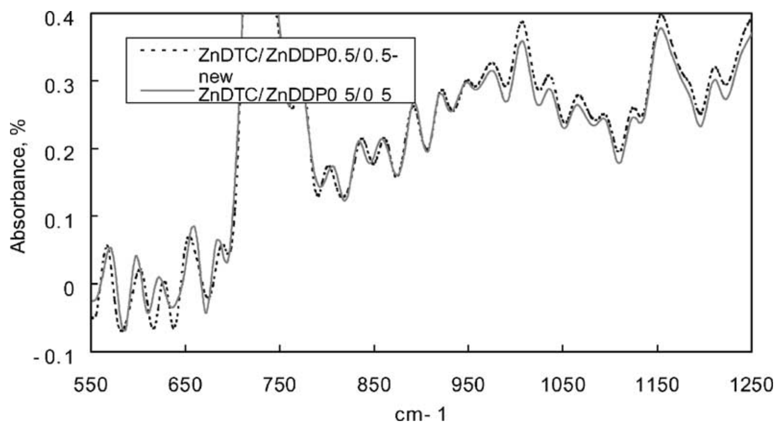

Fig. 3. FT–IR spectra of the oils containing ZnDDP and ZnDTC before and after the oxidation test.

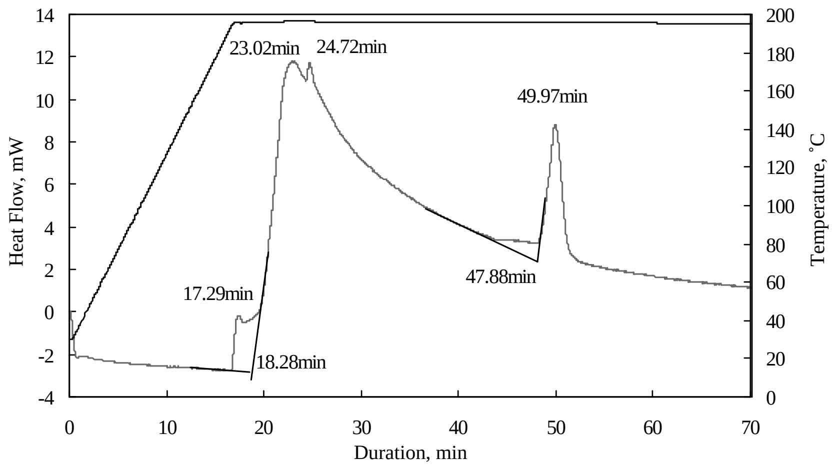

Fig. 4. PDSC exotherm for the oil containing 0.5% ZnDTC alone after the oxidation test.

At 1% additive, the mixture exhibited the longest T_{max}, followed by 1% ZnDTC and the shortest was 1% ZnDDP. With a single additive, ZnDTC-containing oils exhibited a better anti-oxidation performance than ZnDDP-containing oils, in good agreement with RBOT results in Table 3.

The PDSC curves obtained in this paper are quite different from many in the literature in which broad and sharp exothermal peaks are found. In this test, before a main exothermal peak appeared, there was a relatively small exothermal peak except with the oils containing ZnDDP alone. These small exothermal peaks are probably related to primary oxidation products. Oils with good anti-oxidation capacity gave rise to more initial oxidation products and less final aged products. Oils with poor anti-oxidation capacity

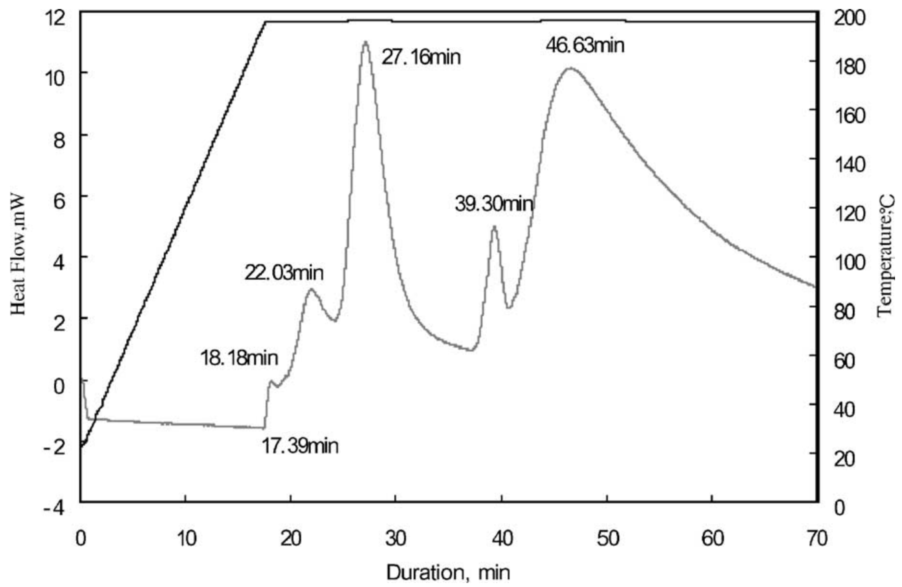

Fig. 5. PDSC exotherm for the oil containing 1% ZnDTC alone after the oxidation test.

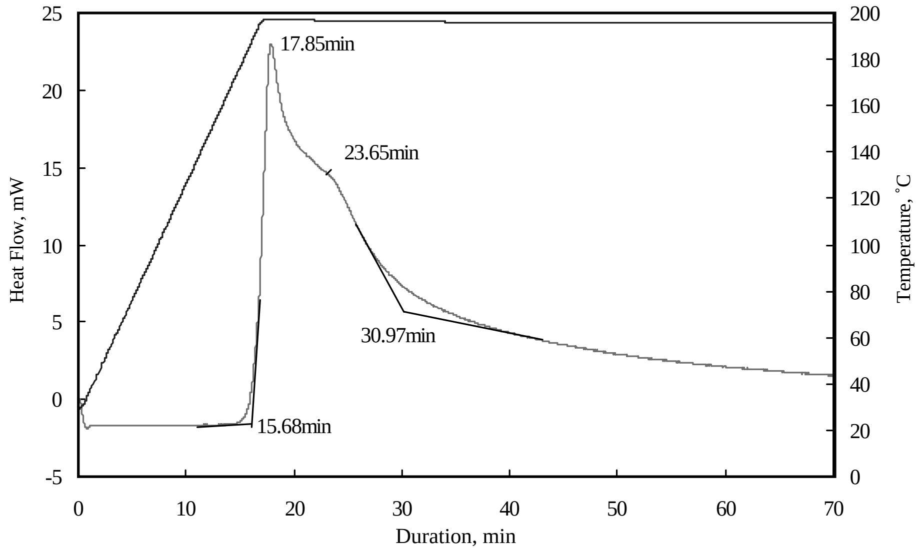

Fig. 6. PDSC exotherm for the oil containing 0.5% ZnDDP alone after the oxidation test.

produced more final oxidation products and less primary oxidation products. Naturally, the more primary oxidation products, the lower the onset temperature. Thus, in the present test, 1% ZnDTC exhibited lower onset temperature than 0.5% ZnDTC. Moreover, the mixture had the lowest onset temperature. Just as RBOT test showed that ZnDDP had the poorest anti-oxidation ability, the thermograms from the oils containing ZnDDP alone exhibited simple sharp exothermal peaks without small companions.

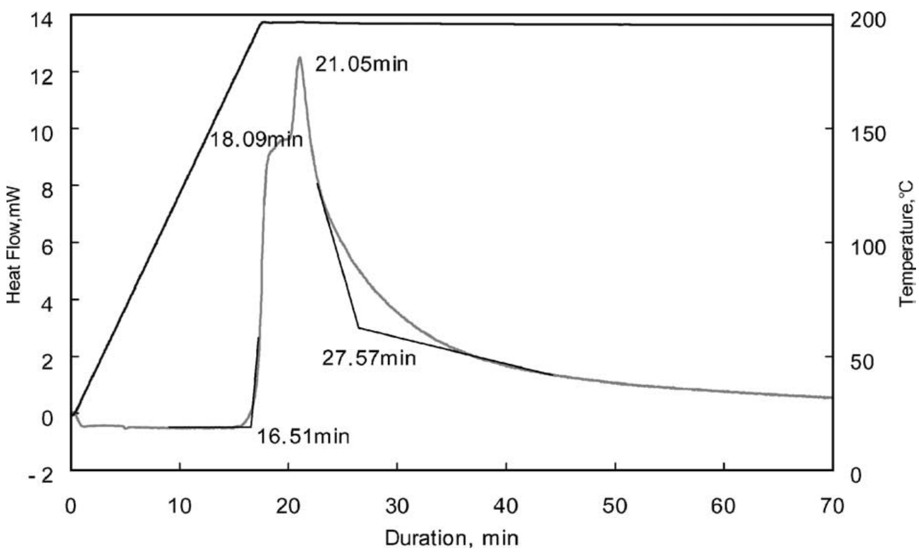

Fig. 7. PDSC exotherm for the oil containing 1% ZnDDP alone after the oxidation test.

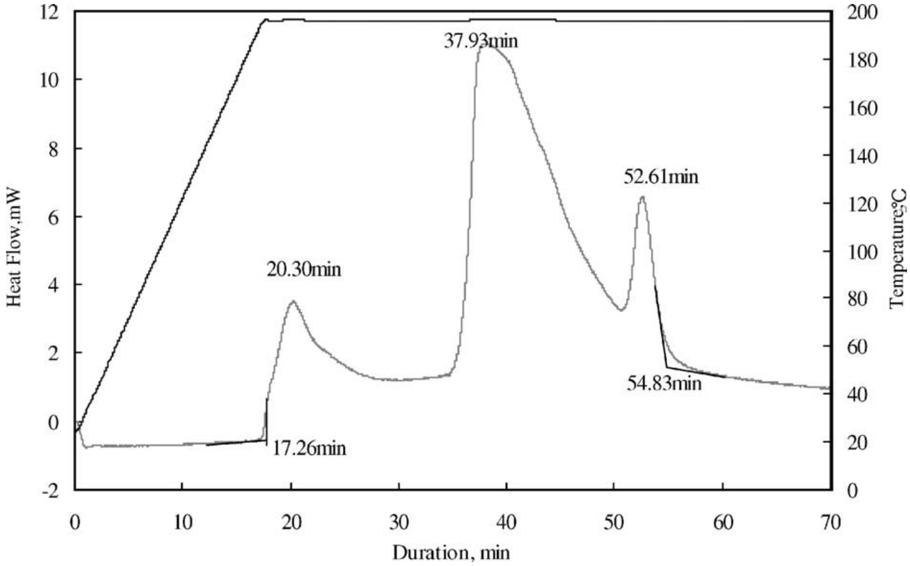

Fig. 8. PDSC exotherm for the oil containing 0.5% ZnDDP and 0.5% ZnDTC after the oxidation test.

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