한국윤활학회지(1995), 제 11 권 제 5 호
Journal of KSTLE(1995) Vol. 11, No. 5, pp.144~149

Frictional Characteristics of the Lubricants Formulated with Non-Conventional Base Stocks

Woo-Sik Moon and Jong-Hun Lee

Yukong Limited, Taejon, KOREA

Abstract—Use of high-quality basestocks is increasing to produce high-performance lubricants. However, their tribological characteristics have not been understood clearly yet. In this study, a newly developed basestock from a fuel hydrocracker and a poly-alpha-olefin are selected and investigated on the properties of lubricants formulated with them. The Lubricants are prepared by blending the basestocks with typical additives such as a zinc dialkyldithiophosphate, a dispersant, a detergent and a dispersant-inhibitor package. Frictional and wear-preventing properties are investigated using an oscillating-type wear-testing machine. The contact is a ball-on-disk mode and the testing temperature is varied from room temperature to 200°C. The results show that their frictional property is varied significantly and that the non-conventional oils result in lower friction and lower wear compared with conventional lubricants, especially at the higher temperatures.

Key words : Friction, Non-Conventional Basestock, Engine Oil, Ball-On-Disk, Wear test, Additives, Interaction

1. Introduction

The requirements for engine oils have become more severe, following the trend to higher performance of engine design. In order to make high-performance lubricants, it is necessary to improve formulation technology as well as to develop better additives and base stocks. In recent years, the use of high-quality basestocks has increased in order to satisfy the requirements for high-performance lubricants. Generally, lower volatility, good oxidation stability and viscometric properties have been required for the lubricants to function successfully under increasingly severe operating conditions.

Recent trend toward lower viscosity of engine oils is directly connected to the improvement of their fuel-economy performance. That is to say, automotive manufacturers tend to recommend the use of 5W/30 multigrades to reduce engine friction losses at all operating temperatures. The traditional formulation approach for these products was to use very low viscosity mineral base oils. However, such products tend to produce high oil consumption and be oxidized and thickened rapidly because of the high volatility of these base oils. Hence, in order to produce fuel-efficient engine oils with higher performance, it is generally necessary for them to be formulated using high-quality base oils in full or partial amount which include synthetic fluids and highly-refined mineral oils. Poly-alpha-olefins and hydrocracked basestocks meet the high performance specifications such as lower volatility, low temperature properties and viscosity-temperature characteristics, because they have higher quality including high viscosity index, low Noack volatility and good oxidation stability compared with conventional base oils.

Synthetic fluids like polyalphaolefin and ester have been used but only for limited purpose due to their high price. However, the so-called VHVI (very high viscosity index) base stocks produced from hydrocracking and/or wax-isomerization reported to be able to solve the problem and to have comparable quality [1,2,3].

It has been demonstrated that a severely hydrocracked VHVI base oil, formulated into friction-modified engine oils, displayed enhanced fuel economy characteristics due to superior oxidation stability and a lower viscosity/pressure coefficient, compared with a conventional mineral oil blend [4]. At a study on the performance of MoDTC friction modifiers, base oils of higher saturate content have been found to enhance their friction-reducing performance, compared with base oils containing higher levels of aromatic and/or polar synthetic components. It was proposed that the effect of base oil composition on the performance is by an adsorption mechanism [5].

Now, it is well understood that tribological behavior of base stocks depends on and is influenced by chemical composition and structure of their hydrocarbon and non-hydrocarbon constituents. In a four-ball-wear test, higher wear was produced with super-refined mineral oils than with conventionally refined mineral oils [6]. Aromatics and sulfurs containing hydrocarbons in solvent-extracted base stocks have been found to provide good wear and friction characteristics, while saturate hydrocarbons usually were markedly poorer [7,8]. However, it is known that increased refining of mineral oils generally enhanced the effectiveness of friction modifiers [9].

In this study, an attempt is made to expand an understanding on the tribological property of representative engine oil additives and the influence of base stocks. A newly developed base stock from a fuel hydrocracker and a polyalphaolefin are selected as non-conventional base stocks and investigated on the tribological properties of lubricants formulated with them. The lubricants are prepared by blending the base stocks with typical additives such as a zinc dialkyldithiophosphate, a dispersant,a detergent and a dispersant-inhibitor-package additive.

2. Experimental Details

2-1. Lubricants

Some characteristics of the base oils used in the experiments are given in Table 1. Four different base oils, which are classified into different API base oil grouping [10], are selected to blend lubricants.

Base oil BO1, which is a solvent-extracted 150 neutral, is classified as Group I. Base oil BO2 produced from a lube-hydrocracker pertains to GroupII, while base oil BO3 produced from a fuel hydrocracker is Group III as its viscosity index is higher than 120. As shown in the table, the VHVI base stock (BO3) has different properties from conventional ones (BO1, 2), containing almost no sulfur and much less aromatics. Moreover, the viscometric properties have been improved remarkably. That is, the VHVI base stock has higher viscosity at high temperature and lower viscosity at low temperature.

Table 1. General properties of base oils

Properties	BO1	BO2	BO3	BO4
API Classification	Gr.I	Gr.II	Gr.III	Gr.IV
Specific Gravity	0.869	0.865	0.844	0.827
Viscosity 100°C,cSt	5.2	5.1	6.0	5.9
Viscosity Index	97	99	123	135
Viscosity @-20°C, cP	2100	2000	1550	800
(CCS) @-25°C	3800	3600	2600	1300
Flash Point, °C	222	212	226	234
Pour Point, °C	-12	-15	-12	-57
Noack Volatility,wt%	17.0	16.6	7.2	7.5
Sulfur, wt%	0.58	0.03	0.00	0.00
Aro., vol% (HPLC)	27.7	3.5	0.6	0
TAN, mgKOH/g	0.02	0.02	0.01	0.01
Aniline Point, 'C	104	111	121	129

Table 2. Composition of BO3 (detail analysis by IP 386/ASTM D2786)

Saturates, %	99.2
Alkanes	33.65
1-Ring Naphthenens	24.98
2-Ring Naphthenens	23.88
3-Ring Naphthenens	11.09
4-Ring Naphthenens	4.48
5-Ring Naphthenens	1.11
6-Ring Naphthenens	0.0

Detailed compositions of BO3 are given in Table 2. It is noted that relatively larger amount of naphthenic components exist. This fact indicates that the greater part of aromatics in the feed stock were converted into naphthenic components during the hydrocracking process.

Among various additives contained in engine oils, the following representative ones are selected, ZnDDP as a dual-functional additive of wear-prevention and oxidation-inhibition, a succinimide as dispersant, and an overbased calcium sulfonate. Their detailed properties are given in Table 3.

One DI-package-type additive of API SH performance grade is also blended to make engine oils. Two kinds of friction modifiers are added up into engine oils to investigate the influence of different base stocks. These additives of commercial grades were blended into different base oils with various combinations to prepare oil samples for the experiments.

Detailed formulations of the representative oils

Table 3. Properties of additives

Properties	ZnDDP	Dispersant	Detergent	DI package	FM 1	FM 2
Viscosity,cSt @ 40℃	130	8000	2000	-	-	168.
@ 100℃	10	420	64	125	15.0	13.0
TBN, mgKOH/g	-	27	300	-	-	-
Elements,	Zn 8.9 wt%	N 1.46 wt%	Ca 11.9wt%	Ca 0.459 wt%	Mo 1.1 wt %	-
	P 8.0 wt%	-	-	Mg 0.370 wt%	-	-
	-	-	-	Na 0.561 wt%	-	-
	-	-	-	Zn 1.19 wt%	-	-
Etc.	Primary-secondary mixed type	PIBSA-PAM type	Overbased Calcium sulfonate	API SH grade	MoDTC type	Glycerol oleate type

Table 4. Preparation of lubricants

Lubricants	Formula			
	Base Oil	ZnDDP 1 wt %	Detergent2 wt %	Dispersant 5 wt %
A	BO1	○		
A1	BO1	○	○	
A2	BO1	○		○
A3	BO1	○	○	○
B	BO2	○		
B1	BO2	○	○	
B2	BO2	○		○
B3	BO2	○	○	○
C	BO3	○		
C1	BO3	○	○	
C2	BO3	○		○
C3	BO3	○	○	○
D	BO4	○		
D1	BO4	○	○	
D2	BO4	○		○
D3	BO4	○	○	○

tested are summarized in Table 4.

Lubricants A,B,C and D are single-additive systems containing ZnDDP by 1.0 wt% concentration in the base oils. Lubricants A1~D1 and A2~D2 are double- additive systems containing other additives plus ZnDDP; the former systems contain the detergent by 2.0 wt% and the later systems contain the dispersant by 5.0 wt%. In lubricants A3~D3, three kinds of additives are contained:1.0 wt% ZnDDP, 2. 0 wt% detergent and 5.0 wt% dispersant. These treating rates of additives are comparable with those of high performance engine oils.

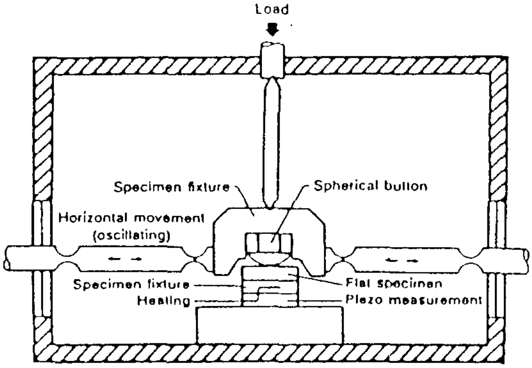

Fig. 1. SRV oscillating machine.

2-2. Experiments

A general view of the SRV oscillating-type wear-testing machine (Optimol Model) is shown in Fig. 1. The sliding system consists of an oscillating upper specimen and a stationary lower specimen. The ball specimen of 10 mm in diameter is rigidly secured into the upper specimen holder. The ball slides over the lower disk specimen, giving the load in contacted state. The load and friction force are measured using a two-phase piezoelectric-type transducer which is located under the disk specimen. Friction coefficient is averaged over each period of oscillating run and recorded continuously. Both the ball and the disk specimens are made of SUJ 2 (which corresponds to AISI 52100) bearing steel.

All the friction experiments and measurements were conducted in the following manner. In Table 5 are given the testing conditions including normal load, stroke, frequency and temperature.

Measurements of friction were conducted on a ball-on-disk configuration operating at 100 Newton, 1.0 mm stroke, 50 Hz and temperature ramped from 30 to 200°C.

Before each run, specimens were cleaned care-

Table 5. Experimental conditions

Test Method	Ball-On-Disk
Load	100 N
Stroke	1.0 mm
Frequency	50 Hz
Temperature	40~200°C

fully in heptane, dried in a hot air stream, and then set in the apparatus. The sliding speed was held constant throughout the run, but the load were increased to the predetermined value during a break-in of five minutes and kept constant thereafter. Specimen temperature was increased from room temperature to 200°C by the speed of 20°C increase over 10 minutes. Friction and specimen temperature were continuously measured through the run.

After a run, the specimens were removed from the apparatus and washed as before. Then the wear scar width on the ball were determined under an optical microscope.

3. Results and Discussion

Variations of friction coefficient with increasing temperature are shown in Fig. 2 for experiments with lubricants A, B, C and D. Friction coefficient shows considerable differences among four oil samples of different base stocks blended. From 40°C to 120°C, friction coefficient is almost the same for all the oils tested increasing gradually from 0.125 to 0. 140. This suggests that the decrease in lubricant viscosity over this temperature range have some influence on friction coefficient. However, after the temperature reaches 140°C, friction coefficient has different values among the lubricant tested, presumably due to the thermal decomposition and/or activation of ZnDDP. Lubricant A, blended with BO1, suppresses the increase in friction coefficient upto 200°C, while lubricant B,C and D give higher friction coefficient and finally result in welding of the specimens at the temperature of 200, 160 and 140°C, respectively.

These frictional characteristics have a correlation with hydrocarbon composition of the lubricants. That is, the lubricants with higher aromatics content give better surface protection.

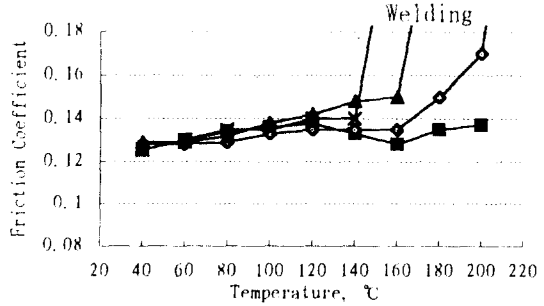

Fig. 2. Influence of basestocks on the friction : one-additive lubricants (ZnDDP), ■, OIL A; ◇, OIL B; ▲, OIL C; ×, Oil D.

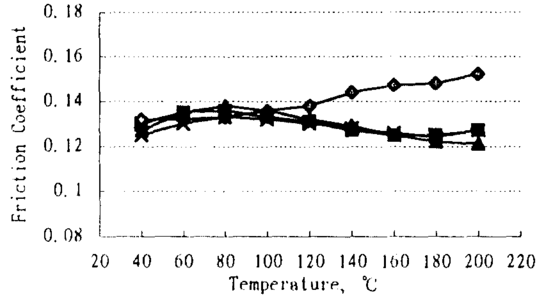

Fig. 3. Influence of basestocks on the friction: two-additive lubricants (ZnDDP+dispersant), -■-, OIL A2; -◇-, OIL B2; -▲-, OIL C2; -×-, Oil D2.

This difference is considered to be caused by the additive solvency of the base oils. Because the ZnDDP is thermally decomposed at around 120°C, the frictional properties of the lubricant should depend on the decomposition products of the ZnDDP at the higher temperature [11]. Oil A has even lower friction at high temperature, as it has good solvency for the decomposed products which is known to have better frictional characteristics than ZnDDP itself [12]. However, with decreasing solvency, they cannot protect the sliding surfaces at higher temperature, because the decomposition products are separated from the oils

The minimum wear amount was produced with lubricant A but other lubricants generated higher wear of similar levels.

As shown in Fig. 3, addition of a dispersant to lubricants A~D changes variations of friction coefficient with increasing temperature. Except for lubricant B, other lubricants have a very similar trend in that friction coefficient decreases gradually to about 0.125 over the temperature range of 100°C to 200°C. Anyway, the dispersant improved both fric-

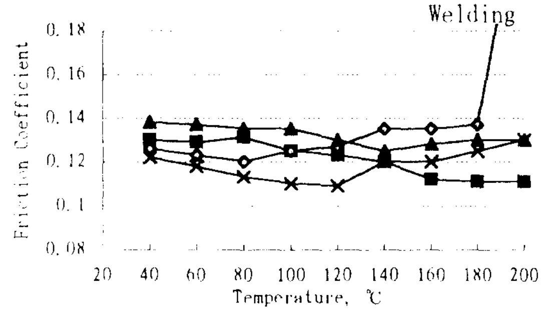

Fig. 4. Influence of basestocks on the friction: two-additive lubricants (ZnDDP+detergent), -■-, OIL A1; -◇-, OIL A2; -▲-, OIL A3; -×-, Oil A4.

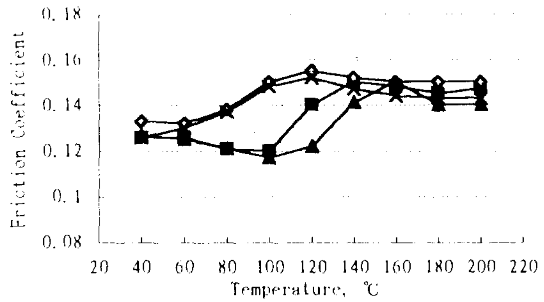

Fig. 5. Influence of basestocks on the friction: three-additive lubricants (ZnDDP + dispersant + detergent), -■-, OIL A3; -◇-, OIL B3; -▲-, OIL C3; -×-, Oil D3.

tion coefficient and wear amount for all the lubricants tested. This result clarifies that the dispersant has a synergistic effect on the activity of ZnDDP, especially at the higher temperature range, whatever the base oil may be.

It is generally understood that dispersants desolve some ZnDDP-decomposition products giving better frictional and wear-preventing properties [11,12]. Now it is clear that when dispersants are added the non-conventional basestocks have the same as or even better than conventional ones in the frictionl properties in spite of their relatively lower solvency.

Addition of a detergents to lubricants A~D generally improves friction coefficient excepting for lubricant B2 which results in welding at 180°C, as given in Fig. 4. It is considered that welding at the higher temperature is prohibited by synergistic effects at sliding surface of ZnDDP and the detergent.

When a detergent is added into lubricants A1~D1 to make three additive systems, friction coefficient responds differently for each lubricant but generally increases over the higher temperature range, as Fig. 5 shows results with lubricants A3~D3. With lubricants B3 and D3, friction coefficient increases over all the temperature range studied. However, transition in friction coefficient is found with lubricants A3 and C3. That is, friction coefficient decreases at the initial lower temperature range but increases rapidly around a critical temperature of 120°C and then levels off.

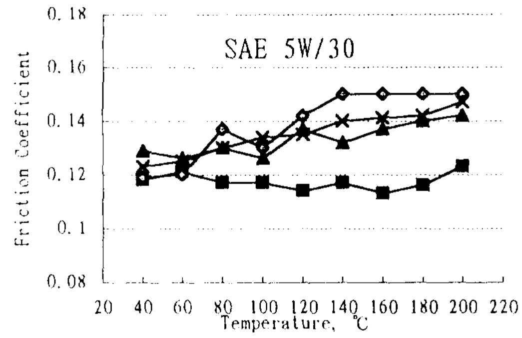

Fig. 6. Influence of basestocks on the friction: full-formulated engine oils, -■-, GROUP III; -◇-, GROUP I; -▲-, GROUP I+GROUP III; -×-, GROUP I(10 W/30).

More study is necessary to understand how the balancing among the three additives influences the frictional characteristics. However, it may be possible to suppress friction coefficient at higher temperature via good combination and selection of additives, as we see in the following results with full formulated engine oils.

Figure 6 gives variation of friction coefficient for full-formulated engine oils using different base stocks but with the same additive systems. The oil blended with a group III base stock has almost constant friction coefficient over all the temperature range investigated, while other oils give friction coefficient increasing gradually with increasing temperature. When the similar group II base stocks are used, the oil of SAE 10W-30 has lower friction coefficient than SAE 5W-30, perhaps due to the higher viscosity. When we add group III base stock into the group I base stock in order to make a SAE 5W-30 oil, friction coefficient decreases slightly compared with the oil blended with a full group I base stock, as shown in the figure.

This result indicates that, when a well balanced

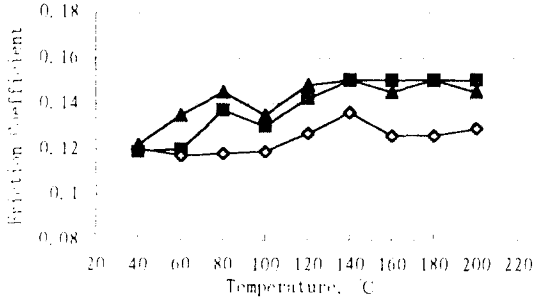

Fig. 7. Influence of friction modifiers on the friction: a full-formulated lubricant (conventional basestock), -■-, GROUP I; -◇-, MoDTC; -▲-, Ashless.

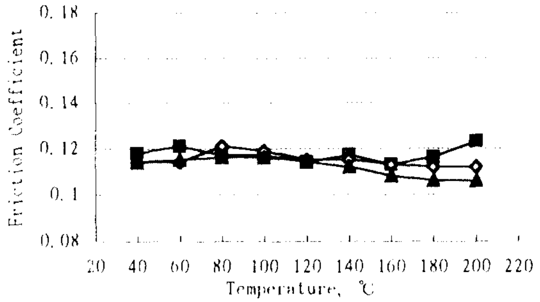

Fig. 8. Influence of friction modifiers on the friction: a full-formulated lubricant(Group III), -■-, GROUP I; -◇-, MoDTC; -▲-, Ashless.

additive system is selected, the group III base stock give excellent frictional properties at all the temperature investigated which are almost impossible with conventional base stocks. That is, excellent surface adsorption and oxidation stability are originated from the base oil and balanced solvency and dispersancy is supported by additives.

When we add a conventional ashless friction modifier (0.2 wt% concentration) to the SAE 5W-30 oil (group I) described in Fig. 6, friction coefficient decreases slightly over the temperature ranging from 60°C to 120°C, as shown in Fig. 7. Addition of a MoDTC friction modifier (0.2 wt%concentration) reduces friction coefficient considerably and is effective upto 200°C. However, friction coefficient of the group I oil with MoDTC is still higher than the untreated group III oil discussed in Fig. 6.

As given in Fig. 8, the effectiveness of friction modifiers is slight when they are added to the SAE 5W-30 oil blended with a group III base stock ,compared with the oil blended with a group I base stock. Reduction in friction coefficient is larger with FM2 and more effective at the temperature range higher than 140°C.

4. Conclusions

(1) Composition of base oils influences greatly on the tribological behavior of additive systems.

(2) Ashless dispersant enhances frictional properties of ZnDDP-containing lubricants at the temperature range higher than 120°C.

(3) A high VI base stock (group III) produced from a fuel hydrocraker bottom feed can reduce friction coefficient in formulated engine oils.

References

1. M. Ushio, Preprint. ACS, 37, 4, 1293-1302, 1992.
2. N. C. Yates, Preprint. ACS, 37, 4, 1303-1312, 1992.
3. W.S. Moon, J.H. Lee and S.K. Hahn, Proc. JAST, Tokyo 1995-5, 429-432.
4. J. Igarashi, Thesis Dr. Eng, 170-187, 1993.
5. A.J. Stipanovic and J.P. Schoonmaker, SAE Paper 932779, 77-88, 1993.
6. E.E. Klaus and H.E. Bieber, ASLE Trans., 7, 1-10, 1964.
7. R.S. Fein and K.L. Kreuz, ASLE Trans., 8, 29-38, 1965.
8. M.T. Benchaita, R.D. Schwartz and F.E. Lockwood, STLE Trans., 33, 1, 85-95, 1990.
9. F.G. Rounds, ASLE Trans., 8, 21-28, 1965.
10. API base oil classification, 1994.
11. I-Ming Feng, Wear, 3, 309-311, 1960.
12. Kawamura, F. Fujita, Y. Esaki, and H. Moritani, SAE paper 852076, 1985.