Mechanism of Carbonaceous Deposit Formation Caused by Lubricating Oil on High Temperature Metal Surfaces

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While formation of deposits in machinery used under high temperature conditions is inevitable, it needs to be minimized as much as possible. Desorption of deposits, though rarely reported, also needs to be addressed, as it could cause secondary damage. There have been a number of reports on the formation of high-temperature deposits and the effects of additives, none of which, however, addresses the desorption phenomenon as part of the deposit formation mechanism. Paying attention to the polar properties of lubricating oils and evaluating the formation, dissolution, and desorption of deposits by lubricating oils, the formation mechanism of high-temperature deposits was considered. Taking notice also of the changes in polar characteristics of oils with the progress of oxidative degradation of oil, we examined the influence of oxidative degradation of oils on the tendency to form high-temperature deposits. Furthermore, the countermeasure to prevent from deposit formation is also considered.

Keywords: lubricant, deposit, formation, desorption, high temperature

1. Introduction

Since lubricating oils have lower viscosity when used in high-temperature environment, their lubricating performance on gears, bearings, and other parts of the machinery needs to be sustained to ensure mechanical integrity. It is also important to consider the influence of oxidative degradation of oils on the service life of machinery, as well as various other effects caused by degeneration of oils. Deposits formed by the contact of oil with heated metal surfaces above 300°C are called high-temperature deposits, the occurrences of which in automotive superchargers and diesel engines [1-5], as well as in gas turbines in aircraft engines, etc. [6-11], have been reported. Various test methods have also been developed, some of which have become standards [12,13] while others have proposed original methods by simulating the actual operating conditions of machinery [14-18]. While formation of high-temperature deposits is inevitable, it needs to be minimized, as excessive deposits could clog oil passages, etc. leading to lubrication failure. Among the methods proposed to reduce deposits, use of optimal additives [19-24] and reduction of temperature are considered to be effective [25]. Though rarely reported, desorption of deposits from metal surfaces also needs to be addressed, as it could cause secondary damage. High polar oils, such as ester-based jet engine oils complied with the MIL-PRF-23699 standard, are said to have deposit-dissolving properties. High-temperature deposits are likely composed of oil content of lubricant, HMW (high molecular weight) products of oxidative degradation, carbon, and inorganic residue of additives; and the high polarity is thought to come from degradation products though it has never been documented. Focusing on the polarity of lubricating oils, we studied how deposits are formed, dissolved, and desorbed by different oils with varying polar properties to investigate the formation mechanism of high-temperature deposits. Taking notice also of the fact that polar properties change with the progress of oxidative degradation process, we examined the influence of oxidative degradation of oils on the tendency to form high-temperature deposits. Furthermore, the countermeasure to prevent from deposit formation is also considered.

2. Experimental programme

2.1. Evaluation of solubility of deposits in high polar oils

In order to determine whether or not high polar oils actually have deposit-dissolving properties, we soaked deposit samples in different high-polar oils for two weeks and then examined how the deposits were dissolved and desorbed under static conditions. Three
kinds of typical high-polar ester-based jet engine oils meeting MIL-PRF-23699, namely, Ester Oil-A, Ester Oil-B, and Ester Oil-C were used. We prepared deposit samples using a panel coker test conforming to FED-STD-791 Method 3462 shown in Fig. 1, a well-known method to evaluate high-temperature deposits, and conducted a test under the conditions shown in Table 1. Preparing several different combinations of oils for generating and soaking deposit samples, each combination by observing the appearance of deposits and measuring changes in weight were evaluated.

High-temperature deposits are thought to be composed of oil content of lubricant, HMW oxidative degradation products, carbon, and inorganic residue of additives. The ratio of each component can be determined by performing thermal analysis, where deposit samples are heated from normal temperature up to 900°C, during which oxidation, carbonization, and ashing reactions occur in different temperature ranges [26-31]. As shown in Fig. 2, amounts of LMW (low molecular weight) component, oil, HMW oxidative degradation products, carbon, and inorganic residue can be calculated from the weight change in each temperature range where a corresponding reaction took place. Before estimating the carbon content, it was made sure that the amount of carbon generated by

<table>
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<th>Table 1 Test condition of Panel coker test</th>
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<tr>
<td>Amount of sample oil (g)</td>
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<tr>
<td>Sample oil temperature (°C)</td>
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<tr>
<td>Test panel temperature (°C)</td>
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<tr>
<td>Splash time (sec)</td>
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<td>Suspend time (sec)</td>
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<td>Duration time (hours)</td>
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<th>Table 2 Conditions of TG-DTA</th>
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<tr>
<td>Amount of sample oil (mg)</td>
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<tr>
<td>Carrier gas(cm³/min)</td>
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<tr>
<td>Temperature increase rate (°C/min)</td>
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<td>Temperature range (°C)</td>
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carbonization reaction during the heating process was a little compared to the original carbon content of the oil. We carried out thermal analysis on the deposit samples under the conditions shown in Table 2 and calculated the ratio of each component as listed in Fig. 3. For comparison, we provide in Fig. 1 the composition of desorbed deposits collected from an actual aero-derivative power-generation gas turbine, which had been running on Ester Oil-C. Deposit-A refers to deposits formed in Ester Oil-A, and Deposit-B and Deposit-C refer to those formed in Ester Oil-B and Ester Oil-C, respectively. Though all deposit samples were formed under the same conditions, the composition of Deposit-C differs from that of Deposit-A or Deposit-B. Deposit-C has a higher carbon content than the other two whereas HMW content is similar for all three. The deposits collected from the actual gas turbine shows even a higher carbon ratio. Increase of carbon content and decrease of oil and HMW oxidative degradation contents likely occur either when the machinery operates in a harsh temperature environment or when the thermal stability of the lubricating oil is lower, which suggests that the deposits collected from the actual turbine were formed under harsher conditions than the deposits formed in the panel coking test apparatus.

2.2. Influence of polar properties of lubricants on deposit-forming tendency

In order to determine whether or not formation of deposits is influenced by polarity difference, we conducted a panel coker test using oil samples with varying polar properties to evaluate the tendency to form high-temperature deposits. In this test, which simulated high-temperature-deposit-forming environment, the panel temperature conditions were set at 2201°C and 315°C. Other test conditions are as shown in Table 1. We prepared oil samples of different polar properties by mixing marine diesel engine fuel (FO), which contains relatively large amounts of oxygenated and aromatic compounds and is said to be high polar [32], with non-polar mineral-based diesel engine oil (LO: Mineral Oil-A) at varying ratios. Although the detergent additive where diesel engine oil acts to dissolve a deterioration product is blended, it is hard to expect the lytic reaction on the high-temperature metal surface. Therefore, by changing the mixture ratio with polarity FO and non-polar as bulk of LO, test sample oils with the smaller ratio of FO lead to lower polar.

FO used in the test has an asphaltene content of 5.4% and a dynamic viscosity of 355 mm²/s at 50°C. LO is a marine diesel engine cylinder oil having an SAE viscosity grade of 50 and a dynamic viscosity of 143 mm²/s at 50°C, which is lower than that of FO.

We carried out the test using the oil samples of varying FO/LO ratios to measure the weight changes of test panels after 6-hour tests.

3. Results

3.1. Evaluation of solubility of deposits in high polar oil

Figure 4 and Figure 5 shows the results of examining the dissolution and desorption of deposits on aluminum plates after being macerated in oil samples at the temperature of 140°C for 14 days. The changes in deposit weight caused by dissolution and desorption are plotted in Fig. 6. The results in all cases revealed that deposits adhered to metal surfaces could dissolve and peel or fall off simply by being soaked in oil. Dissolving and flaking off or falling off were especially evident with Deposit-C irrespective of the type of oil it was immersed in. Dissolution of 5% or more of deposits took place within a relatively short time, and some deposit samples dissolved by as much as nearly 40% at the end of the 14-day test period. The amount of dissolved deposits tended to vary depending on the combination of oils used for maceration and forming deposits. Using the same oil for forming and macerating deposits did not necessarily lead to increased solubility or desorption of deposits, which, however, was noticeably apparent in the combination of Oil-C and Deposit-C. Compared to other deposit samples, Deposit-C has higher carbon content and less HMW oxygen-containing organic compounds, which act like an adhesive that bonds the deposits to the metal surface. HMW components are the products of oxidative degradation of oil and have polarity. We speculate that when deposits containing small amounts of HMW compounds are immersed in polar oil, dissolution of HMW compounds causes embrittlement of the deposits, which encourages the dissolution and desorption of the deposits. The same can be said for the deposits collected from the gas turbine.

High-temperature deposits are formed as a result of rapid oxidization and carbonization reactions in localized areas when lubricating oil in the form of droplets or thin film comes in contact with a heated metal surface. When immersed in oil, deposits formed on metal surfaces will dissolve, and could even peel or fall off in some cases, as described above. Thus, we consider it necessary to...
address the dissolution of deposits by the action of lubricating oil when studying the mechanism of deposit formation. In addition, this dissolving action seems to be influenced by the polar characteristics (dissolvability) of the macerating oil, as well as the composition of the deposits formed, especially the ratio of HMW component to carbon.

3.2. Influence of polar properties of lubricants on deposit-forming tendency

The appearances of deposits formed on the panels after the test are shown in Fig. 7 and Fig. 8. The amounts of formed deposits are provided in Fig. 9. In oil samples with lower FO content than LO, deposit increased with the increase of FO ratio at both 220°C and 315°C, but decreased when FO ratio exceeded that of LO. Deposit
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reached the maximum level when the ratios of LO and FO were equal irrespective of the panel temperature. We conducted a test by mixing different types of LO with the same FO and confirmed similar results separately. Though we have yet to verify the influence of using different types of FO, the results will likely vary because of the quality variance of FO.

The amount of deposits decreases when the oil contains more FO than LO due likely to the polarity of the oil coming in contact with the deposits on a metal surface. The greater the FO content, the higher the polarity of the oil. This means that oil mixtures with higher FO content can dissolve greater volumes of deposits, leaving less on the panel surface. The result of analyzing the composition of deposits formed by the test is shown in Fig. 10, which indicates that, as FO ratio increases, HMW content in deposits tends to decrease while carbon content tends to increase. When the ratio of HMW content to carbon in deposits is lower, the relatively small amounts of HMW compounds in the deposits are dissolved quickly by the contacting oil, which causes the embrittlement of the deposits.

We also analyzed the composition of the oil samples used for the test. Figure 11 shows the composition of oil samples with varying FO/LO ratios. In the composition
The rate of deposit formation, as well as the volume of deposits corresponding to the volume of reaction products, varies depending on the type of oil. Different oil types result in different compositions of deposit contents, especially the ratio of HMW component to carbon, which affects the oil’s ability to dissolve deposits. Polar characteristics variation among different oil types also affects the dissolving action. While formation of high-temperature deposits is a complex mechanism affected by various factors, the amount of formed deposits can be calculated simply by taking the volume of oxidation/carbonization reaction products and subtracting the volume of deposits dissolved by the contacting oil.

Lubricating oils deteriorate with operating time due to oxidation. Products of oxidative degradation are oxygen-containing compounds and have polarity. As the oxidative degradation process progresses, the composition of the oil changes, which also changes the composition of the deposits formed and raises the polarity of the oil. In light of these findings, it is likely that oxidative degradation of oil has a more than small influence on the formation of high-temperature deposits. To find out the influence of oxidative degradation of oil on the deposit-forming tendency, we conducted a panel coker test using oil samples with varying degrees of oxidative degradation.

We used four oils complying with the MIL-PRF-23699 specifications, namely, Ester Oil-A, Ester Oil-B, Ester Oil-C, and Ester Oil-D (equivalent to VG 22-32), as well as Ester Oil-E (VG 100), which is an ester-based lubricating oil for compressors, and Mineral Oil-B (VG 32), which is a hydrogen-refined high-quality mineral-based turbine oil. Only Mineral Oil-B is non-polar. For each oil type, we prepared test samples with varying degrees of oxidative degradation by changing duration time and temperature using the oxidation stability test method conforming to Federal-STD-791. We tested these samples under the conditions listed in Table 1.

The test result with fresh oils is shown in Fig. 12, and the changes in deposit volume with the progress of oil degradation are shown in Fig. 13 and Fig. 14. In these Figures, we described deposit volume as functions of change in total acid number (TAN) and dynamic viscosity, both of which are indicators generally used to measure the degree of oxidation of oil. Figure 15 shows the composition of high-temperature deposits formed using fresh oils.

Generally, the permissible limit for increase of TAN is 2 mgKOH/g, and that for change rate in dynamic viscosity is around 25%. When the oils get extremely degraded and exceed these limits, they tend to form excessive amounts of deposits. However, with respect to Ester Oil-C, Ester Oil-E, and Mineral Oil-B, which have higher HMW content ratio to carbon, we observed exceptional cases, where deposit formation was relatively small despite the TAN at 3 mgKOH/g or higher. This is due likely to the deposit composition that is prone to dissolution and desorption. In addition, we were able to confirm that dissolution and desorption of deposits also occurred in non-polar Mineral Oil-B, as was the case with polar oils, as a result of degradation, which gave polarity to Mineral Oil-B.

Dissolution and desorption of deposits by lubricating oils seem to be also taking place within the permissible limits, leading to variance in deposit volume, which is especially evident with Ester Oil-C. Formation of deposits in fresh oils is charted in Fig. 16, which shows particularly rapid deposit growth in Ester Oil-C. The...
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Noticeable variance is likely due to the formation of excessive deposits, as well as accelerated dissolution and desorption of deposits by the action of the oil.

As mentioned earlier, excessive formation of high-temperature deposits needs to be controlled, as they could clog oil passages, etc., which could lead to lubrication failure. Optimizing additives and reducing temperature have been proven to be effective. Another possible solution would be to cover the metal surfaces with film that has the property to inhibit oxidative/carbonization reactions or repel oil. To find out, we chose, as candidates, two silicon-based coating materials (one contains Al-Ni-Co powder, and the other aluminum powder as pigment) that might inhibit reactions by forming a protective film. Three Ni-P/PTFE composite films (with varying PTFE content) composed of Ni that controls reactions [33,34] and PTFE that repels oil were used for evaluation. We also considered using a film composed only of PTFE because of its oil-repelling property and because it had been verified in a separate test that dried deposits could be easily peeled off of the surface covered with a PTFE film. However, we rejected the idea because of its inability to effectively control deposit formation and intolerance to heat above 300°C, where deposits are formed, though. While Ni-P/PTFE films contain PTFE, they have been used successfully in metal dies, etc. operating above 400°C, exhibiting excellent heat resistance.

We performed a panel coker test to verify each candidate coating ability to inhibit the formation of high-temperature deposits, the result of which is shown in Fig. 13. Fig. 14 shows the effect of oil degradation on deposit formation, and Fig. 15 shows the fraction rate of deposit prepared by Panel coker test using fresh oils.

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in Fig. 17. The graph indicates that deposit formation is inhibited by silicon-based paint products, but more so by Ni-P/PTFE films.

5. Conclusions

Focusing on the polarity of lubricating oils, we investigated the dissolution and desorption of high-temperature deposits to analyze their formation mechanism. In addition, we examined the effects of oxidative degradation of oils on their tendencies to form high-temperature deposits, along with possible methods to reduce their formation, and reached the following conclusions:

1) When contacted by polar lubricating oils, deposits formed on a metal surface dissolve, and peel or fall off in some cases.
2) The polarity of the contacting oil affects the tendency of deposits.
3) The dissolvability of lubricant oil and the composition of formed deposits, especially the ratio of HMW component to carbon, influence the formation of high-temperature deposits. The HMW-component/carbon ratio varies depending on the oil type and is influenced by operating temperature and other conditions.
4) The amount of deposit formation can be calculated simply by taking the amount of oxidation/carbonization reaction products and subtracting the amount of deposits dissolved by the contacting oil.
5) Dissolution of deposits by lubricating oil is influenced not only by the polar properties of the oil, but also by the increase of polarity associated with the production of oxygen-containing compounds as a result of oxidative degradation. Dissolution of deposits also takes place in non-polar mineral oil in such the case.
6) Use of Ni-P/PTFE films, which have the properties to inhibit oxidation/carbonization reactions and repel oil, is effective in reducing high-temperature deposits.

References

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