Organotin Compounds as Multipurpose Additives for Lubricating Oils

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The oxidation inhibitivity of an organotin phosphite containing sulfur and that of an organotin borate also containing sulfur were qualitatively investigated by differential thermal analysis (DTA). These compounds suppressed oxidation of squalane considerably. The organotin borate, especially, was an excellent oxidation inhibitor at high temperatures. Moreover, these organotin compounds were characterized by good load-carrying capacities as, indicated by the results of the Timken Test in spite of their low sulfur contents. These new-type additives, organotin phosphite and organotin borate, could be used as multipurpose additives for lubricating oils.

1. Introduction

Problems related to lubrication have recently become more difficult as developments on lubrication technology, have become highly sophisticated and complex. Therefore further studies and new theories are necessary for the solutions of the problems. Moreover, new-types of lubricating oil additives of better performance are desired. Generally, a lubricating oil system contains a variety of additives, which interact complicatedly, often deleteriously, with each other. These harmful effects, however, may be prevented by using a multipurpose additive which simplifies the lubricating oil system. Zinc dialkyldithiophosphate, for instance, is well known as a multipurpose additive, and Sakurai et al. have reported di- μ -thio-dithio-bis(dialkyldithiocarbamate) dimolybdenum^{1),2)}, as exhibiting good oxidation inhibitivity and extreme pressure performance.

In this paper, the results of the experimental studies made on the oxidation inhibitivity and load-carrying capacity of the sulfur-containing organotin compounds used as multipurpose additives for lubricating oils are discussed. Recently, some studies on organotin compounds used as antiwear additives^{3),4)}, have been made. The organotin compounds investigated here could be considered as new-types of multipurpose additives.

2. Experimental

2.1 Materials

Organotin phosphite (a mixture of $C_8H_{17}Sn(SC_{12}H_{24}O)_3[P(OC_4H_9)_2]_3$, (70%) and $(C_8H_{17})_2Sn(SC_{12}H_{24}O)_2[P(OC_4H_9)_2]_2$, (30%)) and organotin borate (a mixture of $C_8H_{17}Sn(SC_{12}H_{24}O)_3B$, (68%) and $[(C_8H_{17})_2Sn(SC_{12}H_{24}O)_2]_3B_2$, (32%)) were used for studying their oxidation inhibivities and load-carrying capacities. The properties of these organotin compounds are shown in **Table 1**.

Squalane of the following properties: viscosity, 20.40 cSt (at 37.8°C), 4.17 cSt (at 98.9°C); density d_{20}^{20} , 0.811; refractive index n_D^{20} , 1.4535, was used as a base oil for measuring the oxidation inhibivities of these organotin compounds.

Paraffinic mineral oils of 230 cSt and 65 cSt at 40°C, respectively were used as base oils for the Timken Test.

2.2 Oxidation Inhibitivity

The oxidation inhibitivity of the organotin compounds was qualitatively investigated by differential thermal analysis. The temperature at which an exothermic peak appeared due to the oxidation of the base oil was measured by heating at the rate of 5°C/min in air. The time at which the exothermic peak appeared was also measured at constant temperature (135, 155 and 185°C) in air. These tests in air were performed after the temperature of the furnace had become constant at a preset level in nitrogen atmosphere. Oxidation inhibivities of the organotin compounds and zinc dialkyldithiophosphate (**Table 1**), used as a commercial oxidation inhibitor, were compared. All experiments were performed at least three times and reproducible results were obtained.

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Table 1 Properties and Composition of Additives

Additive	Refractive Index (n_D^{25})	Density (d_4^{25})	Composition (wt%)			
			Sn(Zn)	S	P	B
Organotin Phosphite	1.478	1.012	8.9	6.1	5.9	—
Organotin Borate	1.510	1.058	13.3	9.1	—	1.0
Zinc Dialkyldithiophosphate	—	1.123	(8.8)	16.5	8.0	—

2.3 Load-Carrying Capacity

The load-carrying capacity of the organotin compounds was determined by use of the Timken friction machine. Test conditions were as follows: speed, 800 ± 5 rpm; oil temperature, $38\pm2^\circ\text{C}$; volume of test lubricant, $2,840\text{ ml}^{(5)}$.

3. Results and Discussion

The DTA curves obtained with squalane and with squalane containing 1.0 wt% additive heated at the rate of $5^\circ\text{C}/\text{min}$ in air are shown in **Fig. 1**. The temperature at which an exothermic peak appeared by oxidation of squalane was 150°C . The peak-appearing temperatures for the organotin phosphite, organotin borate and zinc dialkyldithiophosphate solutions were 200, 250 and 225°C , respectively. These organotin compounds retarded the oxidation of squalane considerably and they had much the same oxidation inhibitivity as that of zinc dialkyldithiophosphate.

Figure 2 shows the oxidation behavior of squalane obtained by means of DTA at constant temperature. Squalane was hardly oxidized at 115°C within the period of time concerned, but it was oxidized more readily and the appearance of an exothermic peak due to oxidation was marked with increase in temperature.

The time of appearance of the exothermic peak

Fig. 1 Effects of Additives on Oxidation of Squalane

Fig. 2 The Oxidation Behavior of Squalane at Constant Temperature Obtained by Means of DTA

Table 2 Oxidation Inhibitivities of Additives by DTA

Additive	Time* (min)		
	135($^\circ\text{C}$)	155($^\circ\text{C}$)	185($^\circ\text{C}$)
Organotin Phosphite	>480	115	25
Organotin Borate	>480	156	120
Zinc Dialkyldithiophosphate	>480	352	75

* Time of appearance of an exothermic peak by oxidation of squalane

Sample : Squalane solution containing 1.0 wt% additive

by oxidation at constant temperature is shown in **Table 2**. Squalane was oxidized at any temperature from the beginning of the oxidation test, as shown in **Fig. 2**. An induction period, however, was observed with a squalane solution containing 1.0 wt% additive under all temperature conditions. At 135°C all sample solutions hardly oxidized and were not discolored for 480 min. The organotin phosphite and zinc dialkyldithiophosphate solutions became dark brown and sludge-like after the test at 185°C , while the organotin borate solution was still light brown in color and transparent. At this temperature oxidation inhibitivities of these additives were quite comparable with the results shown in **Fig. 1**. From the above results, the oxidation inhibitivities of these organotin compounds and zinc dialkyldithiophosphate are alike, and especially the organotin borate could be expected as an oxidation inhibitor applicable over a wide range of temperature. The mechanism of actions of these organotin compounds containing sulfur as oxidation inhibitors is not yet definite, but it may be similar to that of zinc dialkyldithiophosphate as a

Table 3 Load-Carrying Capacities of Additives by Timken Test

Additive	Concentration (wt%)	OK Load (lbf)	
		65 (cSt)*	230 (cSt)*
Organotin Phosphite	1.0	35	40
	3.0	40	50
	5.0	60	70
Organotin Borate	1.0	30	35
	3.0	40	40
	5.0	40	50
Sulfidized Olefin (S, 47.0%)	1.0	—	35

* viscosities of the base oils

peroxide destroyer^{6),7)}.

The load-carrying capacities obtained with the organotin compounds and with a commercial sulfidized olefin (47.0% sulfur) are shown in **Table 3**. At 1.0 wt% concentration these organotin compounds gave the same value of OK load as that of sulfidized olefin in spite of their lower sulfur contents. The OK load increased with increasing content of the additive, and an especially high value of OK load was obtained with the organotin phosphite.

4. Conclusion

The oxidation inhibitivity of lubricating oil additives can be qualitatively examined by means of DTA. The organotin compounds investigated here seem to possess satisfactory load-carrying capacity and oxidation inhibitivity. Thus, these could be expected as multipurpose additives for lubricating oils.

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要 旨

潤滑油多目的添加剤用の有機スズ化合物

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潤滑油添加剤としての硫黄を含む有機スズ亜りん酸エステルおよび有機スズほう酸エステル(**Table 1**)の酸化防止性と耐荷重能がそれぞれ示差熱分析 (DTA)および Timken 試験によって検討された。スクワランおよび各試料の 1.0 wt% スクワラン溶液に対する酸化試験 (昇温速度: 5°C/min, 空气中)では, 酸化による発熱ピークが現れ始める温度が再現性よく測定された。**Fig. 1** に示すように, この温度はスクワランでは 150°C であるのに対して, 亜りん酸エステル, ほう酸エステルおよび Zn-ジアルキルジチオホスフェート (参考試料, 市販品の酸化防止剤) 溶液ではそれぞれ 200, 250 および 225°C でい

れもスクワランの酸化をかなり抑制することがわかった。定性的な試験ではあるが, 少なくともこれらの有機スズ化合物は Zn-ジアルキルジチオホスフェートに匹敵する酸化防止剤として期待される。また一定温度において, 酸化による発熱ピークが現れ始めるまでの時間が検討された。**Fig. 2** に示すように, スクワランは 115°C でほとんど酸化されなかったが, 温度が高くなると, 測定開始時より発熱ピークが現れ始め, 高温時ほどそのピークは顕著に現れた。各添加剤溶液では 135°C において, 480 分以上もスクワランの酸化が抑制され, 特に有機スズほう酸エステルでは 185°C でもかなりの酸化抑制効果が得られた (**Table 2**)。

Timken 試験機による耐荷重能テストでは, 5.0 wt% の添加濃度でかなりの耐荷重能が得られ, 特に有機スズ亜りん酸エステルによって 60~70 lbf の OK 荷重が得られ極圧性が期待される (**Table 3**)。

Keywords

Antioxidative capacity, Load carrying capacity, Lubricant, Multipurpose additive, Organotin compound