We newly developed the prototype calcium complex grease (Cx-S) which delivered a better temperature performance than traditional calcium complex greases and could keep its structure even over 200°C. This was achieved by combining the common calcium complex thickener technology with a new concept. In this report, the bearing life of several grease types was evaluated by ASTM D 1741. It was demonstrated that the bearing life of Cx-S wasn’t as long as urea grease, although it had excellent anti-oxidation performance. Additionally, leakage rate was calculated by the amounts of leaked grease from bearings during the test. Therefore, it was suggested that a physical factor such as shear stability of the grease is likely to cause shorter bearing life. Then, by using behenic acid instead of stearic acid - to improve shear stability of Cx-S - it was found that behenic type calcium complex grease (Cx-B) forms much thicker and stronger fiber micelles than stearic type (Cx-S). As a result, the shear stability of Cx-B was strongly improved and bearing life was extended by 50% compared to Cx-S.

Keywords: calcium complex grease, heat resistance, oxidation stability, leakage, bearing life, behenic acid

1. Introduction

Due to enhanced progress within various industries such as automotive, wind turbine, steel and so on, requirements are becoming severe year by year. These days, long life greases under high temperature condition are highly demanded in the grease market. Therefore, market share of poly urea greases and lithium complex greases being used in high temperature applications are recently increasing [1]. On the other hand, traditional calcium complex greases which preferably used in former times are now representing commodity product [2]. But, they did not deliver a satisfying performance in terms of heat resistance e.g. dropping point and bearing life under high temperature condition [3]. However, the big advantages of calcium greases are low cost and availability in large quantity as well as they are easy to handle. Lithium greases and lithium complex greases might be more expensive as lithium price recently increased due to high demands of lithium for batteries [4] and for urea greases, some ingredients of urea thickener such as aniline, cyclohexyl amine and so on [2]. This is the major reason we have made the decision for developing novel calcium greases.
It is well known as an indicator of oxidation degradation [7]. It can be calculated from the ratio between the absorption of carbonyl group (>CO) caused by oxidation/degradation of greases (wave number: 1700 ~ 1710 cm\(^{-1}\)) and methylene group (-CH\(_2\)-) derived from its hydrocarbon oscillation (wave number: 720 cm\(^{-1}\)) with FT-IR.

Leakage rate;
It was calculated via amounts of leaked grease from bearing after the test.

2.3. Roll stability test
Shear stability was measured on Roll stability test as defined by ASTM D 1831. Test temperature was room temperature and 100°C. Change rate of penetration before and after testing was calculated.

3. Results
3.1. Traditional calcium complex grease
Current calcium complex greases in the market are using a thickener such as calcium salts composed of two different types of fatty acids (stearic and acetic acids) [2]. Figure 1 shows penetration and dropping point of this calcium complex grease as a function of mole ratio of calcium stearate/acetate. It can be shown that penetration and dropping point are varying by mole ratio of calcium stearate/acetate. This makes the choice of mole ratio very critical to the final grease performance. However, dropping point shows around 200°C at a maximum, and it has limitation in optimizing the composition of grease [5]. Therefore, we studied to improve the heat resistance of traditional calcium complex grease below.

3.2. Prototype calcium complex grease
Basically, calcium complex soap is composed of long chain fatty acid and heat resistant component. As heat resistant component, short chain fatty acid or Aromatic carboxylic acid can be used. Generally, it is well known that heat resistance properties of greases such as dropping point are depending on the decomposition point of the thickener component [2]. As a result of several studies, it was found that calcium soap composed of aromatic carboxylic acids and hydroxide got a high heat resistance due to a benzene ring. Table 2 shows the decomposition points of calcium acetate or benzoate on TG-DTA. The decomposition point of calcium benzoate was around 400°C which was around 60°C higher than the one of calcium acetate. Therefore, it was decided to add calcium benzoate as a third component into thickener system, because it got higher heat resistance and also was easy to handle.

Stearic acid and benzoic acid reacted with calcium dioxide in paraffinic base oil, and then heated gradually. But, it was found that the reaction product separated itself from base oil due to poor solubility and therefore a complex soap couldn’t be formed. The reason is as follows.

Benzoic acid got a poor solubility in paraffinic base oil at around 100°C, which is the temperature of saponification reaction. However, the melting point of benzoic acid is 122°C which seems to be bit too high as well. Several components were studied to improve the solubility of benzoic acid in base oil. The components needed to act as a grease thickener, to show a low melting point and to have a high polarity. Therefore, acetic acid seemed to be an option since it met the needs and was industrially widely used.

Consequently, the prototype calcium complex grease was obtained by combining stearic acid, benzoic acid and acetic acid and optimizing the component compositions and the process of manufacturing. Figure 2 shows penetration and dropping point of this grease. It was found that this grease - which was generated of three types of acids - became harder with lower thickener dosage and improved heat resistance performance than calcium stearate grease and traditional calcium complex grease [5].

<table>
<thead>
<tr>
<th>Bearing type</th>
<th>Grease amount, g</th>
<th>Load, N</th>
<th>Rotating speed, min(^{-1})</th>
<th>Temp., °C</th>
<th>Cycle</th>
<th>Determination of life</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 6306</td>
<td>6.0 ±0.1</td>
<td>221</td>
<td>178</td>
<td>3,500</td>
<td>140</td>
<td>Over torque Temp. increase</td>
</tr>
</tbody>
</table>

Table 1 Test conditions of bearing life evaluation (ASTM D 1741)

<table>
<thead>
<tr>
<th>Decomposition point, °C</th>
<th>Ca acetate</th>
<th>Ca benzoate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>330 ~ 350</td>
<td>390 ~ 410</td>
</tr>
</tbody>
</table>

Table 2 Decomposition point of calcium soap on TG-DTA
3.3. Bearing life test

Table 3 shows the composition and properties of several types of greases. In this report, four types of greases, prototype calcium complex grease (Cx-S), lithium grease (Li), lithium complex grease (Lx), and aliphatic di-urea grease (U) were prepared: all these greases were composed of each type of thickener, paraffin mineral oil and anti-oxidant. The penetration of all greases is NLGI grade No.2. Also, prototype calcium complex grease (Cx-S), lithium complex grease (Li) and urea grease (U) get much higher heat resistance than lithium grease (Li).

3.3.1 Bearing life

First, Fig. 3 shows the result of bearing life test. Bearing life of prototype calcium complex grease (Cx-S) is 360 hours which is longer than lithium grease (Li) and lithium complex grease (Lx) but shorter than urea grease (U) [6].

3.3.2 Carbonyl absorbance ratio

Figure 4 shows the change of carbonyl absorbance ratio as a function of test duration. The higher value indicates that it is more oxidized. Lithium grease (Li) and lithium complex grease (Lx) were oxidized early in the test, while the prototype calcium complex grease (Cx-S) was hardly oxidized.

3.3.3 Leakage rate

Figure 5 shows the change of leakage rate as a function of test duration. Almost all amounts of lithium
grease (Li) and prototype calcium complex grease (Cx-S) leaked from bearing just when reaching end of bearing life. As for lithium grease (Li), the leakage rate was higher due to the thickener structure which was destroyed by oxidative degradation and couldn’t keep base oil. But, as for prototype calcium complex grease (Cx-S), one challenging question remained: Why did almost all amounts of this grease leak from bearing, although hardly oxidized?

3.4. Process until reaching bearing life

Figure 6 shows the process until reaching bearing life [2]. It is well known that the process until end of bearing life is determined by two factors: a chemical factor influencing oxidation and a physical factor impacting mechanical shear performance [8]. Generally both - chemical and physical - factors influence bearing life of greases. However, as for prototype calcium complex grease (Cx-S), it was found that softening of grease under high temperature condition led mainly to shorter bearing life as follows.

Then, shear stability was evaluated by roll stability test (ASTM D 1831). Figure 7 shows change rate of penetration at room temperature and at 100°C. It had good shear stability at room temperature, but got much softer at 100°C. However, this soft grease became hard again when being homogenized with three roller mill (Fig. 8). It doesn’t mean that thickener structure is destroyed by heat and thickener micelles are easier to clump under high temperature, which means softening of this grease. As a result, this grease led to leakage which reduced the bearing life performance. Therefore, it is suggested that the key point is to prevent clumping of thickener micelle.

3.5. Improvement of shear stability and bearing life

Basically, it is proposed that within the thickener the high polarity hydrophilic functions cause the clumping effect. Therefore, there might be two solutions to prevent clumping. One is by adding dispersant additive to disperse thickener into base oil. The other one is by using longer chain fatty acid such as behenic acid for changing polarity in thickener structure. Figure 9 shows the change rate of penetration depending on three greases. Grease1 is prototype calcium complex grease (Cx-S). Grease2 with additional dispersant additive, and Grease3 is similar to Grease1 but with behenic acid as oil-soluble component (Cx-B). It was found that shear stability at 100°C was strongly improved especially when adding behenic acid. Furthermore, as shown in Fig. 10, bearing life of behenic type calcium complex grease (Cx-B) was extended by 50% compared to
prototype calcium complex grease (Cx-S) and delivered nearly same performance as urea grease [9].

4. Discussion

Figures 11, 12 show fiber formations of two greases and the circle portions of these figures show a typical fiber micelle with Transmission Electron Microscope (TEM). Fiber formations of stearic type (Cx-S) look much thinner, while behenic type (Cx-B) looks much thicker and stronger.

Observations can be explained as follows. Figures 13, 14 are showing the model of the fiber formation of stearic type calcium complex grease (Cx-S). White one representing hydrogen, black carbon, red oxygen, and

![Chemical compounds which compose stearic type calcium complex grease (Cx-S)]

(a) Acetic calcium mono-stearate
(b) Acetic calcium mono-benzoate
(c) Calcium di-acetate

![Model of fiber formation of stearic type calcium complex grease (Cx-S)]

(a) Unit micelles
(b) Single fiber micelle
(c) Bundle of 3 to 4 fiber micelles
green calcium in that molecular model (Figs. 13, 14). In this report, XRD (X-Ray Diffraction) and Solid-state NMR (Nuclear Magnetic Resonance) techniques were used to analyze the chemical structure of calcium complex soap. General methods of structural analysis such as GC (Gas Chromatography), LC (Liquid Chromatography) and Liquid-state NMR can’t be used because calcium soaps are very slightly soluble in typical solvents and not easily gasify. In addition, novel calcium complex soap is complex in structure because it is a mixture of several calcium soaps in which calcium hydroxide reacts with three kinds of acids to form, as described above. Therefore, XRD and especially Solid-state NMR-ROSY (Relaxation Ordered Spectroscopy) method were selected. On XRD, it can be guessed whether a mixture which composes novel calcium complex soap is a physical or chemical one by the difference in the crystalline of each components of the mixture. And, Solid-state NMR-ROSY is a technique to separate the overlapping $^{13}$C chemical shift spectra of solid mixtures via an inverse Laplace transform by using the difference in $^1$H longitudinal magnetization relaxation time of each components of the mixture (HT1) [10].

As a result, it was suggested that it was mainly composed of three compounds, acetic calcium mono-stearate (Fig. 13(a)), acetic calcium mono-benzoate (Fig. 13(b)), and calcium di-acetate (Fig. 13(c)), which were combinations derived from the thickener formulation of prototype calcium complex grease (Cx-S). And it was guessed that these compounds would be coordinating in a manner to represent the unit micelle, and then the fiber micelle would be formed in a line, as it can be seen from Fig. 14(a). The diameter of a single fiber micelle can be calculated from molecular length of these compounds. The diameter of a single fiber micelle of stearic type calcium complex grease (Cx-S) is probably around 5nm as shown in Fig. 14(b), since molecular length of acetic calcium mono-stearate is around 2nm which is calculated from its intermolecular distance. As a result, as shown in Fig. 14(c), 3 to 4 fiber micelles are likely to bundle together with a joined diameter of 6 to 7 nm which is measured from a typical fiber micelle in Fig. 11.

On the other hand, Figs. 15, 16 show the model of the fiber formation of behenic type calcium complex grease (Cx-B), which contains acetic calcium mono-behenate, as it can be seen from Fig. 15(a). Since it has a longer carbon backbone chain than stearate, this single fiber micelle got a better higher oil-solubility and stronger van der Waals’ force between the fibers as it can be seen from Fig. 16(a). This prevents clumping as discussed above. As shown in Fig. 16(b), 7 to 9 fiber micelles are likely to bundle together with a joined diameter of 20 to 30 nm which is measured from a typical fiber micelle in Fig. 12. That’s why this fiber is likely to be thicker and stronger. As a result, shear stability and bearing life have been highly improved.

5. Conclusions

It was demonstrated that the prototype calcium complex grease (Cx-S) has not only excellent heat resistance properties such as enhanced dropping point and oxidation stability, but also high performance in other grease properties. However, bearing life of prototype calcium complex grease (Cx-S) wasn’t as long as urea grease. Finally, this report demonstrates strongly the difference of oxidation process depending on several types of greases during a bearing life test. The results are summarized below:

- Bearing life of lithium grease (Li) and lithium complex grease (Lx) is shorter than prototype calcium complex grease (Cx-S) and aliphatic di-urea grease (U).
- As for lithium grease (Li) and lithium complex...
grease (Lx), oxidative degradation was mainly causing shorter bearing life.

- Prototype calcium complex grease (Cx-S) got excellent oxidation stability, but bearing life of prototype calcium complex grease (Cx-S) should be improved. It has been suggested that a physical factor such as shear stability of greases is likely to cause shorter bearing life.

- Behenic type calcium complex grease (Cx-B) has much thicker fibers which are visible via TEM measurement. As a result, shear stability and bearing life have been highly improved.

- It is expected that bearing life of this grease would last longer with further improvement and grease products using this technology could be widely provided to the market in severe high temperature applications.

References


