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R&D on New Friction Modifier for Lubricant for Fuel economy improvement

(Group on New Friction Modifier for Fuel economy improvement)
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1. Contents of Empirical Research

Of the oils sold on the market, those classified as excellent fuel economy engine oils are ones that have reached the rate of fuel economy improvement specified in ENERGY CONSERVING II (EC-II) of API standards in the USA. The purpose of our research is to develop a new friction modifier that realizes an improvement of 50 percent or more in fuel economy as compared to the SH 10W-30 oil sold on the market, which realizes the EC-II standard. In ASTM Seq. VI tests used in API standards, EC-II oil demonstrates an improvement of 2.7% or more in fuel economy over standard oil (20W-30 oil); among oils currently on the market, it offers the highest level of fuel conservation. As shown in Figure 1-1, an improvement of 50% or more in fuel economy, the objective of our research, is equivalent to an improvement of 4.05% or more in fuel economy when compared by ASTM Seq. VI tests.

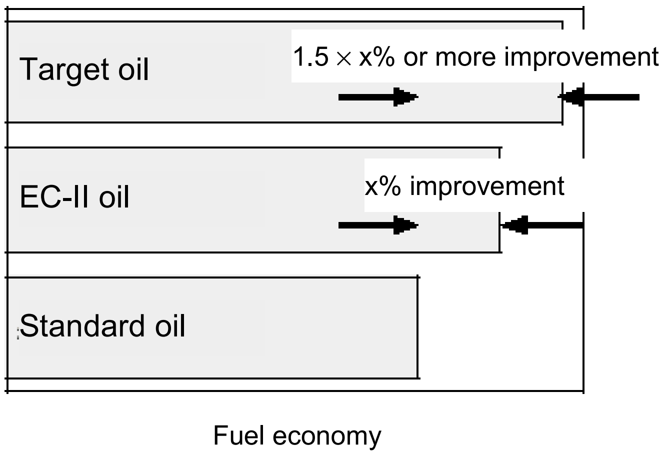

Figure 1-1 Fuel economy improvement targets

The overall plan of our research is shown in Table 1-1. In the development of additives thus far, one common approach has been to search widely for all obtainable additives and to select from among them, through a process of screening, those that are most favorable. In this method, however, great labor is required if the number of samples becomes large, and when attention is focused on obtaining new additives by synthesis, it becomes very difficult to obtain indexes for the molecular designs. In our research, the reaction mechanisms of molybdenum-type friction modifier already in existence were clarified, and the molecules of a new friction modifier which promotes the performance of the same was designed.

Table 1-1 Overall plan

Item	Year of plan				
	7	8	9	10	11
Investigation of friction modifier technology	━				
Clarification of friction modifier reaction mechanisms	━	━	━	━	━
Research and development of new friction modifier	━	━	━	━	━
Laboratory scale evaluations	━	━	━	━	━
Fuel economy bench scale evaluations		━	━	━	━
Evaluation of commercial vehicle with chassis dynamometer					━

From numerous reports it has been recognized that there is a close correlation between friction coefficient and surface generation volume of molybdenum disulfide (MoS_2). In general, it is believed that the MoS_2 generation on surface can easily take place under the severe conditions of high-temperature and high-pressure. Nevertheless the actual state of friction inside an automobile engine is a combination of diverse conditions, and it would be ideal if efficiency in MoS_2 generation were improved under all these conditions. The latest research results have clarified that with the coexistence of zinc compounds, it is possible to promote the generation of MoS_2 and to lower friction coefficient, thereby improving fuel economy. Sulfur in the zinc compounds is labeled by isotope, and the reaction mechanisms are clarified primarily through elucidation of the actual sulfur supply route. Based on the findings thus obtained, a specific zinc compound was proposed.

The newly developed, zinc-type friction modifier was then used in combination with a Mo-type friction modifier to conduct evaluations in the following three stages and confirm performance: a reciprocating friction tester was used to evaluate friction coefficient on a laboratory scale; bench scale fuel economy tests were carried out with a commercial engine, and then tests were performed with a chassis dynamometer using commercial vehicle.

2. Empirical Research Results and Analysis Thereof

2.1. Clarification of friction modifier reaction mechanisms

Stearic acid was selected as a typical organic friction modifier; MoDTC was selected as an organometallic friction modifier, and ZnDTP, an antiwear agent, was selected as coexistent compound. Using an SRV friction tester, the reaction domains and effects of organic friction modifier and of organometallic friction modifier were investigated under diverse conditions of lubrication. The friction coefficient of stearic acid is roughly constant regardless of lubricating conditions, but MoDTC types are effective under high-load conditions. In comparison to MoDTC independent types, stearic acid is effective in domains of low load and of low speed, but the MoDTC + ZnDTP types are even higher in effectiveness than these in all domains. With the aim of developing a friction modifier of even higher performance, our research was focused on organometallic friction modifier.

Comparisons were made of the effect when the additives ZnDTC, ashless DTP and ashless DTC, all of similar structure to ZnDTP, are coexistent with MoDTC. The chemical structures are shown in Figure 2.1-1. The results shown in Figure 2.1-2 indicate that even when the chemical structure is the same, if Zn is included, there is an effective drop in friction coefficient. The results of XPS analysis of surfaces, as shown in Table 2.1-1, indicate that there is a tendency for the volume of MoS_2 generation to increase in the presence of zinc.

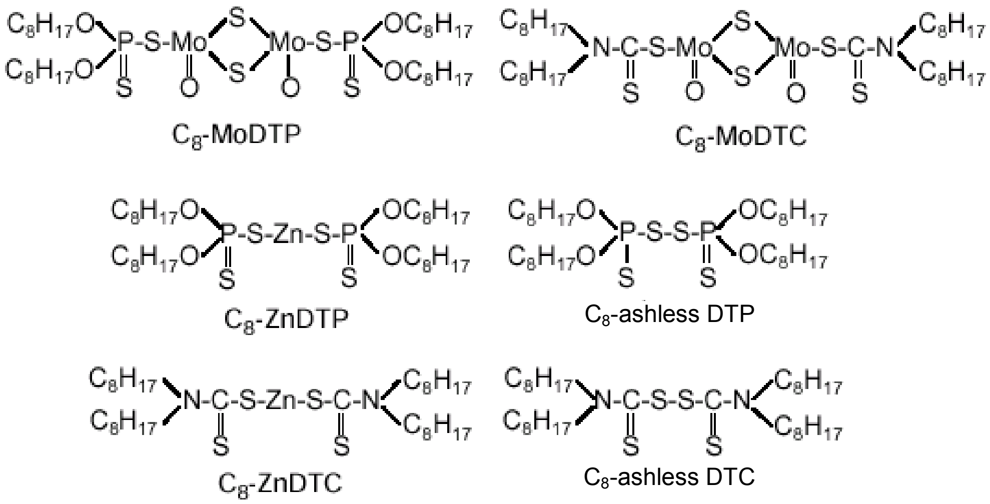

Figure 2.1-1 Chemical structure of additives in use

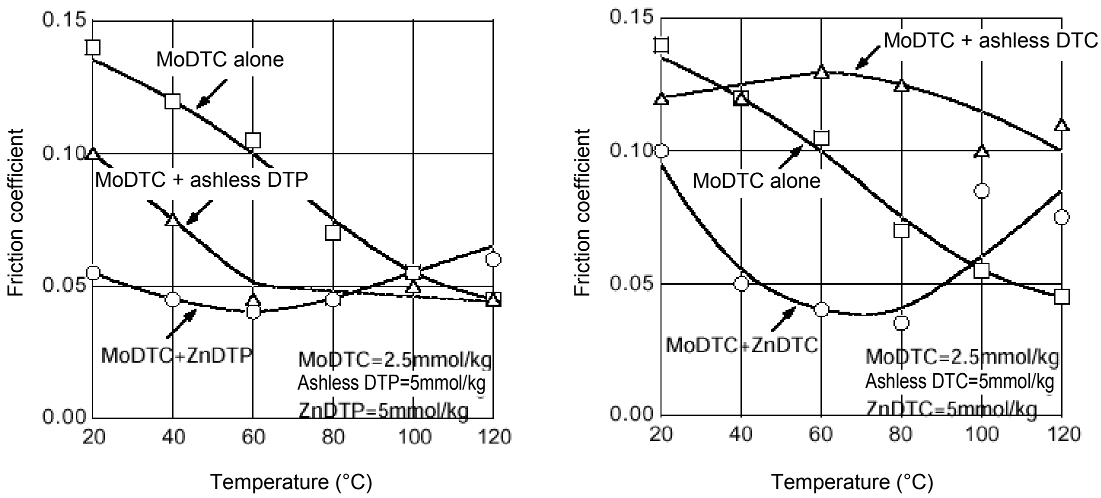

Figure 2.1-2 Effect of coexistence with compounds resembling ZnDTP

Table 2.1-1 XPS analysis of friction surfaces

Coexistent additive	None	ZnDTP	ashless DTP	ZnDTC	ashless DTC
Mo concentration (mmol/kg)	5	5	5	5	5
Additive concentration (mmol/kg)	-	10	10	10	10
Friction coefficient (25°C)	0.13	0.04	0.07	0.07	0.13
MoS_2 adhesion volume (atm%)	0.3	1.3	0.5	1.0	0.1
Zn adhesion volume (atm%)	-	2.7	-	3.5	-
Zn bonding condition	-	Zn-S (partially Zn-O)	-	Zn-S	-

It is believed that control of the volume of MoS_2 generated on a friction surface is an effective means of reducing friction, that is, of improving fuel economy. To develop a new friction modifier effective in improving fuel economy, therefore, it is essential to elucidate the mechanism of MoS_2 generation on friction surfaces. In investigating new additives for effective generation of MoS_2, it is especially important whether the source of sulfur in MoS_2 generated on friction surface is MoDTC or some other sulfur-containing additive in oil, as exemplified by ZnDTP. In the combination of MoDTC and ZnDTP currently in use, an attempt was made to label the sulfur in ZnDTP using ^{34}S, which has a natural isotopic abundance of about 4%, in order to disclose the source of sulfur during MoS_2 generation as indicated in Figure 2.1-3.

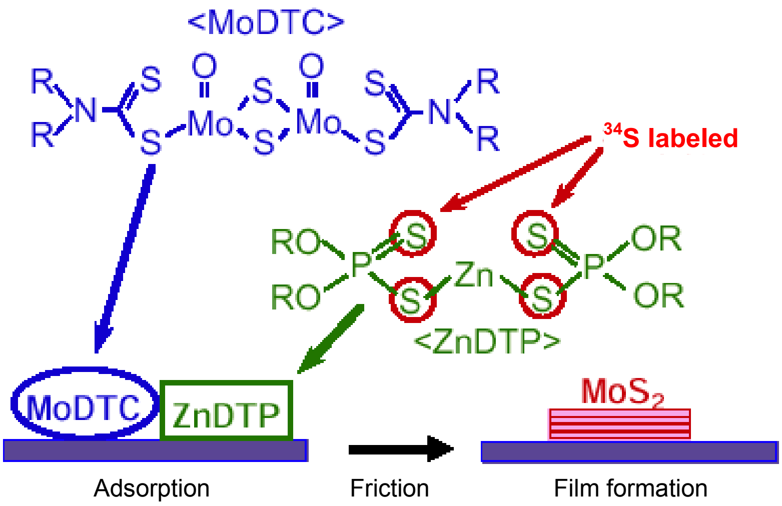

Figure 2.1-3 Friction surface reaction model and use of labled compound

Shown in Figure 2.1-4. is the route of labeled compound synthesis. Table 2.1-2 presents the results of elementary analysis by means of ICP (inductively coupled plasma spectrometry) analysis of ZnDTP and ashless DTP synthesized from natural P_2S_5 and ^{34}S labeled P_2S_5. In either case, a value close to the theoretical ratio was obtained, and it was concluded that synthesis was successful. The results of mass spectral analysis of ZnDTP are given in Table 2.1-3. From comparison of items labeled by ^{34}S with regular products, it was confirmed, also quantitatively, that adequate labeled strength was obtained.

In friction tests, poly α olefin oligomer (PAO) was used as the base oil.

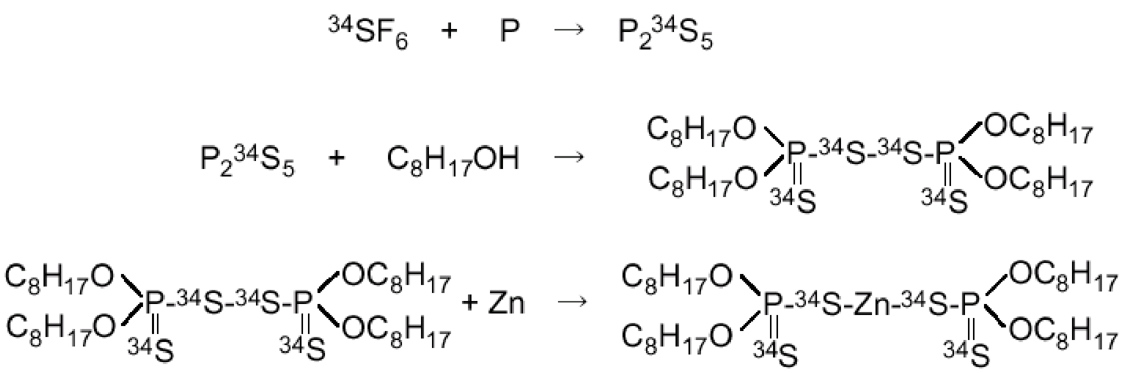

Figure 2.1-4 Route of labeled compound synthesis

Table 2.1-2 Results of elementary analysis of labeled ZnDTP and ashless DTP product

		Zn	P	S	C	H	O	
Theoretical composition	ashless DTP	0.0	8.7	19.0	53.8	9.5	9.0	100.0
	ZnDTP	8.1	8.0	17.5	49.4	8.8	8.2	100.0
Analysis results	ashless DTP	0.0	7.7	17.3	54.6	10.1	10.3	100.0
	ZnDTP	7.3	7.3	16.8	50.3	8.8	9.5	100.0

Table 2.1-3 Results of mass spectral analysis of ZnDTP natural product and labeled product

Mass number	Combination	Calculated value (%)		Measured value (%)	
		Natural	Labeled	Natural	Labeled
771	$^{64}Zn+^{32}S_4$	40.7	0.0	45.1	0.8
773	$^{64}Zn+^{32}S_3+^{34}S$ $^{66}Zn+^{32}S_4$	33.0	0.0	24.9	0.8
775	$^{64}Zn+^{32}S_2+^{34}S_2$ $^{66}Zn+^{32}S_3+^{34}S$ $^{68}Zn+^{32}S_4$	22.1	0.7	20.5	0.4
777	$^{64}Zn+^{32}S+^{34}S_3$ $^{66}Zn+^{32}S_2+^{34}S_2$ $^{68}Zn+^{32}S_3+^{34}S$	3.9	9.0	6.9	1.1
779	$^{64}Zn+^{34}S_4$ $^{66}Zn+^{32}S+^{34}S_3$ $^{68}Zn+^{32}S_2+^{34}S_2$	0.3	46.1	1.5	44.9
781	$^{66}Zn+^{34}S_4$ $^{68}Zn+^{32}S+^{34}S_3$	0.0	27.9	0.8	28.5
783	$^{68}Zn+^{34}S_4$	0.0	16.3	0.3	23.6

To PAO was added 5.0 mmol/kg of MoDTC and 7.5 mmol/kg of ZnDTP having the prescribed quantity of ^{34}S label strength, and SRV friction tests were performed under standard conditions. Friction surface was analyzed using TOF-SIMS (Time Of Flight Secondary Ion Mass Spectrometry), and the percentages of ^{32}S and ^{34}S were determined with respect to cluster ion intensity, including surface Mo-S bonding. Presented in Figure 2.1-5 is a comparison of TOF-SIMS with the conventional SIMS. Because the strength of the incident ion beam in TOF-SIMS (Static-SIMS) is weaker than in the conventional SIMS (Dynamic-SIMS) by about 100-fold, information on the uppermost atomic layer of the surface can be obtained. Also, because the probability of sputtering MoS_2 surface molecules in a cluster state increases, the projection of sulfur bonded with Mo can be detected. Further, under the principle of TOF spectroscopy, because there is almost no control on the upper limit of mass numbers detected, detection sensitivity in the domain of mass number 100 or more, including Mo, is favorable. What is more, because mass resolution is about 100 times that of the conventional SIMS, a peak separation of about 0.05 in the difference in mass number between $Mo^{32}S$ and $Mo^{16}O_2$, for example, is possible, and the interference from mass peak through combination with other elements can be eliminated.

There is a large number of Mo isotopes, including 92 (16%), 94 (9%), 95 (16%), 96 (16%), 97 (9%), 98 (24%) and 100 (10%), and as a result of TOF-SIMS analysis, they can be detected at very good accuracy as Mo^+ independent metal ion, as shown in Figure 2.1-6.

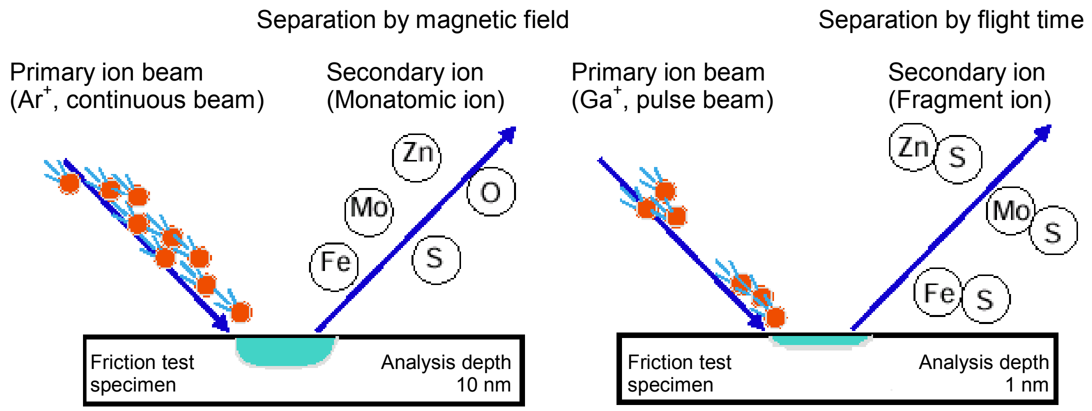

Figure 2.1-5 Conventional SIMS versus TOF-SIMS

As indicated in Table 2.1-4, we find that the $^{92}Mo^+/^{100}Mo^+$ intensity ratio matches the 1.64 isotopic abundance ratio of natural $^{92}Mo/^{100}Mo$ isotope, and that the disparities among specimens are extremely slight. MoS^+, $MoSO^+$ and $MoSO_2^-$ were successfully detected as fragment ions with Mo bonded to S.

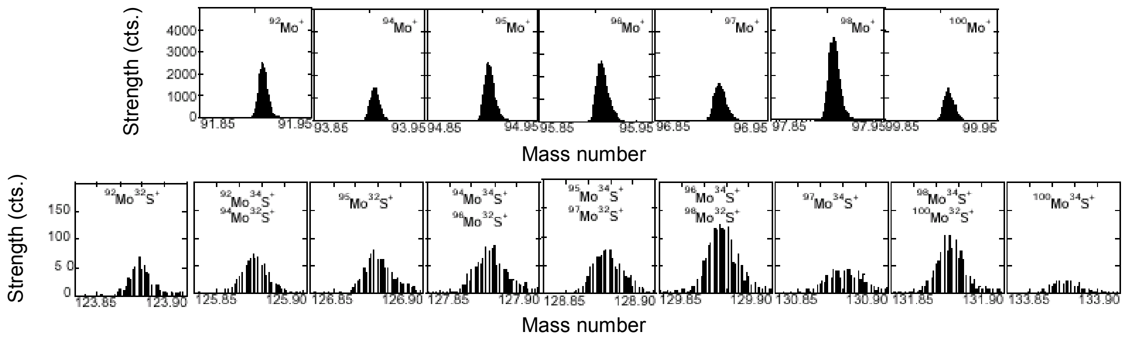

Figure 2.1-6 MoS^+ fragment peaks determined by TOF-SIMS on friction surfaces

Table 2.1-4 Mo fragment strength and sulfur source quantity

Labeled percentage (%) in ZnDTP (%)	$^{92}Mo^+$ (cts.)	$^{100}Mo^+$ (cts.)	$^{92}Mo^+/^{100}Mo^+$	$^{92}Mo^{32}S^+$ (cts.)	$^{100}Mo^{34}S^+$ (cts.)	^{34}S percentage (%)	Percentage of S derived from ZnDTP (%)
0	19674	12060	1.63	623	22	5	-
25	14025	8586	1.63	591	65	15	44
50	11874	7257	1.64	572	121	26	47
75	19234	11758	1.64	516	144	31	39
100	23053	13927	1.66	539	249	43	42

As shown in Figure 2.1-6, detection strength was relatively strong, and the integral strength associated with each peak of $^{92}Mo^{32}S^+$, $^{94}Mo^{32}S^+$, $^{97}Mo^{34}S^+$ and $^{100}Mo^{34}S^+$, where there is no interference among mutual Mo isotopes, was used in quantitative calculations. Table 2.1-1 gives the estimates of ^{34}S percentage in MoS^+ fragment and of S percentage in MoS_2 supplied by ZnDTP. The ^{34}S percentage in MoS^+ was determined from the strength of $^{100}Mo^{34}S^+$ and of $^{100}Mo^{32}S^+$ which were calculated using the metallic ion percentages of $^{92}Mo^+$ and $^{100}Mo^+$, based on $^{92}Mo^{32}S^+$ strength.

The percentage of sulfur derived from ZnDTP was determined from the amount of ^{34}S labeled ZnDTP combination and ^{34}S percentage in MoS^+, in consideration of the abundance of natural ^{34}S and ZnDTP label strength. The percentage of ^{34}S in MoS^+ fragment increases together with an increase in the percentage of ^{34}S labeled ZnDTP, and it was discovered that in either sample, the percentage of sulfur derived from ZnDTP in MoS^+ fragment is around 40%.

From the aforementioned, it can be postulated that the generation of surface MoS_2 is assisted by the mutual reaction of Zn and S. It was determined that in order to promote the generation of surface MoS_2, an effective additive that contains zinc must be sought out.

2.2 Development of new friction modifier

Organic zinc compound additive

In research thus far, it has been disclosed that when Mo and Zn coexist in oil, friction reduction is bolstered. An investigation was conducted, therefore, to see if the performance of MoDTC could be boosted by an oil-soluble additive containing zinc, focusing on organic zinc compound of the carboxylic acid and sulfonic acid groups. Not much effectiveness was demonstrated by the carboxylic acid group, but it was found that salts of the sulfonic acid group are effective in reducing friction in high-temperature domains, so optimization of its structure was investigated. Figure 2.2-1 shows the effect of optimized organic zinc compound in coexistence with MoDTC and ZnDTP. In SRV reciprocating friction tests, the performance of organic zinc compound for MoDTC is enhanced under the coexistence of ZnDTP.

2.3 Establishment of fuel economy evaluation method

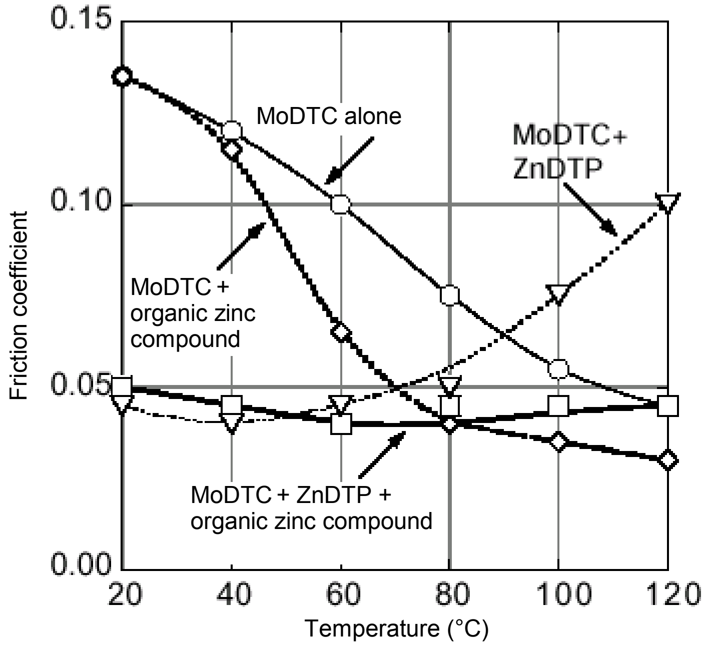

Figure 2.2-1 Friction characteristics of organic zinc compound additives

Evaluations of fuel economy were conducted in three stages: laboratory scale evaluation, bench scale evaluation and chassis dynamo evaluation.

In laboratory scale tests, SRV reciprocating friction tester of the structure shown in Figure 2.3-1 was used, and evaluations were made by the cylinder-on-disk test method in which the cylinder is brought into contact with a flat disk so that its curved outer surface is the line of contact. It is said that this friction test reflects the conditions of cam friction, which are said to account for a large portion of engine friction loss, and it is widely used especially in the evaluation of Mo-type friction modifiers. Standard test conditions were as follows: oil temperature, 80°C; load, 400N; vibrations, 50 Hz; amplitude, 1.5 mm; time, 15 minutes. Parameters were changed as necessary and friction characteristics were measured.

An 1800 cc engine was used in bench scale evaluations. As shown in Figure 2.3-2, five sets of torque and rpm, believed to reflect typical running conditions, were selected, and fuel economy performance was measured while running at constant speed. Driving conditions were established by taking a simple average of the rates of improvement in fuel economy under the five conditions.

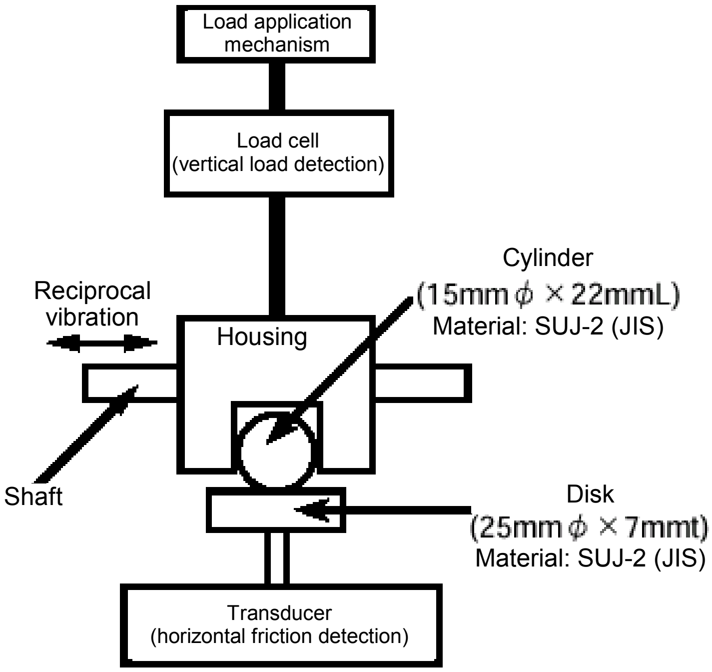

Figure 2.3-1 Structure of SRV reciprocating friction tester

This approach is called the five-point running test. Next, a bench scale fuel economy evaluation was done on API standard oil of the USA, on EC-I qualified oil and on two types of EC-II qualified oil, and the correlation between fuel economy in the aforementioned five-point running test and in Sequence VI was confirmed. As shown in Figure 2.3-3, a regression line was determined from the correlation figure, and the target value which is the fuel economy improvement rate of 4.05% or more by Sequence VI tests, was converted to a fuel economy improvement rate of 0.8% or more in the five point running test.

Based on this, oil was prepared by removing combined friction modifier and ZnDTP from EC-II qualified 10W-30 oil. Fixed quantities of MoDTC, organic zinc compound (Zn-X), ZnDTP and sulfur supplier (SS) were then added to this oil, and rates of fuel economy improvement in the five-point running test were measured. The results, presented in Figure 2.3-4, indicate that the target values could be reached by combining these additives.

Chassis dynamo evaluation was conducted only on the final candidate oil. The test vehicles were a Toyota Vista and Honda Accord, each mounted with a 1800 cc engine. The test mode was 10-15 mode and fuel economy was determined by the carbon balance method.

2.4 Evaluation of candidate oil

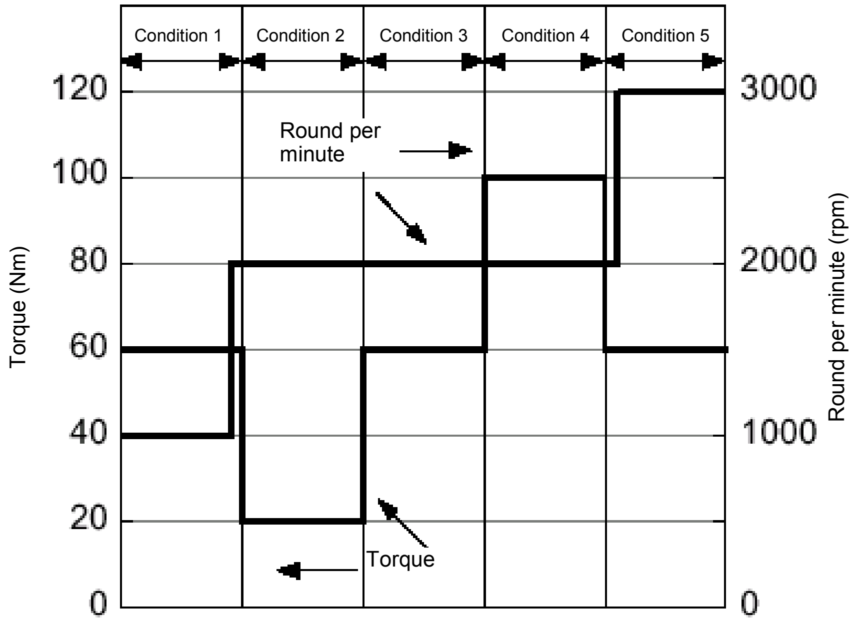

Figure 2.3-2 Conditions of five-point running test

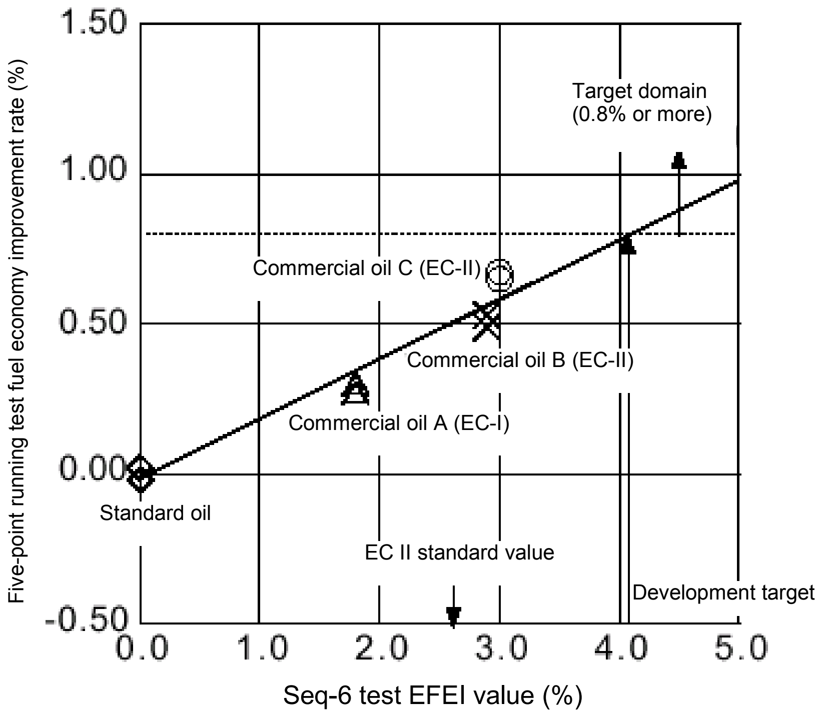

Figure 2.3-3 Correlation between five-point running test and Seq.VI fuel economy test

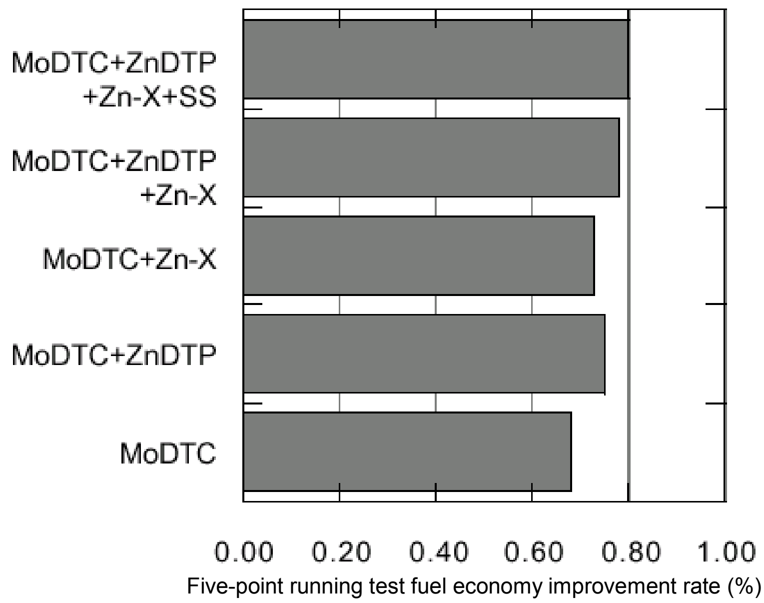

Figure 2.3-4 Fuel economy of market oils and of zinc compound oils

In bench-scale evaluations, it was confirmed that the performance of 10W-30 oil, an additive combination which contains MoDTC and organic zinc compound, clears the target. The contents of this combination are presented in Table 2.4-1. In chassis dynamo evaluations, the most recently developed candidate oil was compared with standard oil and other reference oils, and it was found that in terms of commercial application, 5W-20 grade oil, of lower viscosity than 10W-30, is most feasible for use. In candidate oil for chassis dynamo, therefore, a viscosity grade of 5W-20 was used without changing the fundamental combination of additives.

Figure 2.4-1 presents the results of chassis test using the Toyota Vista. The results indicated that, although the reference oil exhibited only the same performance as the standard oil, the candidate oil was amply effective in improving fuel economy. From these results alone, it is difficult to assess the extent to which targets were reached in the chassis test, but even after considering test errors, it can be concluded that the candidate oil demonstrates adequate performance.

3. Results of empirical research

Table 2.4-1 Additive combinations of candidate oil

Additive		Additive quantity
Metallic detergent	Ca sulphonate	Ca = 2000 ppm
Ashless dispersant	Succinic acid imide	5 wt%
Antioxidant	Alkyl phenol	1 wt%
Antiwear agent	ZnDTP	P = 1000 ppm
Friction modifier	MoDTC	Mo = 700 ppm
	Organic zinc compound	0.5 wt%
Sulfur supplier		S =1000 ppm
Viscosity index improver		Viscosity conditioning
Pour point depressant		Trace amount
Defoamer		Trace amount

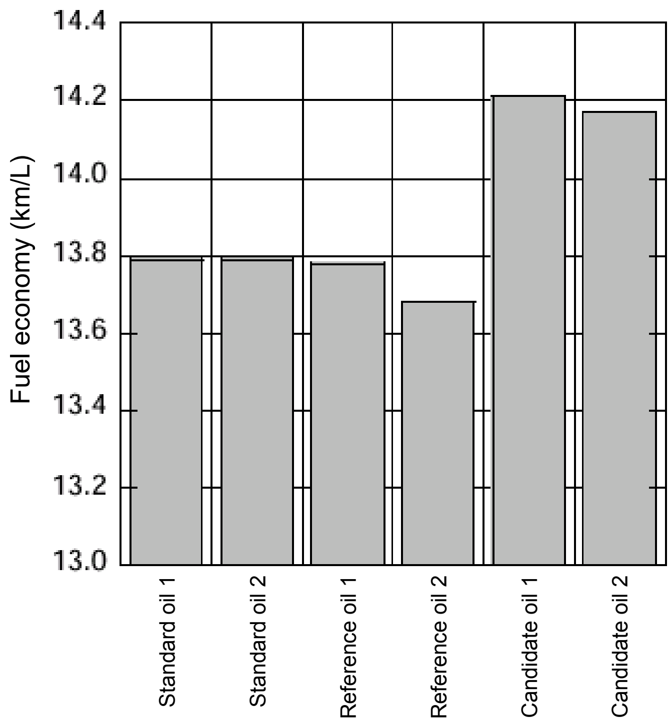

Figure 2.4-1 Chassis dyanmometer fuel economy results for candidate oil

3.1 Elucidation of reaction mechanisms of friction modifier and establishment of new analysis methods

For the first time in the world, synthesis of ZnDTP labeled compound, using ^{34}S isotope, was successful. Also successful was confirmation of assignment of surface sulfur, using TOF-SIMS for analysis of friction surface isotopes. It was thus indicated that in MoS_2 generation on friction surface, sulfur is supplied from other additives in the oil. From the findings thus obtained, it is suspected that the presence of a sulfur source in oil and the presence of Zn are crucial to the promotion of MoS_2 generation on friction surfaces. The catalytic reaction of sulfur supply by ZnS, generated on friction surface, is suggested as the reaction mechanism that bolsters the effectiveness of friction reduction by zinc compounds.

3.2 Establishment of fuel economy evaluation method by bench fuel economy tester

For fuel economy testing, a bench fuel economy tester was introduced; running conditions matching the objectives of our R&D were established, and the procedure was termed the five-point running test. Using each type of market oil, a favorable correlation with Sequence VI was confirmed through this test method, and fuel economy of candidate oil was evaluated.

3.3 Development of new friction modifier and proposal of lubricant oil for fuel economy improvement

Findings on the effects of zinc were actively used; an organic acid zinc additive was proposed to be used together with MoDTC for promoting the generation of MoS_2 on surfaces, and targeted improvements in fuel economy were reached.

A lubricant oil was candidate in which MoDTC, ZnDTP, sulfur supplier and a newly proposed organic zinc compound were combined, and ample effectiveness in improving fuel economy was demonstrated in five-point running test and in chassis dynamo commercial vehicle test.

3.4 Society publications and patent applications

The following society publications and patent applications were made, and results were publicized.

- **Impact of zinc compounds on MoS_2 generation:**
  Hiroyuki Iwasaki, Hirotaka Tomizawa
  November 1997
  Tribology Conference 97 Autumn (Osaka)
- **TOF-SIMS analysis of MoS_2 formed on friction surface, using ^{34}S labeled ZnDTP:**
  Hiroyuki Iwasaki
  October 1998
  Tribology Conference 99 Autumn (Takamatsu)
- **Joint PEC patent application [Lubrication System]:**
  Hiroyuki Iwasaki, Shigeko Taguchi, Hiroshi Nakanishi
  Application on July 13, 1998
  KOKAI number: patent disclosure 2000-026880

4. Synopsis

An attempt was made to elucidate the mechanism of MoS_2 generation on friction surfaces with lubricant oil to which an Mo-type friction modifier has been added. From the findings thus obtained, an organic zinc compound friction modifier was proposed as a coexistent additive for maximizing the effects of Mo-type additive, and improvements in fuel economy were verified. It is believed that through this research the following accomplishments were realized in series: determination of friction surface phenomena, elucidation for friction modifier reaction mechanisms, and development of new additives.

A newly proposed lubricant oil combined with organic zinc compound was candidate, and extensive improvement in fuel economy was demonstrated. Mo-type additive is currently used in high-performance lubricant oil, but indexes of coexistent additive combinations directed at even greater improvement in fuel economy were manifested, and application thereof can be expected. On the other hand, because attention was focused in the present R&D on improvement of initial fuel economy, there is room for further investigation of continuities. In the future, we want to see products developed in a setting where all the performances necessary for commercial application have been added in a balanced fashion.