한국윤활학회지(1991), 제 7권 제 2호
Journal of KSLE(1991) Vol. 7, No. 2, pp.28~35

Effect of Other Additives on Wear-Preventing Property of ZDDP

Woo-Sik Moon
Lubricant Research Laboratory, Ulsan Research center, Yukong LTD

ZDDP의 마모방지특성에 미치는 타첨가제의 영향

문 우 식
(주)유공 울산연구소 윤활유연구실

요약－3원통/링 마모시험기를 사용하여 윤활유 공급하에서 미끄럼 마모시험을 수행하였다. 엔진유에 첨가되는 대표적 첨가제인 ZDDP, 청정제, 분산제의 첨가제 3종과 모델 산화물로서 유성제인 스테아린산을 선택하여, 그 배합유의 마모방지특성을 조사하였다. 청정제 및 분산제 각각의 첨가에 의해 마모방지특성은 향상되었으나, 청정제 및 분산제를 동시에 첨가할 경우 마모방지성능의 향상효과는 없어졌다. 또한, 모델산화물인 스테아린산의 첨가로 인하여 ZDDP의 마모방지작용은 나빠지나, 청정분산제가 그 악영향을 억제하는 작용을 한다.

1. Introduction

Good wear-preventing property of an engine oil is ascribed to ZDDP [1], a dual-functional additive of antiwear and antioxidation which reacts on surface making protective films. The wear prevention by ZDDP has been related to its decomposition by thermal, oxidative or hydrolytic mechanisms. Moreover, the mechanisms become more complex by interactions with other additives, i.e. dispersants or detergents. In addition, the ZDDP activity in real engines is also influenced by such factors as presence of metals and contamination by blowby, oxidation products, etc. Although many studies have been conducted on ZDDP, the detailed mechanism of its functions in an engine oil has not been completely understood.

Since an engine oil contains other additives, the action of ZDDP in mixed systems is affected by their interactions. Several studies have been conducted on the interactions of ZDDP with other additives [2-11]. From the change in the IR spectra of ZDDP by the addition of dispersants, chemical rections have been speculated to occur between ZDDP and the dispersants [4]. Highly polar additives, such as the detergents and corrosion inhibitors, may actively compete with the ZDDP for the rubbing surfaces, and the antiwear performance of a ZDDP can be adversely affected by some friciton modifiers, EP agents, antioxidants, detergent and dispersants [5].

At a study using modified differential vapor pressure osmometry [6,7], no interaction was found between ZDDP and detergents, which form rigid micelles in oil, but there were strong interactions between ZDDP and dispersants, which associate moderately in oil. In a 4-ball test to study the effect of succinimide on wear-preventing performance of ZDDP, it has been observed that above a critical concentration amines can cancel the antiwear performance of ZDDP, but that at amine concentrations below the critical value the antiwear effect is synergistic at high loads [8].

It has also been confirmed that ZDDP adsorption on iron and iron oxide powders is reduced by the presence of the other additives [9]. Moreover, basic barium sulfonates increased the thermal decomposition temperature of ZDDP by about 25℃ [2], while some acid materials accelerated ZDDP decomposition [8].

Table 1. General properties of additives

Addtive	ZDDP	Detergent	Dispersant
Viscosity @ 40℃	225	–	–
@ 100℃, mm^2/s	–	95	600
TAN, mgKOH/g	160	9	0
TBN(HCl), mgKOH/g	2	318	30
($HClO_4$)	2	320	36
Element content			
Ca, wt%	–	12.5	–
S	16.6	2.4	–
P	7.9	–	–
Zn	8.6	–	–
N	–	–	2.0
etc.	Secondary alkyl	Overbased sulfonate	Succinimide type

These results suggest several mechanisms by which second additives affect the ZDDP antiwear performance; first, the decomposition characteristics of ZDDP are affected by direct reaction or forming complexes with other additives, and in addition ZDDP adsorption on surface is reduced by either competing with other additives on surfaces or forming complexes. However, because of the solubilization of decomposition products into the oil with the aid of a dispersant or a detergent, the good antiwear property of used gasoline engine oils was retained [12].

In this paper, an attempt is made to obtain an understanding of the wear-preventing property of representative engine oil additives and the deterioration in their performance caused by their interactions. Stearic acid, which is also an oiliness agent, is selected as a model oxidation product in order to investigate the effects of its interaction with other additives on the wear-preventing property.

2. Lubricants

Among various additives contained in engine oils, the following representative ones are selected, ZDDP as a dual-functional additive of wear-prevention and oxidation inhibition, a succinimide as dispersant, and an overbased calcium sulfonate as detergent, Their detailed properties are given in Table 1. The ZDDP is secondary-alkyl-type with 160 mgKOH/g in TAN. The detergent is 318 mgKOH/g in TBN determined by the HCl method and the dispersant is 30 mgKOH/g in TBN with nitrogen content of 2.0 wt%.

Table 2. Lubricants

Lubricant	Formulation
A	BO(Base oil)+ZDDP (1 wt%)
A1	BO+Detergent (2 wt%)
A2	BO+Dispersant (4 wt%)
B	BO+ZDDP (1 wt%)+Detergent (2 wt%)
C	BO+ZDDP (1 wt%)+Detergent (4 wt%)
D	BO+ZDDP (1 wt%)+Detergent (2 wt%) +Dispersant (4 wt%)

These additives and stearic acid of commercial grades were blended into a paraffinic base oil of about 60 mm^2/s in viscosity at 40℃ with various combinations to prepare the oil samples for the experiments. The detailed formulations of the representative oils tested are summarized in Table 2. Oils A, A1 and A2 are single-additive systems containing each additive in the base oil. Oil A contains the ZDDP with a concentration of 1.0% by weight. Oil A1 contains the detergent of an overbased calcium sulfonate whose added amount is 2.0% by weight. In oil A2, the succinimide-type dispersant is blended by a weight percent of 4.0%. Oils B and C are double-additive systems containing other additives plus ZDDP; oil B contains the detergent by 2.0 wt% and oil C contains the dispersant by 4.0 wt%. In oil D, three kinds of additives are contained: 1.0 wt% ZDDP, 2.0 wt% detergent and 4.0 wt% dispersant. These treating rates of additives are comparable with those of high performance gasoline engine oils.

3. Experimental Details

3-1. Three-roller-on-ring wear test machine

A general view of the three-roller-on-ring machine [13,14] is shown in Fig. 1. The sliding system consists of a rotating upper specimen and a stationary lower specimen. The ring specimen is 34 mm in outer diameter and 26 mm in inner diameter. The three roller specimens of 10 mm in both diameter and length, which were fabricated for cylindrical roller bearings, are disposed between two disks at regular intervals on a circumference of 30 mm in mean diameter to form a three-roller assembly; the rollers are rigidly secured by

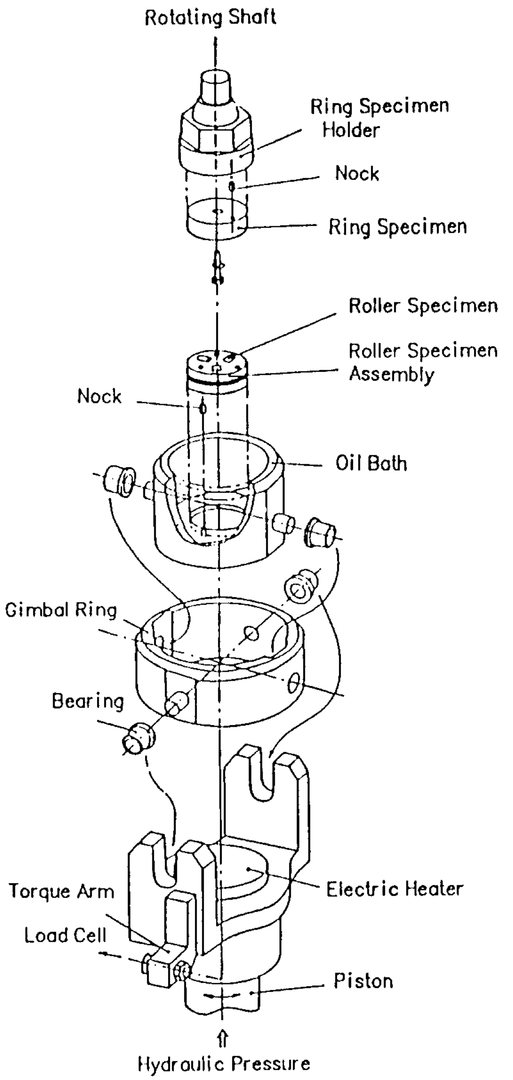

Fig. 1. Main part of the three-roller-on-ring machine

three screws between the two disk plates. With this construction, the rigidly-fixed rollers slide over the cir-the cotacting area increasing from the initial line con-the contacing area increasing from the initial line contact to the suceeding plane contact following the wear of the roller specimens.

Both the ring and the roller specimens are made of SUJ 2 (which corresponds to AISI 52100) bearing steel and were hardened to about HV 750. The sliding surface of the ring was finished to a roughness of about Ra 0.04 μm by lapping, while the surface roughness of the roller specimen was about Ra 0.09 μm.

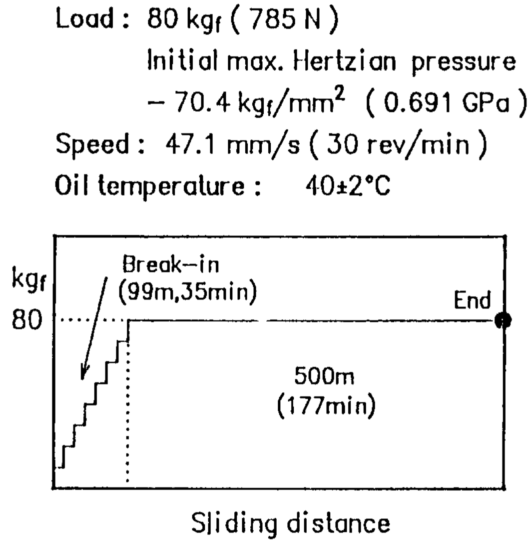

Fig. 2. Experimental conditions

3-2. Experimental procedure

All the wear experiments and measurements were conducted in the following manner. In Fig. 2 are given the testing conditions including normal load, sliding speed and oil temperature. The load of 785 N generates a Hertzian contact width of about 76 μm and an initial maximum Hertzian pressure of about 0.7 GPa, which is compared with the contact between cam nose and rocker arm during severe operation of engines. The conditons were determined so that the effect of hydrodynamic lubrication might be small, which was estimated from the friction during sliding, and that relatively high wear could be produced in short times. An oil temperature of 40℃ was employed. Each experiment consists of a run of 500 m in sliding distance after initial break-in run.

Before each run, specimens were cleaned carefully in petroleum benzene, dried in a hot air stream, and then set in the apparatus as described in the previous section, the sliding speed was held constant throughout the run, but the load and the temperature were increased to the predetermined values during a break-in procedure of 35 min and kept constant thereafter. When the break-in procedure was finished, a run was continued without stopping for a sliding distance of 500 m, which took about 177 min. Friction and oil temperature were continuously monitored through the run.

After a run, the specimens were removed from the

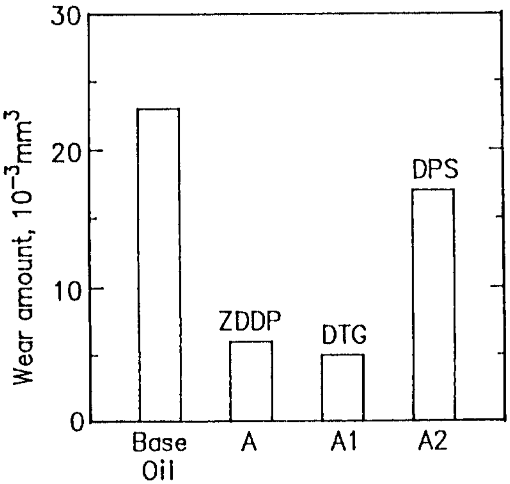

Fig. 3. Wear amounts produced with base oil and oils A, A1 and A2

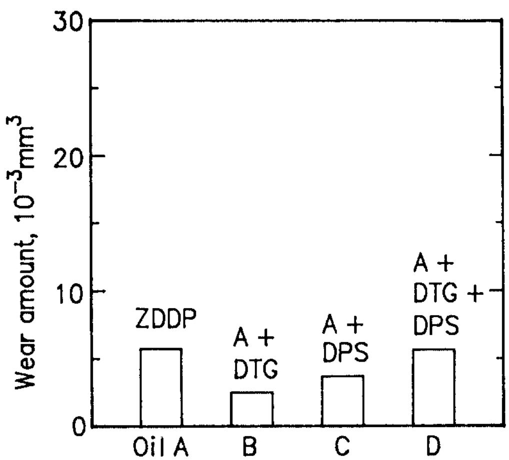

Fig. 4. Wear amounts produced with oils A, B, C and D

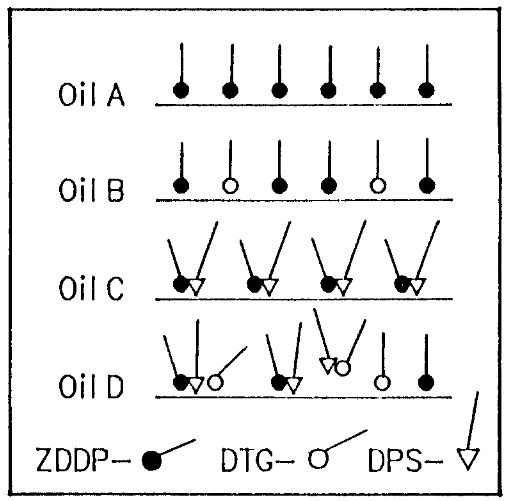

Fig. 5. Schematic explanation of additive interactions on sliding surfaces

apparatus and washed as before. Then the wear scar widths on the three rollers were determined to 1 μm under an optical microscope, equipped with a visual monitor, to provide volumetric wear amount after simple calculation. At the end of each test, surface profiles were taken on wear tracks of the ring and roller specimens using a Talysurf 4 profile-measuring instrument.

4. Experimental Results and Discussion

The wear amounts produced with four kinds of lubricants, including the base oil and the one-additive oils A, A1 and A2, are shown in Fig. 3. With the addition of ZDDP (oil A), wear considerably decreases to about one fourth compared with the base oil. The detergent (oil A1) also has good wear-preventing property or even better than the ZDDP. However, the decrease in wear is moderate with the addition of the dispersant (oil A2). As shown in Fig. 4, the two-additive lubricants, oils B and C, produce lower wear amounts than oil A containing only ZDDP, which indicates the synergistic effect of the ZDDP with both the detergent and the dispersant in the oils. Moreover, the detergent gives better effect than the dispersant [15]. However, the three-additive lubricant (oil D) generates more wear compared with oils B and C, perhaps due to some detrimental interactions among the additives. Complex formation by the succinimide dispersant in the lubricant may be a factor reducing the effective ZDDP concentration [6, 7].

Simple schematic explanation of additive interaction around sliding surfaces is given in Fig. 5. With oil A, only ZDDP adsorbs on the sliding surface reducing wear. As the second and the third additives are added into the one-additive lubricant, interaction among additives is considered to occur both in the bulk lubricants and on the sliding surfaces. With addition of the detergent, oil B, it could compete with ZDDP for the sliding surface, but no interaction occurs in bulk lubricant [6, 7]. However, dispersants are known to interact and

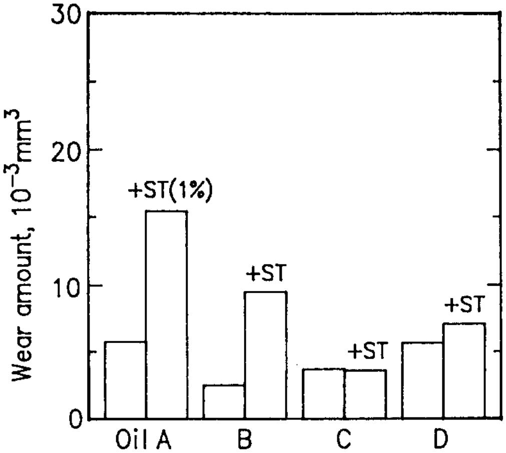

Fig. 6. Changes in wear amounts with stearic acid contamination

make complex with ZDDP and then they adsorb cooperatively on the surface [4-8, 15]. Oil C may be the case as shown in Fig. 5. The interaction in the three-additive lubricant, oil D, becomes more comkplex. That is, interaction between the detergent and the dispersant should be also taken into consideration. For such complicated additive systems, the balance among these additives may become the most important factor to control the wear-preventing property of a lubricant, which is directly related to competitive adsorption, complex formation and cooperative adsorption.

The blended lubricants are also investigated with respect to the effect of their contamination by stearic acid, a model oxidation product, on their wear-preventing property. Fig. 6 shows the changes in wear amounts caused by the addition of stearic acid of 1.0 wt% for the four kinds of oils containing ZDDP and the other additives, i.e. oils A, B, C and D.

With the addition of stearic acid of 1.0 wt% into oil A, the wear amounts become about three times as much as those produced without stearic acid. The result clearly shows that oxidation products, simulated by stearic acid, are harmful to the wear-preventing action of ZDDP. The detrimental effect by stearic acid is also found for oil B, but the wear amounts are less than those with contaminated oil A owing to the inhibiting action of the detergent contained in the oil. On the contrary, oil C completely suppresses the detrimental effect of stearic acid on the wear-prevention; addition of stearic acid causes no increase in wear, perhaps

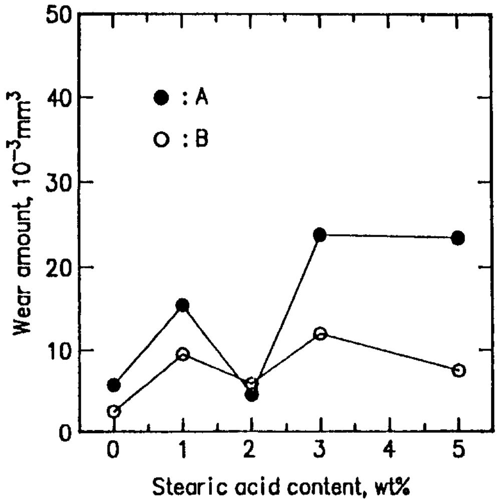

Fig. 7. Variation of wear amounts with stearic acid content: oils A and B.

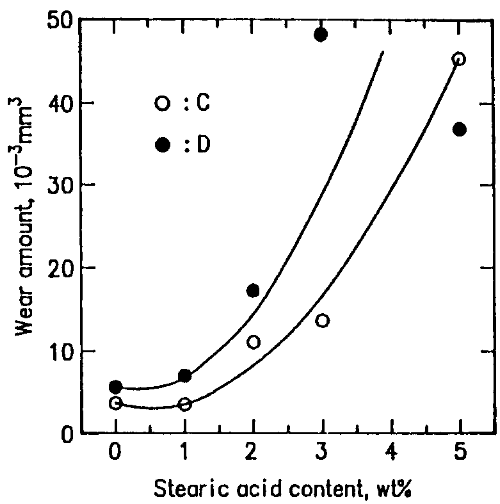

Fig. 8. Variation of wear amounts with stearic acid content: oils C and D.

because the dispersant preferentially reacts with stearic acid and proptects ZDDP from detrimental reaction. The protection of the wear-preventing property by the dispersant is also recognized to be effective with the oil D; the wear increases but only slightly. On the other hand, stearic acid could compete with the ZDDP for the rubbing surfaces and also accelerate ZDDP decomposition, thus reducing the ZDDP effectiveness.

When the content of stearic acid in the oils becomes higher than 1.0 wt%, the variation of wear with the

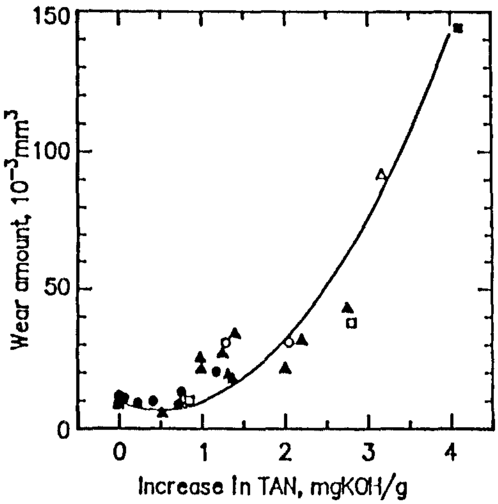

Fig. 9. Variation of wear amounts with increase in TAN [13]

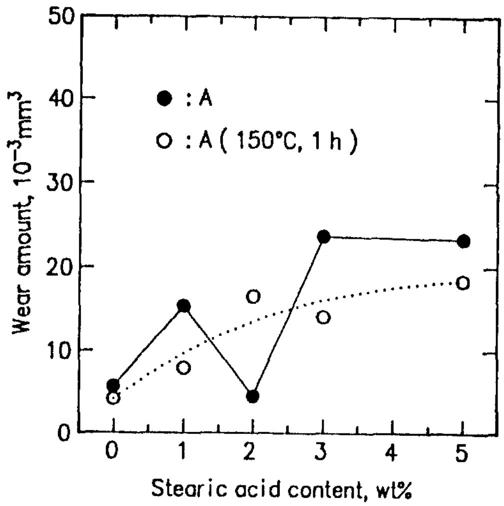

Fig. 10. Variation of wear amounts with stearic acid content in oil A: effect of high-temperature deterioration

increasing content shows complex and different behavior, as shown in Fig. 7 for oils A and B, and in Fig. 8 for oils C and D. With oil A, Fig. 7, wear amounts increase with the content of 1.0 wt%, but the wear with the oil of 2.0 wt% content is even less than the oil containing no stearic acid. With more contamination, over 3.0 wt%, the wear increases to the value of the base oil. The changes in wear for oil B have the same trend as oil A, but both the wear amounts and the degree in the changes are generally less than those with oil A.

Because stearic acid and ZDDP do not react each other in bulk lubricants [14], these changes in wear amounts are considered to be produced due to interaction, adsorption or reaction, between stearic acid and additives in the sliding interfaces. As one possibility, the increase in wear with 1.0 wt% content is due to the decrease in the adsorbed amounts of ZDDP by the influence of stearic acid, and its decrease with 2.0 wt% content is caused by the synergic effect between stearic acid and ZDDP, i.e. the acceleration of ZDDP decomposition on sliding surface by the optimally adsorbed stearic acid, and with the contents over 3.0 wt% the sliding surfaces are adsorbed only by stearic acid to remove ZDDP causing the increase in wear. The less wear and the less changes in wear for oil B than oil A are owing to the reaction of the detergent with stearic acid reducing its effect.

In Fig. 8, variations of wear with increasing content of stearic acid are shown for oils C and D; both oils contain the dispersant in them. The dispersant is considered to control the effect of stearic acid, that is, it protects ZDDP from deterioration in the wear-preventing property when the content of stearic acid is 1.0 wt%, as discussed in Fig. 6. However, as the content becomes higher than 2.0 wt%, the wear increases parabolically with the content. The drastic increase in wear also implies that some wear-increasing components are produced in the oils from the reaction of the additives, perhaps the dispersant, and stearic acid.

Fig. 9 shows variation of wear as a function of increase in total acid number over the initial value [13, 14]. The results had been obtained in an experimental study conducted with gasoline engine oils deteriorated in real engines. Oil D, containing three representative additives, is considered to be most similar to general gasoline engine oils. When the data in Fig. 8 are compared with those in Fig. 9, the wear amounts increase parabolically with increasing amounts of oxidation products, increase in TAN in Fig. 9 and the amounts of stearic acid in Fig. 8. From this comparison, it is indicated that the model lubricants simulate well the deterioration of engine oils.

On the other hand, the oil A is selected to investigate the changes in wear-preventing property caused

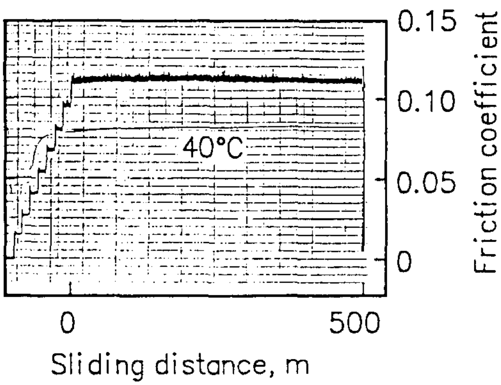

Fig. 11. Original friction record with oil B

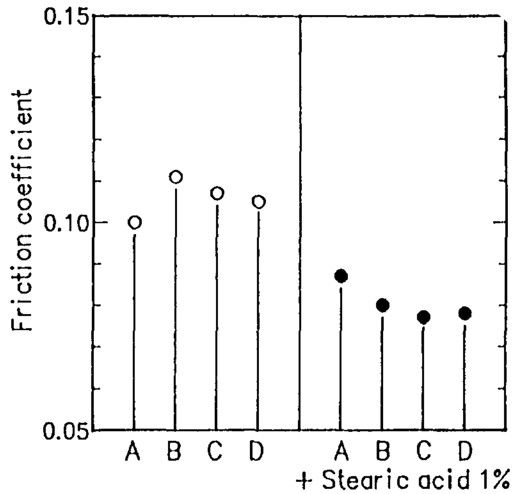

Fig. 12. Changes in friction coefficient with stearic acid contamination

by the high-temperature deterioration of oils. The high-temperature deterioration is simply conducted in a drying oven at a constant temperature of 150℃ under an open air atmosphere for one hour without supplying any catalyst. Stearic acid is blended into the oils before the high-temperature deterioration. The oxidation of the base oil contained in the lubricants is considered to be minimum due to the short period of the deterioration process, but only the decomposition of ZDDP and its reaction with stearic acid are possibly occurred.

As shown in Fig. 10, the wear-preveting property generally becomes better with the high-temperature deterioration for all oils tested with only one exception for the oil of 2.0 wt% content which produced much higher wear. This decrease in wear by high-temperature deterioration indicates that the high-temperature decomposition products of ZDDP have generally better wear-preventing property than ZDDP itself. However, the wear-preventing property of the high-temperature deterioration oils gradually decreases with increasing content of stearic acid in the oils.

Original friction record with oil B is given in Fig. 11. As shown in Fig. 12, friction coefficient at the end of tests is about 0.10-0.11 for the oils A, B, C, and D, which contain no stearic acid. However, friction coefficient with oils B, C, and D is higher than oil A by about 0.005-0.010, indicating that both the detergent and the dispersant increase the friction. By addition of stearic acid into the oils, the friction coefficient decreases to around 0.08 and the decreasing rate is higher with the oils B, C, and D which contain the detergent and the dispersant.

5. Conclusions

To investigate how the interaction among additives and oxidation products influences wear-preveting property of the lubricant containing ZDDP, experiments were conducted with the lubricants prepared by blending various combinations of three selected engine oil additives, i.e. a ZDDP, a detergent and a dispersant, and stearic acid, a model oxidation product.

It has been found that both the detergent and the dispersant give synergistic effect on the wear-preveting property of the ZDDP. Moreover, contamination by stearic acid, a model oxidation product, generally deteriorates wear-preventing property of the ZDDP-containing lubricants. A succinimide-type dispersant suppressed the increase in wear caused by the addition of stearic acid when its addition was small, but a Ca-sulfonate-type detergent decreased the wear over the whole range of addition. A high-temperature deterioration improved wear-preventing property of a ZDDP-containing lubricant.

References

1. Zs. Wittmann and E. Pudmer, Analysis of commerical zinc di(alkylphenyl) dithiophosphate additive, ASLE Trans., 28, 426-430 (1985).
2. N.E. Gallopoulos, Thermal decomposition of metal dialkyldithiophosphate oil blends, ASLE Trans., 7,

55-63 (1964).
3. F.G. Rounds, Some factors affecting the decomposition of three commerical zinc organodithiophosphates, ASLE Trans., 18, 79-89 (1975).
4. N.E. Gallopoulos and C.K. Murphy, Interactions between a Zinc dialkylphosphorodithioate and lubricating oil dispersants, ASLE Trans., 14, 1-7 (19 71).
5. F.G. Rounds, Additive interactions and their effects on the performance of a zinc dialkyldithiophosphate, ASLE Trans., 21, 91-101 (1978).
6. K. Inoue and H. Watanabe, Interations of engine oil additives, ASLE Trans., 26, 180-199 (1983).
7. K. Inoue and H. Watanabe, Interations between engine oil additives, J. Jpn. Petrol. Inst., 24, 101-107 (1981).
8. F.G. Rounds, Some effects of amines on zinc dialkyldithiophosphate antiwear performance as measured in 4-ball wear tests, ASLE Trans., 24, 431-440 (1981).
9. S. Plaza, The adsorption of zinc dibutyldithiophosphates on iron and iron oxide powders, ASLE Trans., 30, 233-240 (1987).
10. W.W. Hanneman and R.S. Porter, The thermal decomposition of dialkyl phosphates and O,O-dialkyl dithiophosphates, J. Org. Chem., 29, 2996-2998 (1964).
11. J.A. McGeehan, E.S. Yamaguchi and J.Q. Adams, Some effects of zinc dithiophosphates and detergents on controlling engine wear, SAE Paper 852133, 1985.
12. K. Fujita, Y. Esaki and M. Kawamura, The antiwear property of zinc dialkyldithiophosphates in used engine oils, Wear, 89, 323-331 (1983).
13. W.S. Moon and Y. Kmura, Wear-preventing property of used gasoline engine oils, Wear, 139, 351-365 (1990).
14. W.S. Moon and Y. Kimura, Deterioration of engine oils and its effect on their wear-preventing property, Proc. Jpn. Inter, Tribo. Conf. (Nagoya, 1990) 433-438.
15. F. Rounds, changes in friction and wear performance caused by interactions among lubricant additives, Lub. Sci., 1, 333-363 (1989).