Antioxidation synergism between ZnDTC and ZnDTP in mineral oil

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Abstract

Antioxidation synergism between ZnDTC and ZnDTP in a kind of mineral base oil was investigated by RBOT. The results indicate that there is antioxidation synergism between the two additives. FTIR analysis show that the oxidation products in the tested oils containing the two additives are much less than those in the tested oils containing the single additive alone.

Keywords: antioxidation, synergism, ZnDTC, ZnDTP, FTIR, ESR, RBOT

1. Introduction

Oxidation failure, caused by oxidation products which leads to the formation of varnish and sludge and to an increase in viscosity, is a main problem for lubricating oil during its service. So many antioxidants have been employed to prohibit this trend. The main antioxidants used in automobile lubricants are zinc dialkyldithiophosphates (ZnDTPs). However, the ZnDTPs have some limited properties, such as lower thermal stability, which cannot adapt to the needs of increasing operating temperatures and prolonging oil drain intervals in the advanced engine systems. Meanwhile, the trend to lower phosphorus levels to reduce poisoning of catalytic converters cannot be avoided, which results in decreasing the contents of the ZnDTPs in the fully formulated engine oils. ZnDTPs alone cannot satisfy these conditions especially when their concentrations are limited to less than 0.1%P in oil, which are the requirements of the API SJ engine oils. Thus, other antioxidants with phosphorus-free should be developed to supplement the action of the ZnDTPs.

It is well known that metals dialkyldithiocarbamtes (MDTCs) with phosphorus-free act as antioxidants for polymers [1-3], which can also be used in lubricating oil as antioxidants [4,5]. There are many reports about the antioxidation action of MDTCs alone in lubricating oils and chemicals, but the effects of MDTCs on antioxidation action of ZnDTPs in lubricating oil cannot be found yet. In this paper, we will study the interaction between ZnDTP and ZnDTC in a kind of mineral base oil.

2. Experimental

2.1. Oil samples

Yubase-6, a kind of mineral-based oil with very high viscosity index, was used as base oil in this test. A ZnDTC (zinc diamyldithiocarbamate) and a primary alkyl ZnDTP were obtained from commercial companies. The data of additives are listed in the Table 1. The data of the base oil and the mixtures are listed in the Table 2. Contents of elemental sulfur and nitrogen in the base oil and additives were analyzed by an elemental analyzer with the model of Vario EL. The elemental zinc and phosphorus were analyzed by ICP. Viscosity at 40ìÉ and total acid number (TAN) are determined for the oils.

Table 1. Elements of test materials

Elemental components	ZnDTC	ZnDTP	Base oil
Zn, %	4.16	8.9	-
S, %	15.08	16.2	<3ppm
N, %	4.873	-	<3ppm
P, %	-	7.9	-

2.2. Oxidation test

The rotary bomb oxidation test (RBOT) is a measure of the oxidation stability of lubricating oils in ASTM D 2272 [6]. In all tests, the sample is placed in a rotating bomb in a heated bath, which is then charged with oxygen with the pressure of 629kPa; a constant elevated temperature is maintained with an maximum temperature 150ìÉ. Catalysts are iron and copper plates. Oxidation stability is expressed in terms of the time required to achieve a specified pressure drop by 175 kPa.

ISOT tests were done according to the method of KS M 2021-1987 [7] under the following conditions: 180ìÉ, iron and copper plates as catalysts, and testing time 24hrs. After testing, viscosity and TAN of the tested oil samples were determined.

2.3. FTIR

Oxidation products in the tested oil samples were analyzed using a FTIR spectrometer. The cell is made of KBr with the thickness of 0.11 mm. The analytical process is automatically. The wave number at the range of 500 to 4000 cm-1 was recorded. The reference is a kind of base oil manufactured by SK without additive.

3. Results and discussions

3.1. Results of oxidation test

3.1.1. RBOT results

The results of RBOT tests and the physicochemical properties of the tested oil samples are listed in Table 2. The RBOT periods of the tested oils with water are shown in Fig.1. Fig.1 indicates that the two additives can improve the antioxidation performance in the mineral oil, but ZnDTC is much better than ZnDTP, and the mixtures are the best except the first point at the concentration ratio of 0.2/0.8 (ZnDTC/ZnDTP). Antioxidation property of ZnDTC increases with increasing concentrations. However, as the increase of additive concentration, the antioxidation property of ZnDTP increases as the concentration being less than 0.5% and then keeps stable in the used concentrations. The mixture exhibits the best antioxidation performance at the concentration of 0.5%/0.5% (ZnDTC/ZnDTP), at which the antioxidation performance is much better than that at the concentration of 1% (ZnDTC or ZnDTP used alone). The RBOT periods for the mixtures 0.5/0.5 and 0.8/0.2 (ZnDTC/ZnDTP) are much longer than the sums of the values of the periods as separative additive used, which suggest that the antioxidation mechanisms between the separations and the mixtures should be quite different.

3.1.2. ISOT test

(1) Physicochemical analysis

The physicochemical results ISOT tests are listed in the Table 2. The data indicate that viscosities have small increases for the cases containing additives and a sharp increase for the base oil after test. The data of TAN before test indicate that ZnDTC and the base oil have very low TAN and ZnDTP has very high TAN that increases with the concentrations of the additive in the oil. After test, TAN increases for the cases containing ZnDTC and sharply increases for the base oil,

Fig.1. RBOT periods of the tested oils

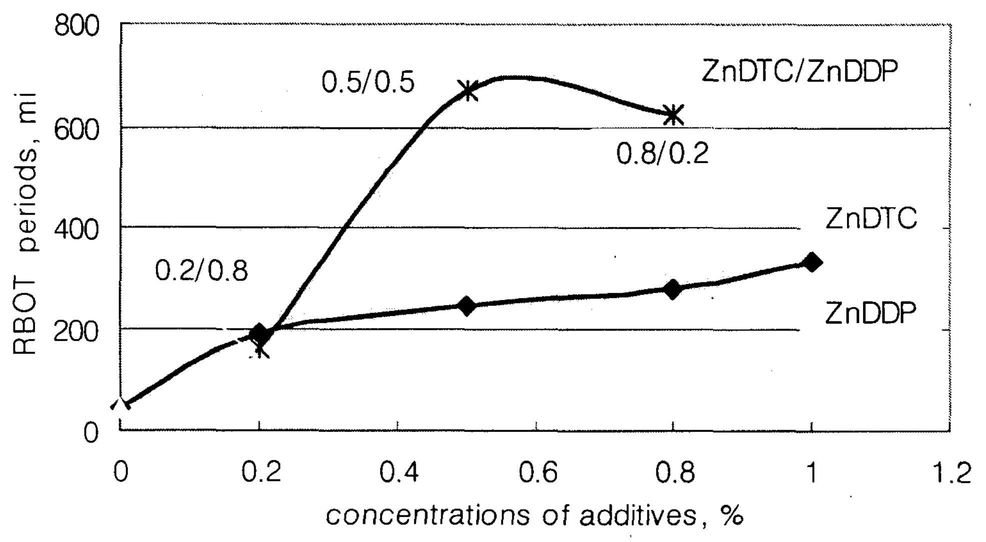

Table 2. Phsicochemical properties and RBOT induction period of the oils

Oil samples	ISOT test				RBOT, min
	Viscosity, cst, at 40℃		TAN, mgKOH/g		
	Before test	After test	Before test	After test	
Base oil	37.65	42.27	<0.01	1.41	45
0.2% ZnDTC	37.62	37.92	0.04	0.11	190
0.5% ZnDTC	-	37.84	<0.01	0.11	245
0.8% ZnDTC	-	37.96	<0.01	0.11	280
1.0% ZnDTC	-	37.91	<0.01	0.24	335
0.2% ZnDTP	-	37.77	0.36	0.16	90
0.5% ZnDTP	-	37.83	0.73	0.06	170
0.8% ZnDTP	-	37.68	1.16	0.13	160
1.0% ZnDTP	-	37.63	1.49	0.09	160
0.2% ZnDTC+0.8%ZnDTP	-	38.2	1.19	0.53	160
0.6% ZnDTC+0.6%ZnDTP	-	38.52	0.73	0.6	670
0.8% ZnDTC+0.2%ZnDTP	-	38.61	0.32	0.29	625

however, TAN changes roughly for the cases containing ZnDTP.

(2) FTIR analysis

FTIR spectra are shown in figures 2, 3, and 4. Main absorption peaks have been marked in the figures. The peaks at 1721.3cm-1 and 1779.2cm-1 belong to vibrations of oxidation products containing C=O, and the broad peak around 3458.1cm-1 should be designated to OH stretching vibration. The peak at 1165.5cm-1 is associated with C-O vibration. These oxidation peaks have been found in the tested base oil, only 1165.5cm-1 absorption existed in all tested oils, which show that oxidation products are carboxylate in the tested base oil and ethers in the tested additives-containing oils. So the base oil is readily oxidized during tests, after added with ZnDTC or ZnDTP, the trend of oxidation has been inhibited significantly. The combinations also indicate that the oxidation conditions are similar to those of the additives used alone.

By comparison with the new oils containing additives in figures 2, 3 and 4, characteristic absorptions of ZnDTC are not obvious owing to the weak absorption of the functional groups in the additive C=N (1430cm-1) and C=S (1000-1060cm-1) bonds; sharply characteristic absorptions of ZnDTP are at 1007.3cm-1 that belong to P-O-C vibration. The intensities of the P-O-C absorptions are reduced both in ZnDTP alone and the combinations after test at different extents.

In fig.3, the P-O-C absorption completely disappeared after test, which indicates that the additive ZnDTP has been depleted during test. In fig.4, the P-O-C absorptions increase with the increase of concentrations of ZnDTP for the mixtures while no P-O-C absorption can be found in the case of oil containing ZnDTP alone, although the content of the ZnDTP reaches 1% more than those of the mixtures.

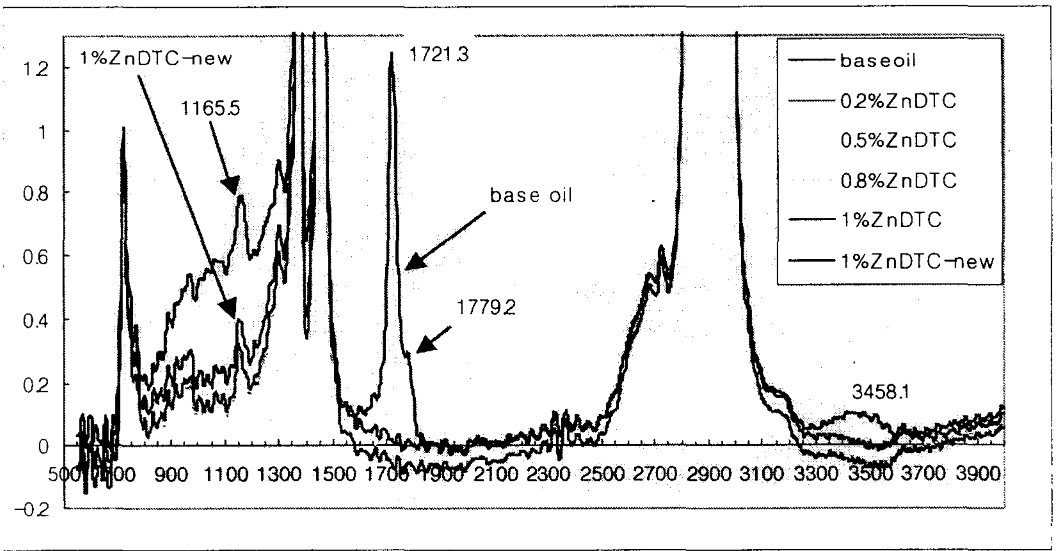

Fig.2. FTIR spectra of the tested ZnDTC-containing oils and base oil

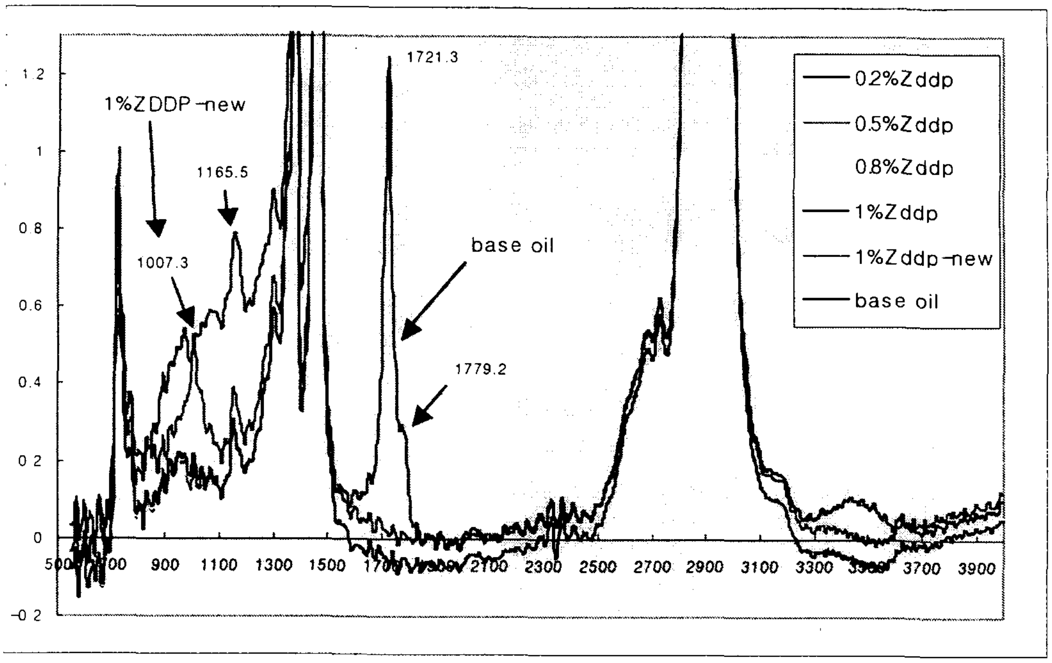

Fig.3. FTIR spectra of the tested ZnDTP-containing oils and base oil

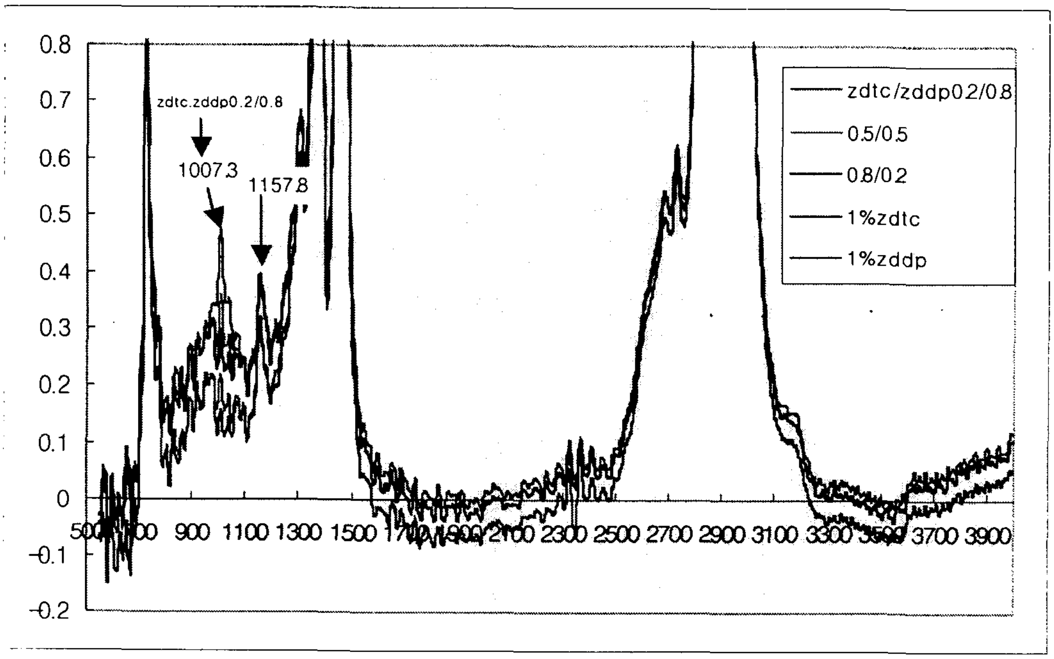

Fig.4. FTIR spectra of the tested combinations

3.2. **Discussion**

Data of TAN indicate that some acidic products have been produced after test as ZnDTC used alone. But the absorptions of oxidation products in FTIR spectra show that few obvious oxidation products have been created after test except for the base oil. So there is a certain substance that is the contributor of the acidic products.

It has been confirmed that ZnDTC inhibited the antioxidation action in a single hydrocarbon system involved both radical scavenging and peroxide decomposition processes [1-3]. The key element was considered to be sulfur. ZnDTC as peroxide decomposer has been attributed to the formation of various sulfur-oxyacids [8]. Al-Malaika et al. [1,2] suggested that sulfur acids should be formed from ZnDTC. Sexton [5] concluded that ZnDTC decomposed the hydroperoxide via the formation of sulfur trioxide-sulfuric acid. Therefore the oxidized oils should be acidic.

Oils containing ZnDTP alone show sharply decreasing the values of TAN after test. FTIR spectra confirmed very few oxidation effects of the base oil. It has been proved that ZnDTP took its antioxidation action through the formation of disulfides without sulfur dioxide [9,10]. Thus the depletion of ZnDTP is responsible for the decreasing TAN.

The mixtures show higher TAN, which is different from the cases of the two agents used alone, although TANs of the mixtures were also completely contributed by ZnDTP before test. The strong intensities of P-O-C in FTIR spectra indicate that ZnDTP still exists in the oils after test, which suggests that ZnDTC play main antioxidation prior to ZnDTP in the combinations. Thus ZnDTC has a great reactivity than ZnDTP in the present tests, which is in directly contradiction to the previous results [4].

.If ZnDTP remains in the combinations after test and the acidity mainly comes from the action of ZnDTC during oxidation, we can diminish the attribution of ZnDTC to TAN and obtain the following results (Table 3). It is reasonable that the differences between TANs of the oils before and after tests are mainly contributed by ZnDTP that remains in the tested oils. So we can calculate the amount of the remained ZnDTP in the oils after tests such as the combination with the ratio of ZnDTC to ZnDTP 0.8/0.2, ZnDTP hardly took part in the oxidation reaction, although results of RBOT show that there is strong interaction between the two additives.

Table 3. The remained ZnDTP in the combinations after ISOT test

Additives, ZDTC/ZDTP	TAN-0.11, mgKOH/g	△TAN ZnDTP	Remained ZnDTP, %
0.2/0.8	0.42	1.03	40.8
0.5/0.5	0.49	0.67	73.1
0.8/0.2	0.18	0.20	90

Generally, ZnDTC has higher stability than ZnDTP. So ZnDTP should be decomposed prior to ZnDTC. The present results show that ZnDTC can improve both of thermal and oxidation stability of ZnDTP in the combinations. This is very important for ZnDTP to keep its friction-reducing and wear resistance in engine oil formulation for a long period during in service [11].

5. Conclusions

(1) ZnDTC exhibits much better antioxidation than ZnDTP and the mixtures have the excellent antioxidation which indicate there is strongly synergistic antioxidation between ZnDTC and ZnDTP.

(2) ZnDTC can improve the stability of ZnDTP in the present combinations.

(3) Oxidation products of ZnDTC after test are acidic materials.

Acknowledgements

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