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Determining the antioxidant activities of organic sulfides by rotary bomb oxidation test and pressurized differential scanning calorimetry

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Abstract

Several typical sulfides were selected and dissolved in hydrotreated base oil, and the antioxidant activities of sulfides studied by rotary bomb oxidation test (RBOT), isothermal pressurized differential scanning calorimetry (PDSC) and non-isothermal PDSC. Four characteristic indexes of constant heating-rate PDSC were chosen and normalized to a comprehensive index by a new method. The sequence determined by the comprehensive index accords partly to the sequence determined by RBOT and accords well with the results reported. The antioxidant activity of sulfide increases with the number of sulfur atoms. Sulfide with long chain has good antioxidant activity, and the antioxidant activity of cyclic sulfides is poor. The method of normalizing the data is useful to determine the oxidation performances of samples, especially when the antioxidant activities vary greatly.

Keywords: Structure–activity relationship; Sulfide; Pressurized DSC; RBOT; Normalization

1. Introduction

Organic sulfur compounds have been used widely in lubricating compositions for their extreme-pressure (EP) as well as their antiwear (AW) properties [1–5]. Extensive work has been done and is reflected by the volume of literature published in characterizing and relating the structure of the organic sulfur compounds to their EP and AW performance [1–4]. Sulfur compounds can also improve oxidation stability of lubricating oil, and some of them are considered natural antioxidants in lubricating oil [6–8]. The oxidation resistance of sulfur compounds differs with molecular structure [9]. The relationship between structures and oxidative stability had been studied by Vasu Bala in solvent-refined base oil, using modified Groupement Francais de Coordination (GFC) oxidation test [10]. Nowadays base oil is mostly hydrotreated, so it is very important to study the antioxidant activities of organic sulfides in hydrotreated base oil.

There are many methods for evaluating the oxidation stability of lubricating oil, for example, pressurized differential scanning calorimetry (PDSC), rotary bomb oxidation test (RBOT), turbine oil stability test (TOST), thin film micro oxidation (TFMO) and hydroperoxide titration test. RBOT is a rapid method for determining the oxidation stability of lubricating oils, and has been used to study the oxidation stability of lubricating oil by many workers [11–18]. Many recent works have shown that PDSC is an effective way to evaluate the oxidation stability of base oils and antioxidants [19–23]. It is claimed that the use of high pressure for PDSC inhibits the rate of volatilization loss of the lubricant and saturates the liquid phase with oxygen. The result is an acceleration of oxidation as well as a sharpening of the lubricant exotherm compared with atmospheric pressure DSC. It allows use of lower test temperatures or shorter test times at the same temperatures. The technology is also a rapid and accurate technique for measuring parameters that correlate with oxidation reactions of oils [24–26]. PDSC applications are run either in an isothermal or a programmed temperature mode, and it has been used to measure either inhibition time (isothermal) [16,22,27–34] or the onset temperature (temperature ramping) [23,33–39] of lubricant oxidation.

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The objective of this study is to determine the antioxidant activities of several typical organic sulfides by rotary bomb oxidation test and pressurized DSC, and to relate the structure of sulfides to their oxidative resistance in severely hydrotreated base oil. Different alkyl/cyclic substitution, chain length and polysulfide functionality of sulfides were studied for their oxidative resistances. PDSC was run in an isothermal and a programmed temperature mode. The data of programmed temperature PDSC were processed by a new method, and the relationship between RBOT and programmed temperature PDSC was clarified.

2. Experimental

2.1. Apparatus

Rotary bomb oxidation tests were performed on a SETA-15200-2 (UK). The test oil, water and copper catalyst coil, contained in a covered glass container, were placed in a vessel equipped with a pressure gage. The vessel was charged with 99.5% oxygen to a gage pressure of 620 kPa, placed in a constant-temperature oil bath set at 140 °C and rotated axially at 100 rpm at an angle of 30° from the horizontal. The number of minutes required to reach a drop of 175 kPa in gage pressure was the oxidation induction time (OIT) of the test sample, which was denoted the oxidation stability of the sample.

The PDSC tests were developed on a NETZSCH DSC 204 Instruments (Germany), which consisted of a measuring unit-part, TA controller 414/3A, a CC 200 cooler, a gas flow control device and a computer for data recording and further processing. The measuring head within the furnace carried two crucibles, one for the sample substance and the other for the reference material, each sitting on a thermocouple. The crucibles were identical, with the material and size dependent on the substance to be measured and the temperature range of interest. Aluminum sample pans were employed, which were solid fat index (SFI) pans. They contained a raised platform in the center of the pan where the sample sat and this prevented the sample from wicking up the sides of the pan.

2.2. Materials and reagents

Mineral hydrotreated base oil was supplied by Kelamayi Petro-Chemical Corporation (Xinjiang, China), which was naphthenic base oil and excellent base stock for manufacturing transformer oil. The following compounds were purchased from J&K CHEMICA: *n*-butyl sulfide, *n*-dodecyl sulfide, tetrohydrothiophene, pentamethylene sulfide, ethyl phenyl sulfide, diphenyl sulfide, diphenyl disulfide, dibenzyl sulfide, dibenzyl disulfide and dibenzyl trisulfide. All sulfides were the purest grade available. All sulfides were weighted and blended into the base oil at 50 °C for approximately 1 h. The concentration of each sulfide was 0.05 mol/l.

2.3. Oxidation stability test by RBOT

The rotary bomb oxidation tests were done according to ASTM D 2112-01a. The sample was measured to 50.0 ± 0.5 g with 5.0 ml of reagent water added to the sample. All oil samples were run in duplicate and the average times were reported.

2.4. Isothermal PDSC under oxygen atmosphere

Isothermal PDSC of oil samples were performed on 1–1.5 mg oil samples in open aluminum pans under 1500 or 3500 kPa of high-purity oxygen. These conditions maintain maximum contact with the sample and eliminate any limitation due to oxygen diffusion in the oil medium. Oxygen flow was maintained at 100 ml/min. After preliminary pressurization of the PDSC cell with oxygen, pressure, oxygen flow and temperature were adjusted. Oil samples were heated from ambient temperature to 165 or 180 °C at a heating-rate of 50 °C/min before being held in isothermal mode until an exothermic peak of oxidation was measured. Isothermal conditions were chosen to provide reasonable exotherm times.

2.5. Constant heating-rate PDSC under oxygen atmosphere

Constant heating-rate PDSC of oil samples were performed on 1–1.5 mg samples in open aluminum pans under 1500 kPa of high-purity oxygen. The reference pan was as identical as possible with the sample pans and was left empty. The oil samples were heated from ambient temperature to 400 °C at a constant heating-rate of 10 °C/min and oxygen flow was maintained at 100 ml/min.

3. Results and discussion

3.1. The antioxidant activities of sulfides determined by RBOT

Table 1 shows the RBOT results for the selected sulfides in hydrotreated base oil. The RBOT times vary from 41.5 to 285 min. The RBOT time of base oil is 68 min. Dibenzyl sulfide shows an unexpected low RBOT time of 41.5 min. In general, the antioxidant activity increases with increasing number of sulfur atoms, and the long chain sulfides have good antioxidant activity.

3.2. The antioxidant activities of sulfides determined by isothermal PDSC

The oxidation induction times of oil samples containing sulfides were determined over a range of temperatures by PDSC. The samples were heated to a pre-determined temperature, before being held at this temperature until an exothermic peak of oxidation was measured. The oxidation induction time was then taken as the time elapsed between reaching the predetermined temperature, and the onset of oxidation, calculated by extrapolation from the maximum heat flow to the extrapolation of the baseline, which was shown in Fig. 1. At 165 °C, base oil, butyl sulfide and ethyl phenyl sulfide have oxidation induction times of 9.0, 9.8 and 10.3 min, respectively, under 1500 kPa. However for dibenzyl trisulfide and dibenzyl disulfide no obvious exothermic peak was observed. For dibenzyl trisulfide, there is

Table 1
The test values of the oil samples matrix determined by ROBT and non-isothermal PDSC

Ranking by RBOT	RBOT (min)	T_e (°C)	T_p (°C)	S_a (J/g)	Φ_m (W/g)
Dibenzyl trisulfide	285	208.27	233.20	522.1	2.093
Dibenzyl disulfide	143	223.20	228.51	1479	15.58
Dodecyl sulfide	122	191.15	204.32	2377	13.69
Tetrohydrothiophene	89	198.71	205.90	4179	49.5
Ethyl phenyl sulfide	78	196.37	204.51	3658	38.48
Butyl sulfide	78	196.47	204.43	4627	49.21
Diphenyl sulfide	76	198.41	206.30	3278	37.6
Base oil	68	198.23	205.82	4020	44.82
Pentamethylene sulfide	67	198.67	205.62	4130	48.52
Diphenyl disulfide	60	182.93	189.70	793.4	3.721
Dibenzyl sulfide	41.5	188.81	205.80	2375	13.39

no exothermic peak at higher temperature (180 °C) and pressure (3500 kPa). It is very difficult to choose a suitable isothermal condition for measuring the oxidation induction times of all oil samples in the matrix. Although the oxidation induction time obtained from isothermal PDSC is a useful index to study the oxidation stability of oil samples, it cannot be used to rank the sulfides in this paper.

3.3. The antioxidant activities of sulfides determined by constant heating-rate PDSC

To evaluate the antioxidant activities of all sulfides under the same condition, constant heating-rate PDSC was applied under oxygen atmosphere. Typical constant heating-rate PDSC thermogram is shown in Fig. 2. T_e, T_p, S_a and Φ_m are used to assess the oxidation stabilities of oil samples containing sulfides. S_a is the total area of the exothermic peaks. Φ_m indicates the maximum heat rate. The four indexes are illustrated in Fig. 2 and the characteristic values of all oil samples are shown in Table 1.

The antioxidant activities are ranked in Table 2. The sequences of antioxidant activities determined by T_p and S_a and Φ_m differ, and the sequences are different from the sequence determined by RBOT. As a result, the antioxidant activities of all oil samples matrix cannot be evaluated by a single index.

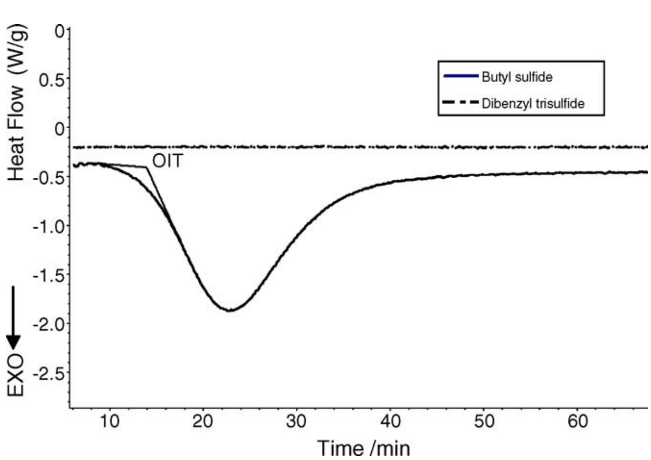

Fig. 1. The typical isothermal PDSC thermogram of oil sample.

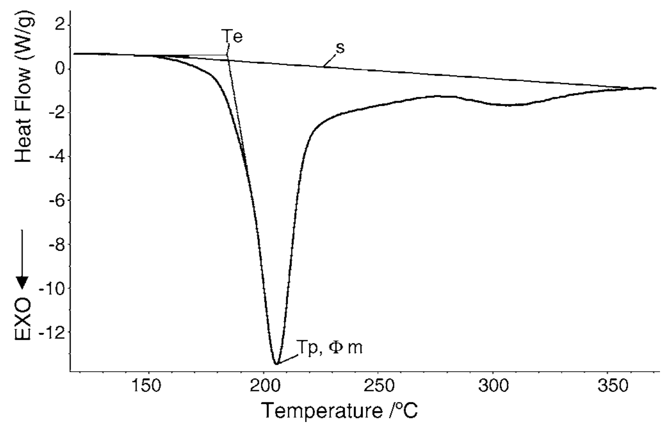

Fig. 2. The typical constant heating-rate PDSC thermogram of oil sample.

The values must be normalized by a standard method to evaluate the antioxidant activity by a suitable index. A new method was used as follows. For T_e, the difference between maximum value and minimum value in Table 1 was used as denominator, and the difference between each value and the minimum value was divided by the difference between maximum value and minimum value to give normalized values between 0 and 1. The same method was applied to normalize T_p. For S_a and Φ_m, the same procedure was used except the difference between the maximum value and the value of oil sample was used as numerator. The normalized values of T_e, T_p, S_a and Φ_m are shown in Table 3. The sum of T_e and T_p can be used to evaluate the antiox-

Table 2
The sequences of antioxidant activities of sulfides rated of by each index

	RBOT	T_e	T_p	S_a	Φ_m
Dibenzyl trisulfide	1	2	1	1	1
Dibenzyl disulfide	2	1	2	3	5
Diphenyl disulfide	10	11	11	2	2
Dodecyl sulfide	3	9	10	5	4
Dibenzyl sulfide	11	10	6	4	3
Diphenyl sulfide	7	5	3	6	6
Ethyl phenyl sulfide	5	8	8	7	7
Base oil	8	6	5	8	8
Pentamethylene sulfide	9	4	7	9	9
Tetrohydrothiophene	4	3	4	10	11
Butyl sulfide	6	7	9	11	10

Table 3
The normalized values of the indexes for oil samples matrix

Ranking by index *A*	T_e	T_p	S_a	Φ_m	Sum of T_e and T_p	Sum of S_a and Φ_m	*A*
Dibenzyl trisulfide	0.6293	1	1	1	1.6293	2	3.63
Dibenzyl disulfide	1	0.8922	0.7669	0.7155	1.8922	1.4824	3.37
Diphenyl disulfide	0	0	0.9339	0.9657	0	1.8996	1.90
Dodecyl sulfide	0.2041	0.3361	0.5481	0.7554	0.5402	1.3035	1.84
Dibenzyl sulfide	0.146	0.3701	0.5486	0.7617	0.5161	1.3103	1.83
Diphenyl sulfide	0.3844	0.3816	0.3286	0.251	0.766	0.5796	1.35
Ethyl phenyl sulfide	0.3337	0.3405	0.2361	0.2325	0.6742	0.4685	1.14
Base oil	0.3799	0.3706	0.1479	0.0987	0.7505	0.2466	1.00
Pentamethylene sulfide	0.3909	0.366	0.1211	0.0207	0.7568	0.1417	0.90
Tetrohydrothiophene	0.3919	0.3724	0.1091	0	0.7643	0.1091	0.87
Butyl sulfide	0.3362	0.3386	0	0.0061	0.6749	0.0061	0.68

idant activities from temperature, and the sum of S_a and Φ_m can also be used to assess the antioxidant activities from heat. The comparison between the sum of T_e and T_p and the sum of S_a and Φ_m is illustrated in Table 3. The sequence of antioxidant activities determined by temperature (sum of T_e and T_p) is different from that determined by heat (sum of S_a and Φ_m). For example, the performance of diphenyl sulfide is good by the index of heat, but it is worst by the index of temperature. The results do not accord well with the results determined by RBOT. As a result, the indexes of the sum of T_e and T_p and the sum of S_a and Φ_m cannot be used to rate the antioxidant activities alone.

The sum of four indexes T_e, T_p, S_a and Φ_m is the comprehensive index *A*, and the values are shown in Table 3. From the result, the antioxidant activity of dibenzyl trisulfide is the best, and the performance of butyl sulfide is the worst. The sequence is showed in Table 3. The antioxidant activity of sulfide increases with increasing number of sulfur atoms, and the oil containing long chain sulfide has good antioxidant activity. The results accord well with Vasu Bala's results [10]. In his study, the organic sulfides were tested in the modified Groupement Francais de Coordination (GFC) oxidation test at 160 °C. Using the solvent-refined mineral base oil, the data indicated alkyl/cyclic substitution, polysulfide functionality and, to a lesser degree, chain length were governing factors for oxidative stability. Collectively, the oxidative stability of the polysulfides tested based on the modified GFC oxidation test in decreasing order of stability was as follows: primary/tertiary alkyl monosulfides > primary/tertiary alkyl disulfids > cyclic disulfides and alkyl trisulfides.

3.4. The relationship between the results of PDSC and the results of RBOT

The DSC/PDSC technique has been used to measure the oxidation induction time, and the relationship between the DSC/PDSC and RBOT has been studied by some researchers [16,29,42,43]. Their oxidation induction times of isothermal PDSC correlate well with results obtained from RBOT. In this paper, because the oxidation induction times of all sulfides cannot be obtained at the same isothermal condition, it cannot be used to study the relationship between isothermal PDSC and RBOT. The comprehensive index *A* of PDSC can be used to determine the antioxidant activities of sulfides. In Table 3, from the sequence rated by the index *A*, polysulfides have good antioxidant activities, and the performance of trisulfide is better than that of disulfide, and sulfide bearing long chain has good performance, and the performance of cyclic sulfides are poor. The relationship between structure and oxidation resistance of sulfides determined by RBOT is similar with what mentioned above. But some sulfides do not accord with the sequence determined by PDSC, for instance, dibenzyl sulfide and diphenyl disulfide. Though the comprehensive rating does not correlate well with the results of RBOT, the index *A* is more suitable to relate PDSC and RBOT than the index of the sum of T_e and T_p. Temperature ramping PDSC is more effective than RBOT to determine the antioxidant activities of different sulfides, especially when the antioxidant activities of sulfides vary greatly.

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