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Analysis of Deposit Formation Mechanism on TEOST 33C by Engine Oil Containing MoDTC

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ABSTRACT

The addition of molybdenum dithiocarbamate (MoDTC) to engine oil improves the fuel consumption of vehicles. However, this is also widely known to cause deposit accretion in the Thermo-Oxidation Engine Oil Simulation Test (TEOST 33C). Thus the effects of additives on TEOST 33C and elemental analysis of the deposits were evaluated to analyze the deposit formation mechanism in TEOST 33C by engine oil containing MoDTC. An elemental analysis of deposits revealed that most consisted of carbide and contained small amounts of molybdenum compounds. Deposit accretion was not caused due to the remarkable increase of compounds derived from MoDTC. It was assumed that they acted as a decomposition catalyst under high temperature and induced carbide to be deposited.

INTRODUCTION

In recent years, the reduction of CO_2 emissions from automobiles has been strongly demanded according to the prevention of global warming. The efficiency of an engine is helpful in improving the fuel consumption of vehicles and many advanced engine technologies such as variable valve timing, direct injection, turbochargers and so forth, have been evaluated. While the turbocharger can increase the power and performance of vehicles without significantly increasing the size or weight, there is a problem whereby the engine oil which lubricates the turbocharger bearing is exposed to relatively high temperatures, especially in air-cooled turbochargers.[1, 2] Excessive oil degradation under high temperatures can cause deposit formation and lead to bearing failure in some turbochargers.[3]

The Thermo-Oxidation Engine Oil Simulation Test (TEOST 33C) was developed as a lubricant test for the evaluation of turbocharger-coking properties.[4, 5] This test was required for the International Lubricant Standardization and Approval Committee (ILSAC) GF-2 specification and is assumed to apply to ILSAC GF-5, the next gasoline engine oil specification.[6] In this test, a mass of deposits occurring on the test piece, called a depositor rod, when the test lubricant passes the depositor rod heated at 200 to 480°C, is evaluated.

The engine oil also plays an important role in improving the fuel consumption of vehicles. There are two methods which are widely accepted for improving the fuel efficiency performance of engine oil. One is lowering the viscosity of the lubricant and the other is an addition of friction modifiers. The addition of friction modifiers helps the engine oil to reduce engine friction under boundary lubrication. Among friction modifiers, molybdenum dithiocarbamates (MoDTC) is reported to be the most effective additive in decreasing engine friction and engine oil containing MoDTC shows high fuel efficiency properties.[7, 8] On the other hand, we examined the effects of MoDTC concentration on TEOST 33C and reported that the mass of deposits in TEOST 33C was significantly increased when accompanied with the addition of MoDTC.[9] Thus, there was a problem with fulfilling both fuel economy and TEOST 33C performance for engine oil containing MoDTC.

In this report, the analysis of the deposit formation mechanism on TEOST 33C by engine oil containing MoDTC was evaluated to estimate the possibility of having both fuel efficiency and acceptable turbocharger-coking properties.

EXPERIMENTAL

TEST OILS

Table 1 summarizes the properties of the test oils used in this study. The oil coded "HMO" was an American Petroleum Institute (API) SM/ILSAC GF-4 0W-20 oil containing MoDTC (Mo=700 ppm). It was prepared from a combination of Group III and Group IV base oil stocks and had ZnDTP with 800 ppm of phosphorus content. Other test oils were arranged by changing additive formulations of HMO. The MoDTC and zinc dithiophosphate (ZnDTP) treatment levels of LMO1 to LMO3 and LPO1 to LPO4 were adjusted respectively. TMO1 to TMO3 were formulated by replacing the MoDTC of HMO with other molybdenum compounds to the level of 500 ppm molybdenum content. These test oils were subjected to TEOST 33C.

Table 1 Test oil matrix

Name	Mo Content (ppm)	P Content (ppm)	Mo Type	TEOST 33C (mg)
HMO	700	800	MoDTC	73.5
LMO1	0	800	MoDTC	24.5
LMO2	350	800	MoDTC	33.5
LMO3	500	800	MoDTC	44.6
TMO1	500	800	Mo Amine	49.6
TMO2	500	800	MoDTP	45.2
TMO3	500	800	MoP	42.6
LPO1	700	0	MoDTC	25.2
LPO2	700	100	MoDTC	41.1
LPO3	700	200	MoDTC	57.3
LPO4	700	500	MoDTC	57.1

TEOST 33C

TEOST 33C was based on ASTM 6335.[4] The test conditions are summarized in Table 2. This test was repeated for 12 cycles, from a depositor rod temperature of 200°C to 480°C. (Figure 1) In this report, two modified tests were carried out in addition to the standard TEOST 33C. One was set to change the number of test cycles to evaluate the effect of test duration. The other was set to stabilize the temperature of the depositor rod for 24 minutes to estimate the effect of the depositor rod temperature as shown in Table 2.

Table 2 Test conditions for TEOST 33C

		TEOST 33C	Mod. 1	Mod. 2
Sample Volume	mL	116	116	116
Catalyst (Fe)	ppm	100	100	100
Reactor Temp.	°C	100	100	100
Depositor Rod Temp.	°C	200-480	200-480	400, 440, 480
Test Cycle		12	3, 6	1
Test Duration	min	114	28.5, 57	24
Pump Rate	g/min	0.4	0.4	0.4
Wet Air Flow	mL/min	3.5	3.5	3.5
N2O	mL/min	3.5	3.5	3.5

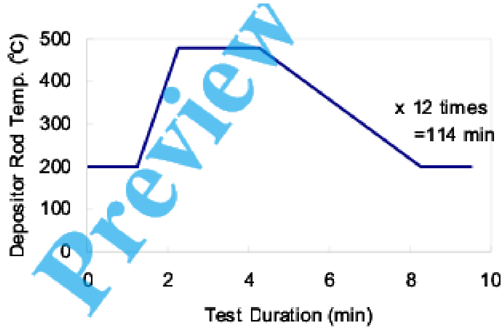

Figure 1 Depositor rod temperature cycle for TEOST 33C

RESULTS AND DISCUSSION

ANALYSIS OF DEPOSIT FORMATION FACTORS

Effects of engine oil additives

The test results for HMO and LMO1 to LMO3 showed the relationship between MoDTC concentration and the mass of deposits in TEOST 33C.[9] (Figure 2) The mass of deposits increased along with increases in the addition of MoDTC. In particular, with more than 350 ppm of molybdenum content, the addition of MoDTC permitted a significant increase in deposit formation.

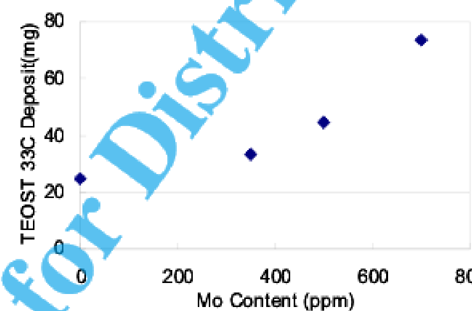

Figure 2 Effects of MoDTC content on TEOST 33C

The effects of molybdenum type on TEOST 33C is detailed in Figure 3. In Figure 3, all test oils contained 500 ppm of molybdenum content. The type of molybdenum compounds for LMO3, TMO1, TMO2 and TMO3 were MoDTC, molybdenum amine complex, molybdenum dithiophosphate (MoDTP) and molybdenum phosphorus complex, respectively. All of these provided the same level of deposit formation regardless of the molybdenum compound type. This revealed that high concentrations of molybdenum compounds induced deposit accretion in TEOST 33C in spite of their complex structure.

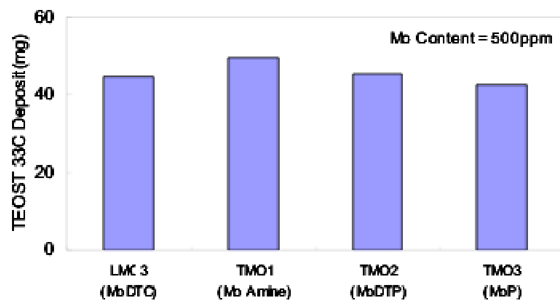

Figure 3 Effects of Mo type on TEOST 33C

The relationship between ZnDTP content and the mass of deposits in TEOST 33C was determined through the test results for HMO and LPO1 to LPO4. (Figure 4) A reduction of ZnDTP caused the suppression of deposit formation. In particular, deposit formation was significantly suppressed with less than 200 ppm of phosphorus content, even if the test oil contained a high concentration of MoDTC. It was suggested that the coexistence of MoDTC and ZnDTP would lead to an increase in deposit formation on TEOST 33C.

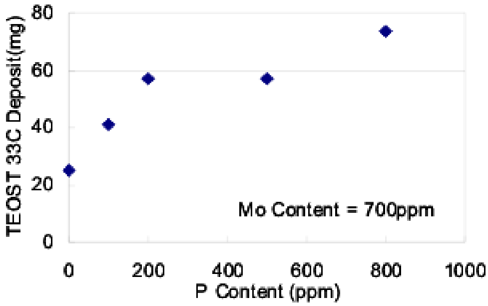

Figure 4 Effects of ZnDTP content on TEOST 33C

Engine oil containing MoDTC and no ZnDTP was able to satisfy appropriate TEOST 33C properties. However, a deterioration of antiwear performance was apprehended due to the lack of ZnDTP.[10] In addition, it was generally accepted that the low friction property mechanism of MoDTC forms a molybdenum disulfide (MoS_2) layer under boundary lubrication.[11, 12] In forming MoS_2 single sheets, ZnDTP and other sulfurized compounds played a significant role as a sulfur source for MoS_2. Engine oil without ZnDTP could not maintain the low friction properties of MoDTC during mileage accumulation. The addition of ZnDTP was essential for low friction retention and oil without ZnDTP was not able to fulfill both fuel consumption and TEOST 33C performances.

Effects of test temperature

The depositor rod temperature of TEOST 33C was set to 200 to 480°C. The maximum temperature simulated a very hot turbocharger impeller shaft.[5] The HMO was subjected to TEOST 33C for which the depositor rod temperature was set to a stable condition from 400°C to 480°C for 24 minutes in order to evaluate the effects of the test temperature. The test results are shown in Figure 5.

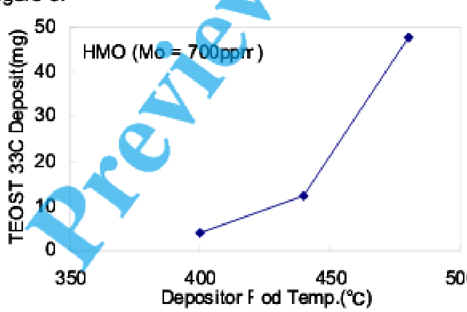

Figure 5 Effects of Depositor Rod Temperature on TEOST 33C

When HMO was applied to the modified TEOST 33C with a temperature of 480°C, the HMO caused a substantial amount of deposit (47.8 mg), although this was not as much as standard test with 73.5 mg. However, the deposit formation was remarkably reduced when the depositor temperature was set to a stable temperature below 440°C. These results indicated that the high temperature test condition such as 480°C promoted deposit accretion by engine oil containing MoDTC in TEOST 33C. As previously described, the coexistence of MoDTC and ZnDTP was suggested to lead to an increase in deposit formation on TEOST 33C. They were reported to be thermally decomposed at below 400°C.[13,14] It was revealed that thermal decomposition of MoDTC and ZnDTP would not influence deposit accretion in TEOST 33C.

ELEMENTAL ANALYSIS OF DEPOSITS

After TEOST 33C, the deposit was collected from the depositor rod and then subjected to CHN-O analysis, fluorescent X-ray analysis and XPS to estimate the deposit formation mechanism. Figure 6 showed the elemental analysis results of the deposit from HMO, LPO1 and LPO4. In all test oils, 40 to 50% of the deposit was comprised of C, H, N, O and the remainder were elements derived from engine oil additives and ferric naphtenate which was used as a catalyst. The elemental analysis also suggested that the ratio of C, H, N, O in the deposit increased along with the deposit accretion.

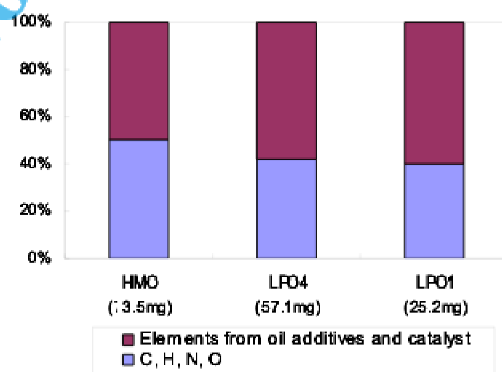

Figure 6 Elemental analysis of deposit

The detailed elemental analysis results for the deposit are described in Figure 7-9. Figure 10-12 shows the elemental composition of each fresh oil. In comparison with the elemental composition of fresh oil, elemental analysis of the deposit indicated that Ca would be deposited more easily than other elements derived from oil additives. Though coexistence of MoDTC and ZnDTP induced deposit accretion, elements such as Mo, Zn and P derived from MoDTC and ZnDTP did not accumulate in the deposit in excessive amounts. The deposits of HMO, LPO1 and LPO4 presented similar Mo contents in spite of the deposit mass, and the ratio of Mo, Zn and P to elements from oil additives was at almost the same level as that in fresh oil. XPS analysis indicated that most of the Mo in the HMO deposit existed as MoS_2 and molybdenum trioxide (MoO_3). This revealed that deposit accretion by adding MoDTC was not caused due to a remarkable increase in molybdenum compounds in the deposit. The addition of MoDTC to engine oil was assumed to accelerate deposit accretion by accumulating carbide in the deposit.

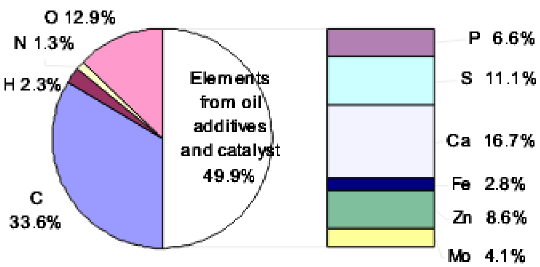

Figure 7 Elemental analysis of deposit by HMO (73.5mg, P=800ppm)

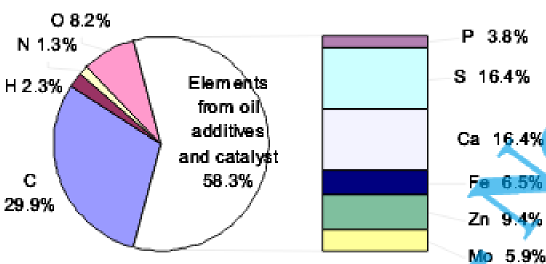

Figure 8 Elemental analysis of deposit by LPO4 (57.1mg, P=500ppm)

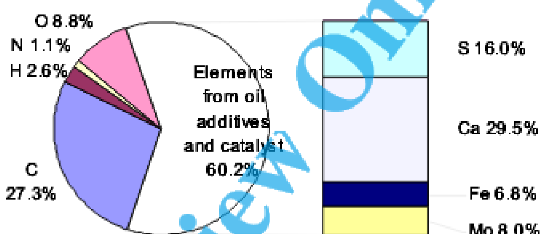

Figure 9 Elemental analysis of deposit by LPO1 (25.2mg, P=0ppm)

Though it was assumed that oxidative degradation of test oils caused the deposit of carbide, little change was seen in the neutralization numbers of HMO after TEOST 33C. (Table 3) Meanwhile, molybdenum compounds were widely accepted to have a catalytic effect. It was supposed that reactants of MoDTC and ZnDTP acted as a decomposed catalyst to induce deposit accretion. This idea was supported by the results of a modified TEOST 33C. As previously described, a stable depositor rod temperature test showed that deposits were significantly increased by the addition of MoDTC only when the depositor rod temperature was set to 480°C. (Figure 5) The results of a test with a varying number of cycles also confirmed the behavior of Mo compounds as a catalyst. (Figure 13)

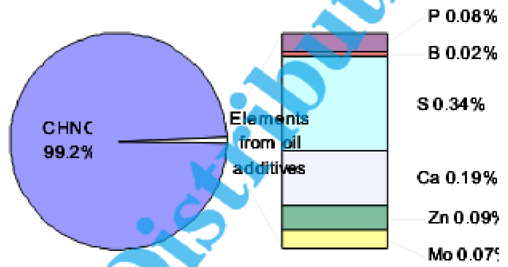

Figure 10 Elemental composition of HMO

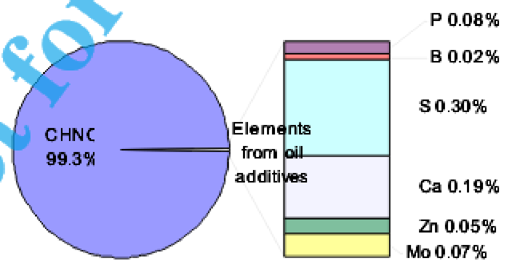

Figure 11 Elemental composition of LPO4

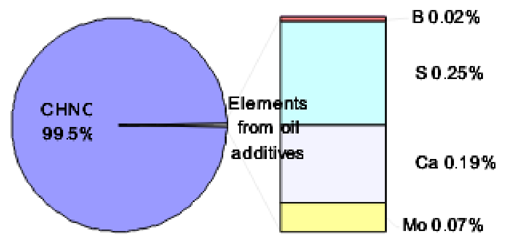

Figure 12 Elemental composition of LPO1

Table 3 Changes in the neutralization numbers in HMO

		Fresh Oil	After TEOST 33C
Acid number	mgKOH/g	2.13	1.59
Base Number (HCl)	mgKOH/g	5.86	4.66
Base Number ($HClO_4$)	mgKOH/g	6.54	6.44

In LMO1 which contained no MoDTC, an increased ratio of deposit mass was reduced with an increase in test cycles. In contrast, the deposit mass of HMO was increased with an increase in test cycles. The mass of each element in the HMO deposit in tests of both 6 and 12 cycles was calculated based on elemental analysis. (Figure 14) The mass of elements with the exception of C and O for the 12 cycle test was twice as much as that of the 6 cycle test. The mass of C and O for the 12 cycle test was significantly increased compared with that of the 6 cycle test. This suggested that the increase resulted in deposit accretion by engine oil containing MoDTC. This result coincided with the result that indicated the ratio of C and O in deposits was increased with deposit accretion. Thus, it was assumed that the reactant of molybdenum compounds and ZnDTP induced the oxidization or decomposition of engine oil under high temperatures such as 480°C and led to increased deposit formation by inducing deposits of carbide in engine oil containing MoDTC.

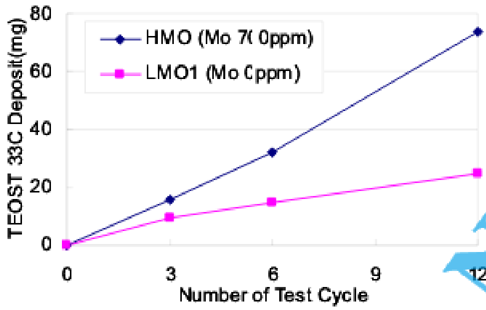

Figure 13 Effects of the number of test cycles

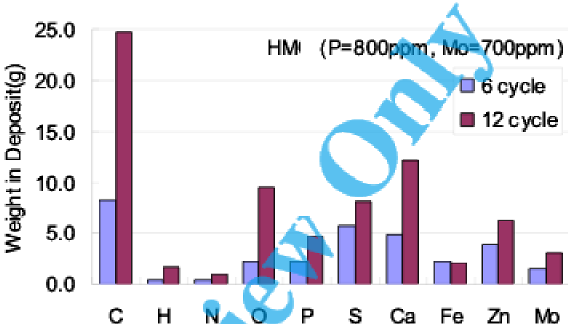

Figure 14 Calculated value of elemental mass in 6 and 12 cycle tests

CONCLUSION

In this report, the analysis of the effects of engine oil additives and deposit composition was evaluated in order to analyze the deposit formation mechanism in TEOST 33C by engine oil containing MoDTC. The conclusion is as follows.

- The addition of molybdenum compound and ZnDTP I caused remarkable deposit accretion in TEOST 33C.
- Engine oil containing MoDTC induced deposit formation under high temperatures such as 480°C.
- Approximately half the deposit was comprised of carbide and compounds derived from MoDTC; ZnDTP did not accumulate in deposits in excessive amounts.
- The ratio of C and O increased along with deposit accretion.
- The ratio of deposit accretion increased with an increase in test duration for engine oil containing MoDTC. C and O were especially induced to be deposited.

These results indicated that the reactants of molybdenum compounds and ZnDTP induced the oxidization or decomposition of engine oil under high temperatures such as 480°C and led to increased deposit formation by inducing carbide to be deposited in engine oil containing MoDTC. Meanwhile MoDTC and ZnDTP were essential for fuel efficiency properties. In ILSAC GF-4 specification oils, no engine oil with more than 500 ppm of molybdenum has been confirmed to show relatively good TEOST 33C performance (less than 25 mg of deposits[6]), which does not necessary mean they cause deposit formation and lead to bearing failure in turbochargers.

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