INFLUENCE OF PHYSICAL STATES OF AMIDE TYPE GEL-LUBRICANTS ON THEIR TRIBOLOGICAL AND RHEOLOGICAL PROPERTIES

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ABSTRACT

The authors studied how changes in the physical states of amide type Gel-Lubricants (Gel-Lubes) affect their tribological and rheological properties. In the hydrodynamic lubrication region, viscosity varied dramatically around the melting point of Gel-Lube. Compared to a base oil, lower traction coefficients were observed in EHL with Gel-Lube in both the gel and liquid states. Friction coefficients under boundary lubrication conditions were lower than those of the base oil and a conventional grease, while much lower friction properties were obtained with Gel-Lube in a liquid state. Bearing friction torque measured in the liquid state was lower than that in the gel state. Results suggest that the viscosity reduction caused by changes in the physical state of Gel-Lube enable it to spread over the friction surfaces more easily and that the boundary film, composed of an adsorption layer of aliphatic amides, remains unchanged in both the gel and liquid states.

Keywords: gel-lubricant, low friction, lubricants, rheology

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INTRODUCTION

In recent years, the impact of global warming has become even more serious, as evidenced by the destruction wrought by huge typhoons, tornadoes, and heavy snows. Lubricants can play a significant role in protecting the environment to help reduce CO_2 emissions. For instance, high performance lubricants featuring energy-saving, long-life, and anti-wear properties have been developed. Not only liquid lubricants, such as motor oils and industrial lubricants, but also greases have been developed with improved energy-saving properties, such as low friction and torque properties [1]. Quite aside from these lubricant developments, the authors have been developing a unique amide type Gel-Lubricant (Gel-Lube), which could be described as being something between an oil and a grease [2]. One of distinctive features of Gel-Lube is thermo-reversibility. A substance that is thermo-reversible can reversibly change physical states depending on its temperature. Somewhat like butter, Gel-Lube has the appearance of a gel or grease at room temperature, and changes to a liquid at higher temperatures as shown in Fig. 2. These physical state changes are temperature dependent and reversible. The key to the thermo-reversibility of Gel-Lube lies in its composition.

Gel-Lube consists of base oils and gelling agents. Aliphatic amides were used as the gelling agents in this study and the general molecular structure is shown in Fig. 1. At low temperatures, Gel-Lube has the appearance of a gel because the gelling agents form three-dimensional networks through hydrogen bonds and Van der Waals forces, holding the base oils like a thickener. However, at high temperatures, the hydrogen bonds break and the gelling agents move freely in the base oils, and Gel-Lube behaves like a liquid. The melting point of Gel-Lube can be controlled within a range of approximately 70-150°C by selecting an aliphatic amide of the proper molecular structure. Furthermore, the gelling agents function not only as thickeners but also as oiliness agents, since polar groups contained in the aliphatic amides will adsorb onto metal surfaces. The oiliness effect gives Gel-Lube low frictional and anti-wear properties under boundary lubrication conditions [3].

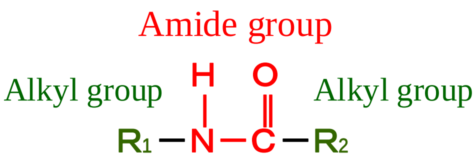

Figure 1. Molecular structure of aliphatic amide.

These characteristic features of Gel-Lube, namely its thermo-reversibility and low friction properties, can be useful in a variety of lubrication applications. In light of the melting points of Gel-Lube, there are several potential applications depending on the environmental temperature, as illustrated in Fig. 2. At temperatures below the melting point, Gel-Lube can be used as a grease substitute (Type A applications). In addition, a new application approach, in which a bearing is used at a temperature above the melting point of Gel-Lube, was tried in this study. At high temperatures, machine parts can be impregnated with liquid Gel-Lube and used after cooling (Type B). Finally, in Type C applications, oil leaks could be prevented because Gel-Lube does not flow when at rest at low temperatures, but when in use, at high temperatures, partially liquefied Gel-Lube would lubricate the friction surfaces. Thus, the ways that the tribological properties of Gel-Lube change due to physical changes are quite important for these applications, especially in the case of Type C applications.

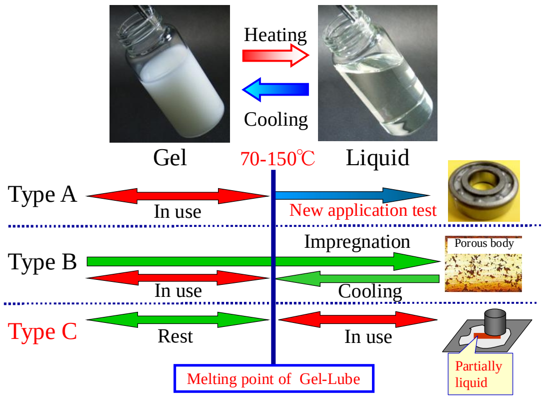

Figure 2. Physical state changes and potential applications of Gel-Lube depending on temperature.

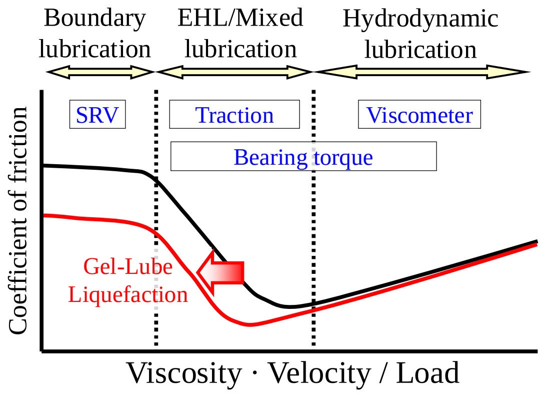

Figure 3. Correlation between lubrication conditions and measurements.

A detailed understanding of the tribological and rheological properties of Gel-Lube as they are affected by changes in its physical state was not sufficient. Therefore, we evaluated these properties, focusing on how the physical state of Gel-Lube is affected by changes in temperature, and compared them with those of an oil and a conventional grease. Changes in the rheological properties of Gel-Lube associated with changes in its physical state were measured using a cone-plate viscometer. Traction and oil film thickness were measured using a ball-on-disk tribometer. Friction properties were evaluated using an SRV reciprocating tester. A bearing tester was used to elucidate the friction torque properties. These measurements were studied in each lubrication condition, as shown in Fig. 3. We then proposed lubrication mechanisms of Gel-Lube based on the results of XPS surface analyses.

EXPERIMENTAL

Samples

For this study, VG68 Poly-α-olefin (PAO) was used as the common base oil. The gelling agent in Gel-Lube was an aliphatic amide whose melting point is around 70°C. The alkyl groups of the aliphatic amide are R_1:$C_{18}H_{37}$ and R_2:$C_{17}H_{33}$ as shown in Fig. 1. To represent a conventional grease, a lithium grease containing a lithium soap thickener (Lithium hydroxystearate) with a melting point of around 220°C was prepared. Tricresyl phosphate (TCP) was added to all the lubricants as an anti-wear additive. The compositions of the test samples, referred to as Gel-Lube, Li-Grease and Base-Oil, are shown in Table 1. 60 worked penetration and dropping point were measured in accordance with ASTM D217 and ASTM D2265, respectively.

Table 1. Compositions of samples.

	Gel-Lube	Li-Grease	Base-Oil
PAO	69%	93%	99%
Aliphatic amide	30%	-	-
Lithium soap	-	6%	-
TCP	1%	1%	1%
Penetration	324	338	-
Dropping point	61°C	207°C	-

Hydrodynamic lubrication

For the evaluations in hydrodynamic lubrication, the rheological properties of the lubricants were measured using a cone-plate type rotational viscometer. The cone was 20 mm in diameter and had an angle of 1 degree. The viscosity of each lubricant was measured at a shear rate of $100s^{-1}$ at temperatures from 25°C to 80°C, a range that includes the melting point of Gel-Lube.

Elasto-hydrodynamic lubrication

A ball-on-disk tribometer was used to study EHL behavior. The test conditions are summarized in Table 2. The traction coefficients and central film thicknesses were measured for Gel-Lube and Base-Oil.

Table 2. Test conditions.

		Traction coefficient	Central film thickness
Specimen	Ball	Steel, 25.4 mm	
	Disk	Steel	Glass
Pressure, MPa		460	260
Velocity, m/s		0.5	0.03-1.0
Slide roll ratio, %		3	0
Temperature, °C		25, 70	

Boundary lubrication

Friction tests were performed using an SRV ball-on-disk type reciprocating tester to evaluate behavior under boundary lubrication conditions. These test conditions are summarized in Table 3. The friction coefficients were measured at temperatures from 25°C to 125°C, with the temperature being increased by 25°C every 10 minutes. To elucidate the lubrication mechanisms, the surfaces of the test specimens after the friction tests were analyzed by XPS.

Table 3. Friction test conditions under boundary lubrication conditions.

		SRV
Specimen	Ball	Steel, 10 mm
	Disk	Steel
Velocity, mm/s		100
Pressure, GPa		1.5
Temperature, °C		25, 50, 75, 100, 125
Duration, min.		10 each
Evaluation		Coefficient of friction

Bearing Lubrication

To study a new application approach, as mentioned in Fig. 2 (Type A), bearing tests were conducted using radial ball bearings. The lubrication conditions in bearings generally range from hydrodynamic lubrication to EHL, depending on the operating conditions. In this study, Gel-Lube and Li-Grease were evaluated and the test conditions are shown in Table 4. These tests were conducted by using a modified Soda-type grease life testing machine. Bearing torques were detected by a wire fixed in a bearing housing and a load cell when a main shaft attached with an inner race of a bearing rolled at some rotation speed. With each lubricant, bearing friction torques were measured for five minutes each at several discrete speeds ranging from 200 rpm to 8000 rpm. The operating temperatures were 25°C and 70°C.

Table 4. Bearing friction torque test conditions.

Bearing	6204
Lubricant content, g	2
Rotation speed, rpm	200, 500, 1000, 2000, 4000, 8000
Temperature, °C	25, 70
Duration, min.	5 each
Evaluation	Friction torque

RESULTS

Hydrodynamic lubrication

The effects of temperature on the viscosities of the lubricants are shown in Fig. 4. The viscosities of Li-Grease and Base-Oil decreased logarithmically and consistently with increasing temperature. The viscosities of Li-Grease were higher than those of Base-Oil due to a structural viscosity, which can be attributed to the Li soap thickener. Meanwhile, the viscosities of Gel-Lube were similar to those of Li-Grease at temperatures in the range of 25° to 55°C. At temperatures above 55°C, the viscosities of Gel-Lube dropped dramatically and approached those of Base-Oil.

The changes in viscosity of Li-Grease and Base-Oil were caused by the predictable reduction in oil viscosity as temperature increased. Meanwhile, the dramatic decrease in the viscosity of Gel-Lube can be attributed to the physical state change, from gel to liquid. The characteristics of Gel-Lubes made using different types of aliphatic amides had been studied previously [4], but Gel-Lube had not been tested against other greases. The results this time indicate that, in terms of viscosity, Gel-Lube behaves like a grease at low temperatures, but like an oil at high temperatures. In hydrodynamic lubrication conditions, the liquefaction of Gel-Lube helps to reduce viscosity resistance.

EHL lubrication

The drop in viscosity of Gel-Lube associated with its liquefaction might have significant effects in EHL regions. The central film thicknesses of Gel-Lube and Base-Oil are shown in Fig. 5 and Fig. 6. At 25°C, Gel-Lube formed thicker films than Base-Oil, and the thickness was proportional to the two-thirds power of velocity in the higher velocity region. Meanwhile, at 70°C, the film thicknesses of Gel-Lube were quite similar to those of Base-Oil. The decrease in the difference in film thicknesses between Gel-Lube and Base-Oil can be attributed to the liquefaction of Gel-Lube, and these results correlate with the viscosity results described above.

Using the same EHL tester, the traction coefficients of Gel-Lube and Base-Oil were measured. The results are plotted in Fig. 7. At 25°C, the traction coefficient of Gel-Lube was about 20% lower than that of Base-Oil. At 70°C, the traction coefficient of Base-Oil had decreased dramatically, but that of Gel-Lube was still about 30% lower. The low traction properties of Gel-Lube at low temperatures were also reported in a previous study, and shown to be linked to the oiliness effect of an adsorption layer composed of gelling agents [5]. However, the fact that Gel-Lube in a liquid state also shows these properties suggests that it would retain its low torque and friction properties at high temperatures. In comparison, the film thickness and traction properties of Li-Grease at 25°C were quite similar to those of Base-Oil. It was impossible to measure Li-Grease at 70°C due to a limitation of the tribometer.

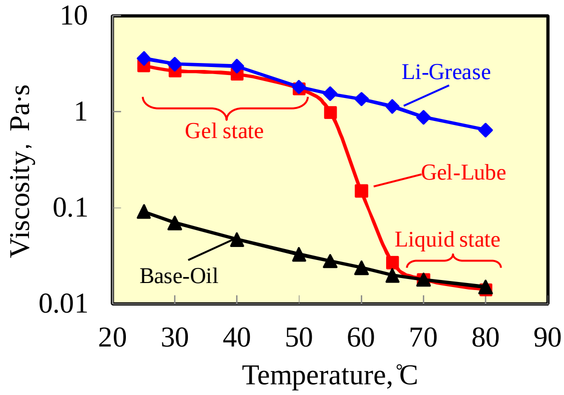

Figure 4. Effects of temperature on viscosity.

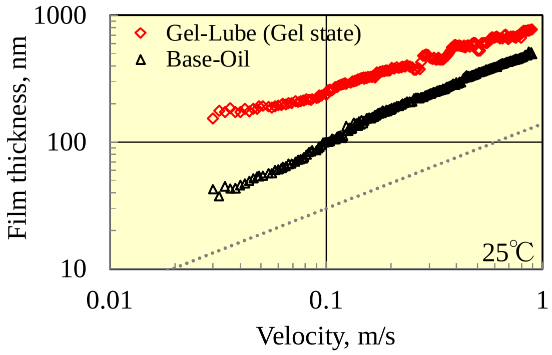

Figure 5. Central film thickness of Gel-Lube and Base-Oil.

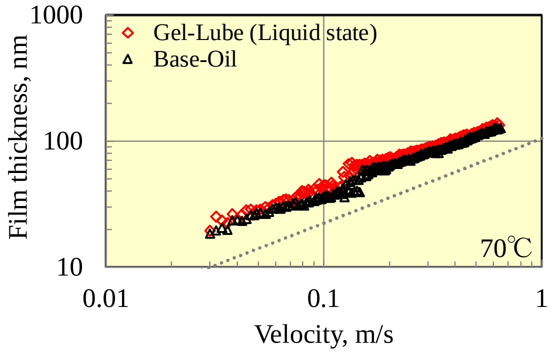

Figure 6. Central film thickness of Gel-Lube and Base-Oil.

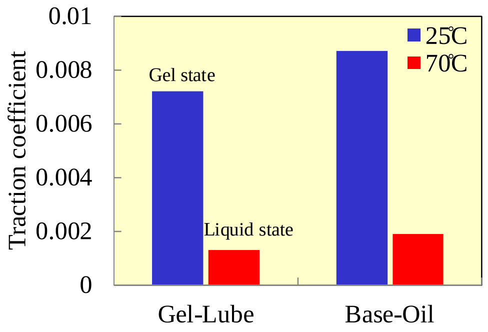

Figure 7. Traction coefficients of Gel-lube and Base-Oil.

<u>Boundary lubrication</u>

The low traction properties of Gel-Lube in the liquid state under EHL conditions could also translate to friction reducing properties in boundary lubrication conditions. We therefore conducted friction tests using an SRV ball-on-plate reciprocating tester to study the temperature dependence of the coefficient of friction. The friction coefficients of the lubricants and images of the sliding surfaces after the friction tests are shown in Fig. 8 and Fig. 9, respectively. Base-Oil showed stable friction coefficients of around 0.11 throughout the test temperature range. The coefficients of friction of Li-Grease were somewhat higher at around 0.12. The effect of temperature on friction coefficient of these two lubricants was negligible. Meanwhile, the friction coefficients of Gel-Lube were similar to those of Base-Oil at lower temperatures up to 50°C, when it was in the gel state. At temperatures above 50°C, Gel-Lube in the liquid state showed lower friction coefficients than Base-Oil. The difference increased with temperature, until the value was 0.094 at 125°C. These low friction properties of Gel-Lube are mainly attributed to the oiliness effect of the gelling agents used in its formulation. In addition, the reduction in viscosity associated with liquefaction at higher temperatures could result in further reductions in friction. The wear conditions with each lubricant were similar. This may be the effect of the anti-wear additives.

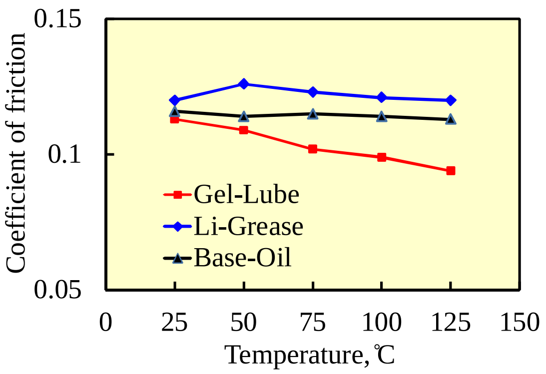

Figure 8. Friction coefficients measured by a SRV tester.

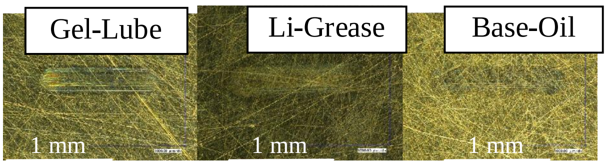

Figure 9. Photographs of sliding surfaces of disks after SRV friction tests.

Bearing lubrication

Using the insights gained into the improvement in tribological properties associated with the liquefaction of Gel-Lube, we investigated a new application in which Gel-Lube was used in a bearing at temperatures above its melting point. Friction torque tests using radial ball bearings were conducted and the results are shown in Fig. 10 and Fig. 11. The friction torque of Gel-Lube at 25°C increased with the bearing rotation speed. At 70°C, Gel-Lube in the liquid state significantly reduced friction torques, especially at higher bearing rotation speeds. Meanwhile, the friction torques of Li-Grease at 25°C were similar to those of Gel-Lube and were somewhat lower at 70°C, although still significantly higher than those of Gel-Lube.

The temperature dependence of the reduction in friction torque observed with Gel-Lube is attributed not only to the drop in base oil viscosity but also the change in physical state. Because the bearing tests were performed in an unloaded condition in this study, the lubrication condition may have been hydrodynamic lubrication. The significant difference in torque reductions between these lubricants was due to the viscosity properties illustrated in Fig. 4. In addition, the low traction properties of Gel-Lube may have affected these torque reductions.

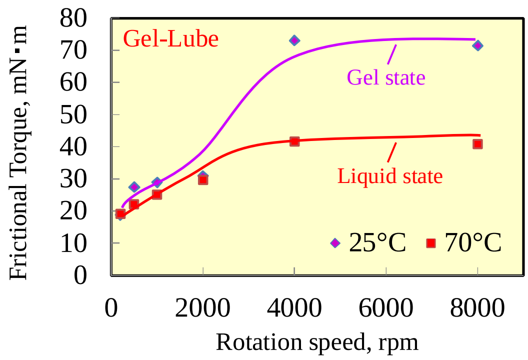

Figure 10. Friction torques of ball bearings using Gel-Lube.

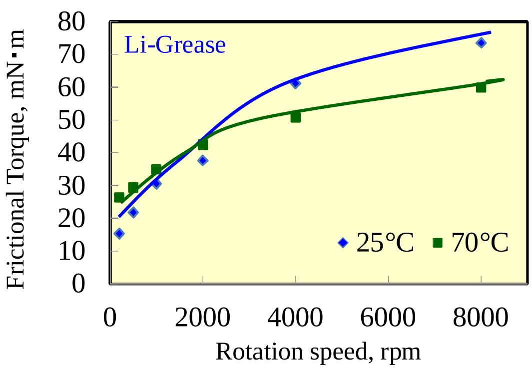

Figure 11. Friction torques of ball bearings using Li-Grease.

DISCUSSION

As for the rheological behaviors of Gel-Lube, the measurement results with the rotational viscometer reflect a state of hydrodynamic lubrication. The rheological behavior of Gel-Lube in the gel state is similar to that of the conventional grease, and that of Gel-Lube in the liquid state is close to that of Base-Oil. These characteristics of Gel-Lube could make it more effective than grease at reducing viscous resistance at higher temperatures. For instance, in the case of Type C applications (Fig. 2), as long as the lubrication conditions were maintained within the hydrodynamic region, Gel-Lube could be applied to machine parts in a grease-like state and then, when the machine is operated and temperatures rise, Gel-Lube would liquefy and significantly reduce viscosity resistance. This possibility was demonstrated in the bearing tests. The torque reduction observed when using Gel-Lube at higher temperatures is mainly attributed to its rheological properties, as Gel-Lube transitions from gel to liquid. Because the bearings were tested in an unloaded condition, it was thought that the results reflected a state of hydrodynamic lubrication. But due to the potential for EHL lubrication in bearings depending on usage conditions, it would also be important to consider the behavior of Gel-Lube in EHL conditions.

Meanwhile, the EHL test results showed that film thicknesses of Gel-Lube are thicker than those of Base-Oil when in the gel state, and comparable when in the liquid state. However, the traction coefficients of Gel-Lube in both the gel and liquid states are lower than those of Base-Oil. Gel-Lube in the liquid state is rheologically similar to Base-Oil but reduces traction due to a thick adsorption layer composed of aliphatic amides. The phase diagram indicates that Gel-Lube exists in a pseudo-solidified state at high pressures even at temperatures above the melting point [5]. This solidified Gel-Lube formed thick adsorption layers in the liquid state and lowered traction coefficients in EHL regions. The low traction properties of Gel-Lube in the liquid state could be useful for applications involving machinery parts operating in EHL regions.

Meanwhile, under boundary lubrication conditions, the low friction properties of Gel-Lube are mainly a function of the oiliness effect of the aliphatic amides. In addition, the drop in viscosity as Gel-Lube changes from a gel to a liquid helps reduce friction, because Gel-Lube in the liquid state is better able to spread over friction surfaces.

To verify the oiliness effect of Gel-Lube in the reciprocating tests, XPS analyses of the sliding surfaces (shown in Fig. 9) were conducted after the tests. As shown in Fig. 12, the results showed that nitrogen was present in a shallow area of the sliding surface, from 0 to 10 nm deep. This suggests that amides had adsorbed on the friction surfaces. However, the concentration was low and the chemical species could not be defined. In a previous study, nitrogen was detected on the sliding surfaces after a similar test conducted with a Gel-Lube made using a different type of amide at a temperature below its melting point [6]. We confirmed that Gel-Lube in the liquid state behaves similarly to that in the gel state.

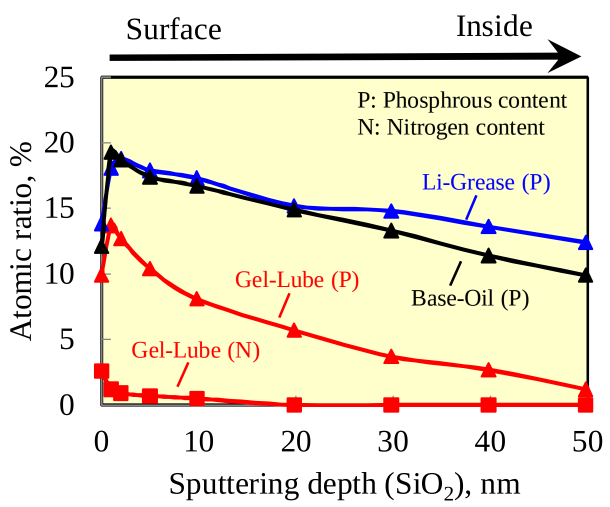

Figure 12. XPS phosphorous and nitrogen depth profiles of sliding surfaces lubricated with each lubricant.

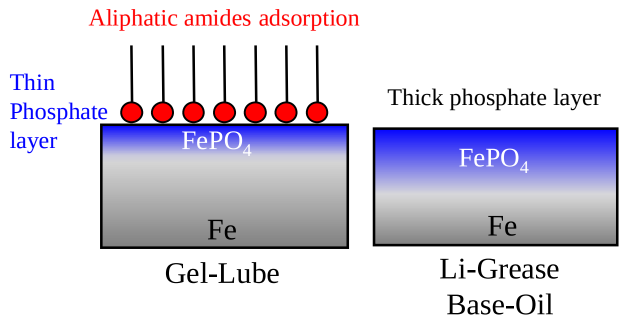

Figure 13. Lubrication mechanisms under boundary lubrication conditions.

Furthermore, phosphorous was detected in all sliding surfaces. With the Base-Oil and Li-Grease, thick films of iron phosphate had formed, which could be traced to the TCP that was added as an anti-wear agent. The phosphate extended from shallow areas to deep ones, of at least 50 nm in depth. Meanwhile, with Gel-Lube, a similar phosphate layer was clearly detected but the concentration was lower. Compared to Base-Oil and Li-Grease, the gelling agents in Gel-Lube and TCP might interact with one another to a greater degree. As a result, it may be that a thinner iron phosphate layer forms and the amide groups adsorb onto that layer. The synergistic effect on friction reduction of the combination of Gel-Lube and TCP had been confirmed previously [6]. Therefore, this thinner phosphate layer might be effective at reducing friction. Lubrication models under boundary lubrication conditions are proposed in Fig. 13. Even in boundary lubrication conditions, in which oil films are significantly thinner, Gel-Lube exhibits excellent friction reducing performance.

CONCLUSION

We studied the changes in the tribological and rheological behaviors of Gel-Lube associated with changes in its physical state, which depend on temperature. The rotational viscosity of Gel-Lube declined dramatically with liquefaction at higher temperatures. This phenomenon led to a reduction in bearing friction torque resulting from the liquefaction of Gel-Lube at higher temperatures. Gel-Lube in the liquid state formed oil films of roughly the same thickness of those of Base-Oil, but showed lower traction coefficients than Base-Oil due to an adsorption layer composed of the aliphatic amides which are used as gelling agents. In SRV tests, friction coefficients declined with the liquefaction of Gel-Lube due to an oiliness effect and an increased supply of lubricant on the friction surfaces. With Gel-Lube, the formed tribo-film consisted of a thinner iron phosphate layer and amide species adsorbed on the surface. Interactions between the aliphatic amides and TCP may have occurred on the friction surfaces since the phosphate layer was different from that observed with Base-Oil. Gel-Lube in the liquid state showed superior tribological characteristics in each lubrication condition. Therefore, Gel-Lube could have ground-breaking potential for a variety of energy-saving machinery applications based on its thermo-reversibility and the oiliness effect.

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