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The Antiwear Performance of Dialkyl 3, 5-di-t-butyl 4-hydroxy Benzyl Phosphonates as a New Additive in the Four Ball Wear Test

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Abstract—The antiwear performance of dialkyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonates was investigated using a four ball wear test machine. Diethyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonate (DEP) and dibutyl 3,5-di-t-butyl 4-hydroxy benzyl phosponate (DBP) among them showed excellent antiwear performances compared with conventional additives, ZDDP and TCP as the bulk oil temperature and the sliding velocity increased. The surface analysis through an optical microscopy was conducted for tribological studies.

Key words : Lubricant additives, Antiwear performance, Thermal behaviour, Plastic deformation

1. Introduction

Zinc dialkyl dithio phosphate (ZDDP) and tricresyl phosphate (TCP) have been used widely as an antiwear additive for lubricating oils for over forty years, and their wear performance has been investigated more completely than any other additives [1-11]. All of the load carrying additives including ZDDP and TCP are the protective film formation of chemical reactions between the substrate and the inorganic elements (e.g. sulphur, phosphorus and chlorine), and their antiwear capability is depending upon the shearing strength of film formed [12-14]. However, under severe lubrication systems, viz, high temperature and speed conditions, these accelerate the rupture of film which is formed, in terms of exothermic reactions of thermal decompositiion of the hydrocarbons and pyrolysis phenomenon of additives at the frictional contact junction [15-17]. By the reasons, it is difficult to solve failure phenomenon which is occurred in tribosystems fundamentally.

To improve this problem, the new additives, dialkyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonates have synthesized and investigated. The new additives provide excellent antiwear performance under severe conditions. The aim of this study is to consider the wear characteristics of dialkyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonates represented an alkyl group having from 1 to 8 carbon atoms, and to obtain the optimum alkyl group and concentration. And also to describe the antiwear performance between the new additive and conventional additives. The surface analysis of worn balls was conducted for tribological studies.

2. Experimental Work

A shell four ball wear test machine operated under the following conditions was used to evaluate the antiwear performances of the blended oils:

Load	392N
Sliding velocity	30 cm/sec., 40.1 cm/sec, 69.1 cm/sec
Bulk oil temp.	30°C, 75°C, 120°C, 150°C
Time	60 min

The balls were made of EN31 steel and had a diameter of 12.7 mm and hardness (Rc) in the range of 64-66. After each test, the results reported were the mean wear scar diameter of the three balls.

The base oil used was a liquid paraffin, SAE 10# with kinetic viscosity of 26.5 cst at 40°C and a viscosity index of 100. The new additives, dialkyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonates were synthesized, and represented an alkyl group having from 1 to 8 carbon atoms, and that is, these are dimethyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonate

(DMP), diethyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonate (DEP), dibutyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonate (DBP), dihexyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonate (DHP) and dioctyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonate (DOP). Their concentration was varied over a range from 0 to 1.5 weight percent. The conventional additives, ZDDP and TCP were obtained commercially, and their results were evaluated at the ZDDP concentration of 0.5 weight percent and the TCP concentration of 1.0 weight percent. After each wear test, the surface analysis of worn balls was observed through an optical microscope for tribological properties.

3. Results and Discussion

To determine the effect of carbon chain length of dialkyl 3, 5-di-t-butyl 4-hydroxy benzyl phosphonates on the wear performance, studies such as that illustrated in Fig. 1 were conducted by varying an alkyl group having from carbon chain 1 to 8, viz. methyl, ethyl, butyl, hexyl and octyl. The results were obtained under load to 392N, sliding velocity of 40.1 cm/sec, running time of 60 min and bulk oil temperature of 75°C by the ASTM D2266 [18], and each test was evaluated at its concentration of 1.0 weight percent. It showed that wear was rishing with increasing carbon atoms, probably because they are less chemically active or decomposed product by long carbon chains. DMP among them showed lower antiwear performance relatively due to its low oil solubility, while DEP and DBP were not, and they showed higher antiwear performances. That is, DEP and DBP provide excellent antiwear performances.

The effect of the DEP and DBP concentrations on the wear performance is illustrated in Fig. 2. The results were obtained at concentrations of 0.5, 0.75, 1.0 and 1.5 weight percent, and each test was conducted at the same conditions above mentioned. The results over the concentration of 0.75 weight percent in Fig. 2 showed that wear remained constantly, and their wear performance showed relatively similar trend. Throughout the studies, 0.75 weight percent is decided to be optimum concentration.

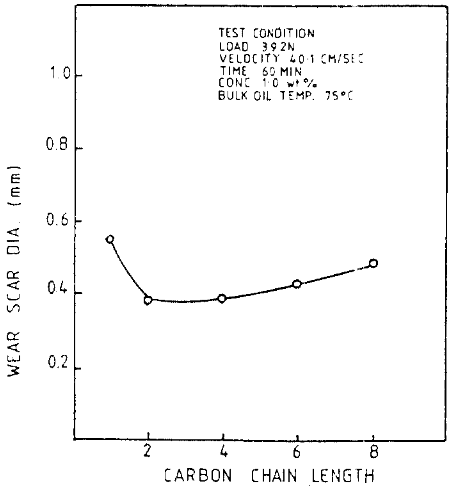

Fig. 1. Effect of chain length on wear performance of dialkyl 3.5-di-t-butyl benzyl phosphonates.

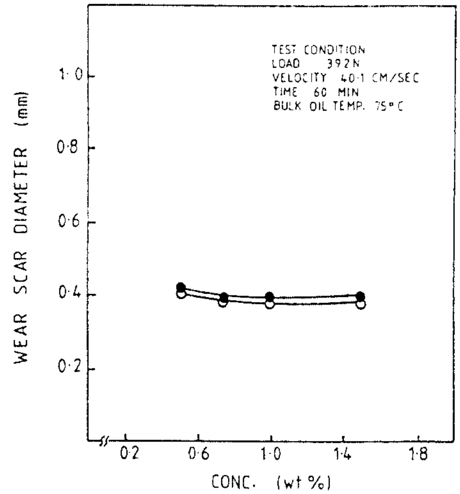

Fig. 2. Effect of DEP and DBP conc. on wear perofmance (● -DBP, ○ -DEP).

To investigate the antiwear performance under severe conditions, viz, high temperature and speed conditions, studies were conducted by varying bulk oil temperature and sliding velocity. The effect of the bulk oil temperature on the antiwear performance is illustrated in Fig. 3. The sample oils, which were included with TCP concentration of 1.0 weight percent, ZDDP of 0.5 weight percent, and DEP and DBP of 0.75 weight percent concentrations were used, and also base oil without any additive was investigated. Their antiwear performance was investigated at the same conditions above mentioned, and the bulk oil temperature was varied in the range of 30°C, 75°C, 120°C and 150°C. As shown in Fig. 3, wear showed rising trends with

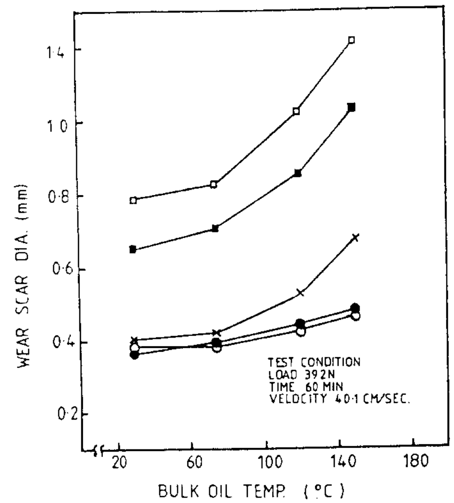

Fig. 3. Effect of bulk oil temp. on wear performance (□: BASE OIL, ■: 1.0 wt% TCP, ×:0.5 wt% ZDDP, ●:0.75 wt% DBP, ○: 0.75 wt% DEP).

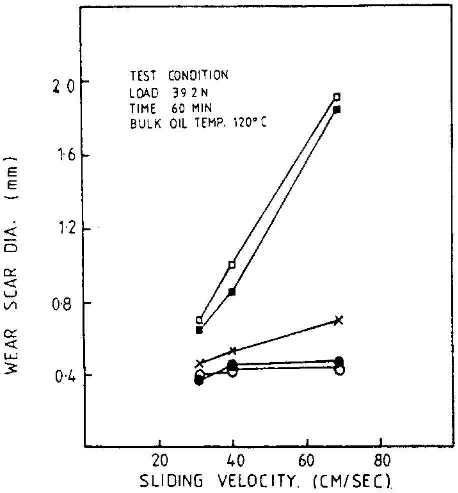

Fig. 5. Effect of sliding velocity on wear performance (□: BASE OIL, ■: 1.0 wt% TCP, ×: 0.5 wt% ZDDP, ●: 0.75 wt% DBP, ○:0.75 wt% DE).

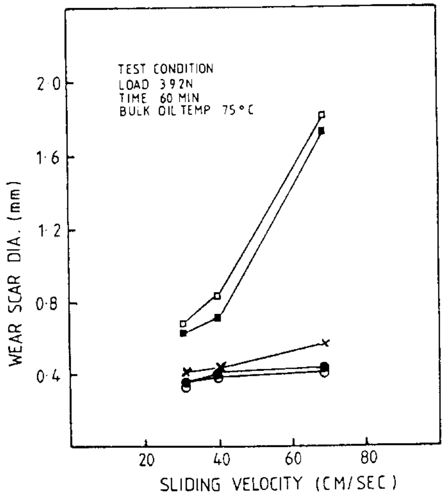

Fig. 4. Effect of sliding velocity on wear performance (□: BASE OIL, ■: 1.0 wt% TCP, ×: 0.5 wt% ZDDP, ●: 0.75 wt% DBP, ○: 0.75 wt% DEP).

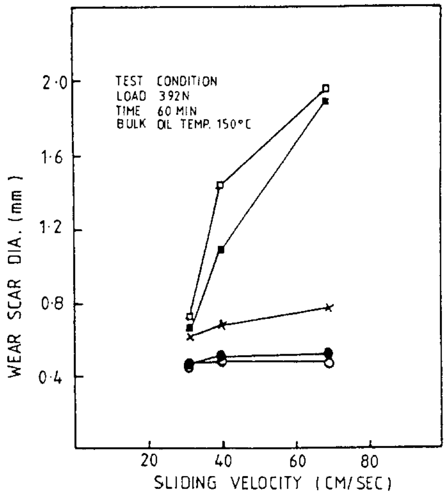

Fig. 6. Effect of sliding velocity on were performance (□: BASE OIL, ■: 1.0 wt% TCP, ×: 0.5 wt% ZDDP, ●: 0.75 wt% DBP, ○: 0.75 wt% DEP).

increasing bulk oil temperature, and especially wear for TCP additive was much greater than any other additive. It means that its antiwear capability has a limit. Compared with newly additive and ZDDP, the one showed lower antiwear performance than the other, and wear ratio for DEP and DBP was relatively constant with increasing bulk oil temperature, while ZDDP was not. It is deduced that greater antiwear performance of conventional additives is caused by thermal instability in frictional contact junction. This can be proved by the surface analysis of worn balls.

The effect of sliding velocity on the wear performance is shown by the data in Figs. 4, 5 and 6. Five sample oils above mentioned were used, and the results were obtained at the load to 392N, test duration of 60 min, and sliding velocity in the range of 30.7 cm/sec, 40.1 cm/sec and 69.1 cm/sec. The bulk oil temperatures were also varied. The results of antiwear performance at the bulk oil temperatures of 75°C, 120°C and 150°C are illustrated in Figs. 4, 5 and 6.

As shown in Figs. 4, 5 and 6, wear rose with increasing sliding velocity and bulk oil temperature. Without the additive function, the transition from mild wear to severe wear with sliding velocity was inevitable in such high shear stress and temperature conditions due to the accumulation of heat and the subsequent thermal instability of frictional contact junction [16]. Addition of TCP additive influenced the phemomenon little in spite of the improvement on wear performance. When ZDDP additive was added, it restrained the transition considerably while poured with increasing bulk oil temperature. But the new additives, DEP and DBP showed relatively constant wear ratio in spite of increasing sliding velocity and bulk oil temperature, and higher antiwear performance compared with conventional additives under severe condition. As above mentioned, this difference is due to thermal behaviour, and the new additive may be reduced thermal energy occurred in contact junction.

On the basis of experimental results, the newly synthesized additives, DEP and DEP showed excellent antiwear performance under severe conditions, and acted as very effective antiwear additives. And so, if used in tribo-systems, it may be reduecd wear.

4. Surface Analysis

The surface of worn balls after each test was conducted at the bulk oil temperature of 120°C and the sliding velocity of 40.1 cm/sec were observed through an optical microscopy, and these are shown in photographs 1 to 5. Strains of sludge or oil an the ball surface were removed with solvent before the photomicrograph was taken. Worn balls in sample oil without any additives and with TCP additive occurred in scuffing wear by plastic deformation (photo. 1 and 2). And also, in the case of sample oil with ZDDP additive, it showed that plastic deformation caused by thermal instability was occurring. Scoring marks shown in the bottom of worn ball is due to the abrasive of hardened material transferred (photo. 3). A very remarkable phenomenon was observed that there was no evidence of any plastic deformation at the contact junc-

Photo 1. Micrograph of worn surface of EN31 steel ball (×150)-non-additive.

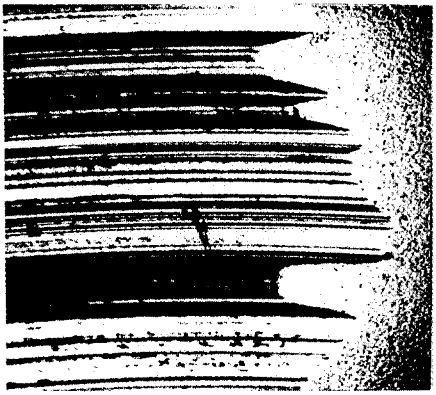

Photo 2. Micrograph of worn surface of EN31 steel ball (×150)-1.0 wt% TCP.

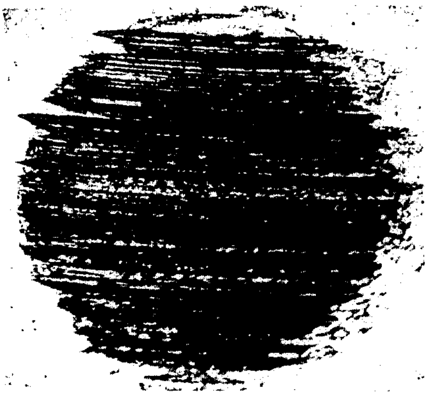

Photo 3. Micrograph of worn surface of EN31 steel ball (×150)-0.5 wt% ZDDP.

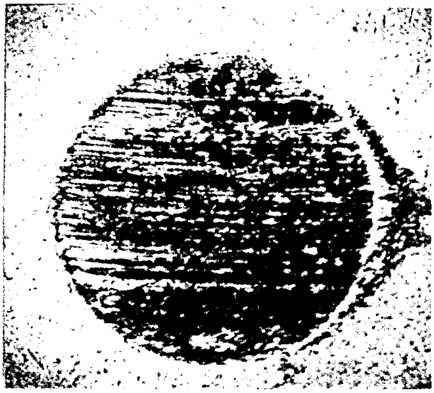

Photo 4. Micrograph of worn surface of EN31 steel ball (×150)-0.75 wt% DEP.

Photo 5. Micrograph of worn surface of EN31 steel ball (×120)-0.75 wt% DBP.

tion tested with the sample oils containing new additives, DBP and DEP, and it showed clear wear surface (photo 4 and 5), and thus the constant wear ratio with increasing bulk oil temperature and sliding velocity can be proved.

5. Conclusions

Of the dialkly 3, 5-di-t-butyl 4-hydroxy benzyl phosphonates tested, DEP and DBP wre very effective derivatives, and these showed excellent antiwear performances compared with conventional additives, ZDDP and TCP as the bulk oil temperature and sliding velocity increased. The wear ratio of the new additives showed relatively constant with increasing the bulk oil temperature and the sliding velocity, while conventional additives were not. From the results of worn contact surface analysis, it was observed that there was no evidence of any plastic deformation at the contact junction tested with sample oils contained with new additives, DEP and DBP, while much occurred for ZDDP and TCP additives, respectively. It is deduced that this difference is due to thermal behaviour at the contact junction. And thus if the new additive used in tribosystems is may be reduced wear.

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