Soft Semi-Solid Deposit Formation of Lubricating Oil at Lower Temperatures below 200°C

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(Manuscript received 10 January 2014; accepted 3 June 2014; published 15 July 2014)

In the compressor housing of a turbocharger with oil mist atmosphere, soft semi-solid deposit could be observed even at the lower temperatures below 200°C. Sticky or hard deposit at higher temperatures above 300°C is well-known, which can be demonstrated by standard test such as the Panel Coker Test. However, the semi-solid deposit formation has not been reported and understood. In this research, the deposit in the compressor housing was analyzed and the formation mechanism was presumed basing on the composition of the deposit. To validate the presumption, the deposit formation was demonstrated using newly designed test method. Furthermore, the dependence of conditions on the formation and the countermeasure to prevent from deposit formation are also considered.

Keywords: deposit, low temperature, oil, oxidation, turbocharger

1. Introduction

The deposit is one of major problems in oil lubrication at higher temperatures above 300°C. The problems are common for variety of machines such as turbocharger [1,2], diesel engine for marine [3], aero engine [4-8] and gas turbine for power generation [9]. Deposits, are named “high-temperature oil deposit” have variety of appearance and origin, and are adhesive or hard. It cannot be removed easily. Such deposit is due to the remarkable thermo-oxidation reaction of oils on hot metal surfaces, and can be demonstrated by the Panel Coker Test conforming to FED TEST METHOD STD No.791 Method 346 and other methods developed [10-12]. It can be controlled by selecting proper oils with high thermo-oxidation stability and reducing the metal surface temperature [13-18].

On the other hand, at relatively low temperatures below 200°C, deposits, are named “low-temperature oil deposit”, may form on the compressor housing of a turbocharger with oil mist atmosphere. It can be observed under very severe conditions such as endurance engine bench tests. It is easily removable, because it is non-adhesive semi-solid and relatively softer than those on the turbine side.

The turbocharger is a key accessory for automobile engines. The turbine wheel captures hot exhaust gas from

the engine to generate rotational force for the compressor, which helps boost engine efficiency and performance. The turbine side of the bearing housing is heated by exhaust gas to a high temperature, with the oil line surface inside the bearing housing rising to around 300°C, or more during heat soak due to the engine stopping. Such high temperatures could cause the high-temperature oil deposit to form inside the oil line and possibly block it. Conversely, although the compressor side is cooler than the turbine side, other types of deposits, the low-temperature oil deposit, may form on the housing surface there under specific severe conditions. On the compressor side, oil mist enters the suction air pass with blow-by gas from the crankcase and oil pan when the crankcase ventilation system is used and could cause the low-temperature oil deposit to form.

In terms of turbocharger, it has been requested to avoid both types of deposit. However, as mentioned, lots of studies have been made about the high-temperature oil deposit, but little studies about the low-temperature oil deposit were made. Therefore, the consideration of the formation mechanism and the demonstration were focused on in this study.

In this research, the low-temperature oil deposit was analysed to make sure of the formation mechanism and an experimental deposit formation method is considered. Furthermore, the dependence of atmosphere, such as

Table 1 Conditions of TG-DTA

Carrier gas	200 cm ³ /min (Ar: 80%, O ₂ : 20%)
Temperature increase rate (/min)	20
Temperature range (°C)	Room temperature - 900
Pressure	Atmosphere

Fig. 1 Example of TG-DTA curve

temperature and oxygen pressure, coating of metal and lubrication oil was evaluated using the proposed experimental deposit formation method.

2. Experimental

2.1. Analysis of deposits

Two kinds of engine deposits, both high-temperature oil deposit and low-temperature oil deposit, were collected from the turbochargers used in actual service and analysed as follows. The high-temperature oil deposit which was made by panel coker test was also analysed for reference.

Deposits were subject to organic element analysis (CHNO analysis) and X-Ray Fluorescence spectrometry (XRF). CHNO analysis can analyse concentrations of C, H, N and O elements, while other inorganic elements are residues. XRF can provide the semi-quantitative analysis of inorganic elements. In addition, Thermogravimetry - Differential Thermal Analysis (TG-DTA) was conducted to estimate the composition of the deposits. Table 1 shows the test conditions for TG-DTA, while Fig. 1 shows the TG-DTA typical curve. As the temperature escalates within the range of Room temperature-900°C, the deposit loses gravity due to reactions such as evaporation, oil oxidation, carbonization and carbon oxidation. The gravity loss corresponding to each reaction indicates the amount of fractions contained, such as low molecular weight fraction, oil fraction, high molecular weight fraction including oxidized product

fractions, namely sludge, carbon fraction and residues as shown in Fig. 1 [19-23].

2.2. Experimental method for demonstrating low-temperature oil deposit formation

2.2.1 Method of test

Modified rotary pressure vessel oxidation test conforming to ASTM- D-2272, as shown in Fig. 2, was used for demonstrating low-temperature oil deposit formation. This method can enable the key conditions under which low-temperature deposits form; the enclosing oxygen accelerates the engine oil oxidation, while rotation causes a thin film of oil to form on the test beaker surface in the vessel and the temperature is controlled by a thermostatic bath. Table 2 shows the test conditions. Some conditions such as temperature and oxygen pressure were changed in order to understand the dependence of the atmosphere on the deposit formation.

2.2.2 Test oils

Fresh commercial engine oil and degraded used commercial engine oil collected from a passenger car were evaluated. Both engine oils are 0W20 viscosity grade lubricating oils which are generally used by low-fuel-consumption specification. Degradation of lubricating oil is not avoided during operation in actual services, and the deposit characteristic may change with degradation [24-27]. Therein, degraded oil was also evaluated.

Table 2 Test conditions

Gas in test vessel	Oxygen
Gas pressure in test vessel (MPa)	0.2-0.6
Temperature (°C)	140-180
Rotation of test vessel (rpm)	100
Oil amount (g)	1
Duration time (hours)	24

Fig. 2 Evaluation test method for low-temperature deposit

3. Results

3.1. Deposit composition

Figure 3 shows the element content of deposits which indicate the atomic ratio. In terms of high-temperature oil deposit, engine deposits collected from the turbochargers in actual service and deposit made by panel coker test, have similar composition. On the other hand, the low-temperature oil deposit has different composition from high-temperature oil deposit.

High-temperature oil deposits included inorganic residues much, primarily composed of Ca, Zn, P, and S and possibly originating from engine oil additives. Conversely, the low-temperature oil deposit has smaller residues than high-temperature oil deposit, also primarily composed of Ca, Zn, P, and S. In addition, the CHO content differs between high- and low-temperature oil deposits. High-temperature oil deposit has relatively higher levels of oxygen, which mean they are caused by remarkable oxidation and composed of fewer organic compounds. Conversely, low-temperature oil deposit is composed of high levels of organic compounds.

Figure 4 shows the deposit content obtained from the TG-DTA results, which indicate the weight ratio of each ingredient such as low molecular weight fraction, oil

Fig. 3 Element content of deposits

Fig. 4 Fraction of deposits

fraction, high molecular weight fraction, carbon fraction and residues. It was confirmed that low-temperature oil deposit comprises much of organic fractions, including oil fraction and high molecular weight fraction, while the high-temperature deposits comprised around 70% of residues and carbon. From this result, it was confirmed that there is little inorganic residues in low-temperature oil deposit, and there is inorganic residues in high-temperature oil deposit so much. Usual grease contained of about 20% solid composites in order to make fluid oil into the semisolid. The low-temperature oil deposit has also 20% solid composites including carbon and inorganic residue. Therein the low-temperature oil deposit has distinctive feature of being non-adhesive semi-solid and relatively soft like grease.

Analytical results indicate some differences between high- and low-temperature deposits as mentioned. The condition of the turbocharger suction air pass means engine oil mist comes into the compressor airflow with blow-by gas and forms a thin film on the compressor housing surface. Additionally, the partial pressure of the oxygen in the suction air exceeds the atmospheric level because the suction air is compressed. Since these conditions facilitate oxidation reactions, engine oil can be oxidized rapidly, hence oxidized products easily form on the compressor housing surface even at lower temperatures below 200°C.

Fig. 5 Dependence of temperature on deposit formation (Post-oil in evaluation test for low-temperature oil deposit, 0W20)

3.2. Demonstration of low-temperature oil deposit formation

Figure 5 shows the results of deposits as demonstrated under three temperature conditions at the oxygen pressure of 0.6 MPa. Appearance of oils was changed with temperature and both of fresh oil and degraded used oil turned into semisolid resembling actual deposits at the temperature of 180°C. At the temperatures below 160°C, oils after tests were still liquid, even if the glass container was leaned. In addition, there is little difference of temperature

conditions in which remarkable semisolid-ization advances between fresh oil and degraded used oil. The analytical results of deposits, which were estimated by TG-DTA, are shown in Fig. 6. It can be seen that the oil tested in 180°C which obvious semisolid-ization generated have little inorganic residue and comprise much of organic fractions. And they have high molecular weight fraction and carbon much. In endurance engine bench tests, it is actually 180°C that obvious soft semi-solid deposit can be observed. Accordingly, it is can be seen that this method devised newly is appropriate for

Fig. 6 Dependence of temperature on deposit formation (Fraction of Post-oil in evaluation test for low-temperature oil deposit, 0W20)

Fig. 7 Dependence of oxygen pressure on deposit formation (Post-oil in evaluation test for low-temperature oil deposit, 0W20)

demonstrating the low-temperature oil deposit which forms on the compressor side of turbocharger.

The results of deposits which were evaluated under three oxygen pressure conditions at the temperature of 180°C, furthermore, are shown in Fig. 7. Appearance of oils was changed with oxygen pressure. Semi-solid deposits resembling actual deposits were observed at 0.6 MPa for fresh oil and at 0.4 MPa for degraded used oil. The degraded used oil can lead to the deposit formation under lower oxygen pressure than fresh oil.

The analytical results of deposits, which were estimated by TG-DTA, are shown in Fig. 8. The post-oils

which obvious semisolid-ization generated have high molecular weight fraction and carbon much. Considering that degraded used tends to form deposit easily, it might be due to the difference of compositions between fresh oil and degraded used oil. The degraded used oil for tests contains high molecule composition a lot.

4. Discussions

Fraction analyses of deposit were carried out using TG-DTA as mentioned. The results can indicate the feature of deposit and could use not only for external observation but for the quantitative evaluation of deposit

Fig. 8 Dependence of oxygen pressure on deposit formation (Fraction of Post-oil in evaluation test for low-temperature oil deposit, 0W20)

Fig. 9 Dependence of oxygen pressure on deposit formation (Solidification index in evaluation test for low-temperature oil deposit, 0W20)

Fig. 10 Dependence of temperature on deposit formation (Solidification index in evaluation test for low-temperature oil deposit, 0W20)

formation. The feature of low-temperature oil deposit is significant fractions of high molecular weight fraction and carbon. Focusing on these contents, the deposit formation can be evaluated quantitatively. A new factor 'Solidification index (Deposit index)' was considered, which was defined by formula (1). In this formula, though it was small, the inorganic residue which is a solid was also put in, and the ratio with oil with fluidity was considered. However, since the low molecular components are easy to be evaporated in actual condition, it was not put into the formula.

Solidification index (Deposit index)

$$= \frac{\text{High MW} + \text{Carbon} + \text{Residue}}{\text{Oil} + \text{High MW} + \text{Carbon} + \text{Residue}} \quad (1)$$

The quantitative analytical results of deposits are shown in Figs. 9 and 10. In these figures, the value calculated from the fraction of oils before tests were also added. As the degraded used oil for tests contains high molecule composition a lot, the index of the degraded used oil for tests is higher than fresh oil for tests. In these figures, it can be seen that indexes of post-oils of which

Fig. 11 Dependence of coatings on deposit formation (Post-oil in evaluation test for low-temperature oil deposit, 10W30)

Fig. 12 Dependence of coatings on deposit formation (Fraction of Post-oil in evaluation test for low-temperature oil deposit, 10W30)

remarkable semisolid-ization was observed are higher. The change in state of oils with temperatures and oxygen pressures can be expressed quantitatively by deposit index. Considering reaction rate, temperature is a multiplier of a reaction rate constant and that of oxygen concentration corresponds to oxygen pressure is a constant. Therefore, the influence of temperature is exponential and oxygen concentration is direct proportion-like. Although it was hard to consider whether influence of which of temperature and oxygen pressure is significant, in the range supposing the actual system of conditions, the results that the influence of oxygen pressure is relatively than temperature significant was brought.

In the compressor housing of a turbocharger with oil mist atmosphere, which forms a thin film on the metal surface, low-temperature oil deposit formation is thought

Fig. 13 Dependence of coatings on deposit formation (Solidification index in evaluation test for low-temperature oil deposit, 10W30)

to be promoted by the rapid oxidation under the condition of high oxygen pressure. In order to find the solution which control the deposit lower, fitting coatings on the metal and oil formulations can be possible candidates. The aim is in the minimization of inhibiting oxidation reaction and the amount of oil on metal surface. The optimal coatings can be expected the decrease of the reaction rate and the oil repellent. The optimization of oil formulations also can lead to decrease the reaction rate.

At first, the dependency of some coating on the deposit reduction was evaluated. The coatings which could be potential were used. They compose of the nickel which cannot generate carbide easily and repellent PTFEs having different content. In terms of test method, the test which was used for the demonstration of deposit formation, in the modified rotary pressure vessel oxidation, though glass test container is usually used so far, the steel test container used for evaluation of coating

effect on the deposit formation. It is the reason that the test specimen for evaluation is the steel disk which coating can form. The disk specimen was installed in the bottom of test container and was checked the appearance of oils, if deposit forms or not, for evaluations. In addition, the deposit index was evaluated using the fraction data of oil on the disk. The index can help in understanding the effect verification, but cannot indicate the amount of deposit. It just can indicate the reactivity.

Tests were carried out at 180°C with oxygen pressure of 0.6 MPa, using 10W30 commercial engine oils. The results are shown in Figs. 11, 12 and 13. It can be seen that Ni-P PTFE coating can lead to the decrease of deposit on the whole. However, coating with higher content of PTFE had few inhibiting effects to the semisolid-ized propagation by oxidation reaction. Nickel content ratio becomes smaller with the increase in a PTFE content ratio, and the reaction inhibiting effect might be decreased.

In addition, though tests, it was observed that the propagation of semisolid-izing with steel test container becomes quick rather than with glass test container. It might be due to the catalytic effect of the oxidation reaction by steel.

Subsequently, the dependency of oil formulations was evaluated using nine sorts of trial engine oil. Oil-A is standard formulated engine oil of 5W30 with sec-ZnDTP and mixture of detergents, which is standard oil for formulations as follows. Oil-B is the oil changed the antioxidant to prim-ZnDTP. Oil-C includes double content of sec-ZnDTP. Oil-D is the oil without viscosity index improver (VII). Oil-E is the oil changed the base oil to volatile base oil. Oil-F is the oil changed the base oil to the base oil which cannot volatilize easily. Oils-G, H, I have different type of detergents.

Fig. 14 Dependence of lubricants on deposit formation (Fraction of Post-oil in evaluation test for low-temperature oil deposit, 5W30)

Fig. 15 Dependence of lubricants on deposit formation (Solidification index in evaluation test for low-temperature oil deposit, 5W30)

Figures 14, 15 show the results of tests carried out at 180°C with oxygen pressure of 0.6 MPa. Trend of the effect of formulation of oil on deposit formation can be obtained. Lower volatile oils can lead to small deposit. The change of anti-oxidant from sec-ZnDTP to prim-ZnDTP as well as redoubling of sec-ZnDTP can affect the decrease in deposit. The effect of VII is small. Salicylate type of detergent is effective rather than other type of detergents.

Accordingly, optimal coating and oil formulation can reduce the deposit. However, in terms of oil formulation, even if it reduces low-temperature oil deposit, high-temperature oil deposit may increase conversely, and careful consideration including other characteristics besides deposit required [28,29].

5. Conclusions

The deposit in the compressor housing was analyzed and the formation mechanism was presumed basing on the composition of the deposit. To validate the presumption, the deposit formation was demonstrated using newly designed test method. Furthermore, the dependence of conditions on the formation and the countermeasure to prevent from deposit formation are also considered. As a result, followings were drawn.

- (1) Organic fractions, including oil fraction and high molecular weight fraction, form much of the so-called “low-temperature oil deposit” formed at relatively low temperatures below 200°C, while so-called “high-temperature oil deposit”, formed on high-temperature surfaces, mainly comprise residues.
- (2) Using a modified rotary pressure vessel oxidation test, which replicates actual conditions, low-temperature oil deposit formation can be demonstrated. Low-temperature oil deposit can be formed under conditions favouring oxidation

reactions.

- (3) Low-temperature deposits comprise significant high molecular weight fraction and carbon. Although oils were not seen to transform from a liquid to a soft semi-solid state, a “deposit index”, capable of quantitatively evaluating low-temperature oil deposit formation, was proposed.
- (4) The atmosphere conditions such as temperature and oxygen pressure affect the deposit formations.
- (5) Coating and oil formulation can lead to decrease in the oxidation reaction of oil and the deposit formation.

Acknowledgements

The authors are grateful to IDEMITSU KOSAN for providing some sample oils for evaluations and valuable discussions.

References

- [1] Diaby, M., Sablier, M., Le Negrate, A., El Fassi, M. and Bocquet, J., “Understanding Carbonaceous Deposit Formation Resulting from Engine Oil Degradation,” *Carbon*, 47, 2, 2009, 355-366.
- [2] Keller, J. A., Lowther, H. V. and Rogers, T. W., “Lubricant Performance in Passenger Car Turbochargers,” *SAE Technical Paper*, 1981, 810016.
- [3] Dong, L., Liang, X. and Shu, G., “The Influence of Lubricating Oil on Deposits Formation in a Diesel Engine under the Operation Condition of High Power Density,” *Lubrication Science*, 25, 7, 2013, 441-451.
- [4] Edge, R. G. and Squires, A. T. B. P., “Lubricant Evaluation and Systems Design for Aircraft Gas Turbine Engines,” *SAE Technical Paper*, 1969, 690424, 1-21.
- [5] Siouris, S., Shepherd, T., Wilson, C. and Blakey, S., “Development of an Apparatus for the Degradation of Aviation Gas Turbine Lubricants,” *Tribology Transactions*, 56, 2, 2013, 215-223.
- [6] Dohaty, B. W., “Aircraft Fuels, Lubricants and Fire Safety,” *Advisory Group for Aerospace Research and Development Paris*, August, 1971, AD-729-570.
- [7] Yokoyama, F., “Evaluation of Thermal and Oxidation Stability for Gas Turbine Lubricants under High Temperature,” *Proceedings of International Tribology Conference*, Yokohama Japan, 1995.
- [8] Blenkiron, T. and Sawyer, W. J., “Lubrication of the Olympus 593 engine,” *SAE Technical Paper*, 1968, 680318.
- [9] Dowse, D. G., Janstan, E. and Maier, K., “Deposition in Gas Turbine Oil Systems - Part1: Analysis and Classification,” *SAE Technical Paper*, 1985, 851869, 115-131.

- [10] Kawaguchi, M., Isoda, T., Tamai, K. and Takezawa, Y., "Development of a Laboratory Bench Detergency-Dispergence Test for Automobile Crankcase Lubricants and Its Application to the Lubricating Oil Technology," Proceedings of the JSLE-ASLE International Lubrication Conference, Elsevier, Amsterdam, 1976, 758-766.
- [11] Chao, K. K. and Saba, C. S., "Tribo-Evaluation of High Temperature Candidate Fluids in a Sliding "TBOD" Bench Tester," Tribology Transactions, 38, 1, 1995, 63-68.
- [12] Dyer, W. G., Slater, B. B. and Witt, D. G., "Lubrication of Turbocharged Passenger Car Engines," SAE Technical Paper, 1985, 852177, 19-29.
- [13] Klaus, E. E., "Thin Film Deposition Behavior of Lubricants as a Function of Temperature: Lubricant Stability Maps," Lubrication Engineering, 48, 7, 1992, 599-605.
- [14] Gunsel, S., Klaus, E. E. and Duda, J. L., "High Temperature Deposition Characteristics of Mineral Oil and Synthetic Lubricant Basestocks," Lubrication Engineering, 44, 8, 1988, 703-708.
- [15] Gunsel, S., Klaus, E. E. and Duda, J. L., "High Temperature Deposition Characteristics of Mineral Oil and Synthetic Lubricant Basestocks," ASLE Preprint Presented ASLE/ASME Tribology Conference (American Society of Lubrication Engineers), 1987, 87-TC-3B-3, 1-6.
- [16] Kagaya, M. and Ishikawa, S., "An Evaluation and Optimization of Lubricants for Turbocharged Gasoline Engines," SAE Technical Paper, 1984, 840261.
- [17] Burrows, A. L., "Optimized Lubricants for Turbocharged Passenger Car Engines," SAE Technical Paper, 1981, 811227.
- [18] Yoshida, S. and Naitoh, Y., "Analysis of Deposit Formation Mechanism on TEOST 33C by Engine Oil Containing MoDTC," SAE Technical Paper, 2008, 2008-01-2480.
- [19] Covitch, M. J., Gundic D. T. and Graf, R. T., "Microstructure of Carbonaceous Diesel Engine Piston Deposits," Lubrication Engineering, 44, 2, 1988, 128-138.
- [20] Mitsumoto, S., Mitamoto, T. and Yamamoto, H., "Effect of Lubricant Viscosity, Additives and Ash Content on Durability in a Heavy Duty Engine," SAE Technical Paper, 1989, 892050.
- [21] Teixeira, M. A. G. and Goncalves, M. L. A., "The Combination of Thermal Analysis and Supercritical Extraction as a Tool for the Characterization of Mixed Deposits and Sludges," Journal of Petroleum Science and Engineering, 32, 2-4, 2001, 249-255.
- [22] Husnawan, M., Masjuki, H. H., Mahlia, T. M. I. and Saifullah, M. G., "Thermal Analysis of Cylinder Head Carbon Deposits from Single Cylinder Diesel Engine Fueled by Palm Oil-Diesel Fuel Emulsions," Applied Energy, 86, 10, 2009, 2107-2113.
- [23] Retief, E., Taylor, A., Strachan, P. and Homayoun, M., "Oil Degradation in Light Commercial Vehicles," SAMEA, The South African Mechanical Engineer, 49, 11, 1999, 27-29.
- [24] "The Long Road Ahead. Extending Drain Intervals Promises Miles of Trouble-Free Motoring. But Formulating the Lubricants is not as Simple as It May Seem.," Lubrication Engineering, 56, 11, 2000, 14-16.
- [25] Dennis, A. J., Garner, C. P. and Taylor, D. H. C., "The Effect of EGR on Diesel Engine Wear," SAE Technical Paper, 1999, 1999-01-0839.
- [26] Iwakata, K., Onodera, Y., Chikugo, K., Mihara, K. and Ookawa, S., "Deterioration of Oil in Heavy-Duty Diesel Engine," Komatsu Technical Report, 38, 1, 1992, 30-39 (in Japanese).
- [27] Bijwe, J., Garg, A. and Gandhi, O. P., "Reassessment of Engine Oil Periodicity in Commercial Vehicles," Lubrication Engineering, 56, 1, 2000, 23-29.
- [28] Smolenski, D., "Component Performance in Engine Oil Formulation," Tribology and Lubrication Technology, October, 2013, 34-41.
- [29] Kasrai, M., Cutler, J. N., Gore, K., Canning, G., Bancroft, G. M. and Tan, K. H., "The Chemistry of Anti-Wear Films Generated by the Combination of ZDDP and MoDTC Examined by X-ray Absorption Spectroscopy," The Society of Tribologists and Lubrication Engineers: Technical Preprints, World Tribology Congress London, 1997, 60-68.