Out-Particling of Rolling Bearings Lubricated with Urea- and Fluorine-Based Greases

If semiconductor wafers, liquid crystal panels or hard disk surfaces are contaminated by fine liquid particles, solid particles or gas, product performance is impaired. Consequently, in semiconductor, liquid crystal and hard disk manufacturing, the rolling bearings in the equipment for transporting the wafers, liquid crystals or disks must use greases with low out-particling and evaporating, or a solid lubricant coating must be applied to the bearings to minimize the wear particles they emit. The authors previously reported on lithium soap-based grease (1) and a special fluororesin coating (2) with superior out-particling performance. Recently, demand has been increasing both for a grease that does not contain metallic components and can be used at high temperatures and in vacuum applications. In response to this demand, the authors analyzed the relationship between low out-particling and various compositions of urea- and fluorine-based greases. Focusing on producing a grease with no metal content, including in the base oil and additives, the authors developed a urea grease with no metallic components which has excellent out-particling performance almost equivalent to that of the lithium soap grease. By adding a compound to improve the lubricity of the fluorine grease, the authors overcome its primary shortcoming, the low wear resistance it imparts to bearings. The resulting grease performs very well in vacuum environments, has superior out-particling performance and contributes to excellent bearing durability.

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INTRODUCTION
If semiconductor wafers, liquid crystal panels or hard disk surfaces are contaminated by fine liquid particles, solid particles or gas, product performance is impaired. Consequently, in semiconductor, liquid crystal and hard disk manufacturing, the rolling bearings in the equipment for transporting these components must use greases with low out-particling and evaporating properties. An addition to the requirement of grease, a solid lubricant coating must be applied to the bearings to minimize the formation of wear particles. Previously, the authors reported (1) that when rolling bearings, linear motion guide bearings or ball screws are used at normal temperature under normal atmospheric conditions, a grease made of a blend of poly-alpha-olefin and mineral oils with lithium soap as a thickener is superior in out-particling and lubricating performance to a fluorine grease, which had been widely used for its perceived low-out-particling characteristics. The authors also reported (2) that for applications in high temperatures and ultra-high vacuum conditions, a special fluororesin coating consisting of nickel and fluororesin (PTFE) layers had superior out-particling and lubricating performance to a calcined PTFE coating or silver coating.

Recently, as the density of semiconductor and hard disks has increased, cleanliness control has become an increasingly important consideration for enhancing productivity in the manufacture of these products. For this reason, the performance requirements for rolling bearings and other products for clean environments are becoming more severe and diversified. One of the key requirements was to develop a low-out-particling lubricating grease that does not contain metal or sulfur components. Another was to develop a high-performance lubricating grease for vacuum and high-temperature conditions.

In response to these requirements, the authors focused their research on urea and fluorine greases. Specifically, the authors analyzed the relationship between the composition of the greases and the out-particling and lubricating performance. In this report, the authors present the results of our analysis of urea and fluorine greases for use in clean environments.

TEST METHOD
Test Greases
The authors decided to analyze the urea greases in order to find an effective grease that does not contain metal or sulfur components. Table 1 shows the compositions and properties of the test greases. Because the highly refined mineral oil contains traces of sulfur, poly-alpha-olefin was used as the base oil. For greases A, B, and C, poly-alpha-olefin with kinematic viscosity of 100 mm/s at 40°C was used as the base oil and diurea compounds with different structures were used as the thickener. For greases B, D, E, and F, on the other hand, the same aromatic diurea compound was used as the thickener but the kinematic viscosity of the base oil was 30 – 400 mm/s at 40°C. Though greases A and C, with 13 and 12% urea, had worked penetration of 210 and 220, respectively, greases B, D, E, and F had worked penetration of 266, even with urea content of 22 and 27%. Regarding oil separation, grease D was high (2.0%) and the others were low (0.2 to 0.6%).

As discussed in the authors previous report, fluorine grease is suitable for vacuum applications because of its low evaporation (1). However, in comparison with mineral oil and synthetic oil-based greases, it is inferior in terms of the protection from wear it provides to bearings, and it has problems with rust prevention and torque performance that require improvement. Figure 2 shows the compositions and properties of the fluorine test greases. For greases G, H, and J, polytetrafluoroethylene polymer (PTFE) was used as the thickener and straight-chain perfluoroalkyl polymer (PFPE) as the base oil. For greases K and L, branched perfluoroalkyl polymer was used as the base oil and PTFE telomer and PTFE polymer were used as thickeners, respectively. No additives were included in the test greases except in grease J, Grease J included 3 mass % of an anti-wear additive (perfluoroalkyl polymer with a carboxylic acid end-group).

Equipment and Method for Measuring Bearing Out-particling in Normal Atmospheric Conditions
Figure 1 shows the equipment for measuring the quantity of out-particles generated by a bearing. The bearing used in the test was a deep groove ball bearing (695VV) with non-contact rubber seals. It had a bore diameter of 5 mm and an outside diameter of 13 mm. The quantity of test grease was 20 percent of the free internal space in the bearing, which amounted to 19 mg of urea grease and 38 mg of fluorine grease, respectively. The testing equipment with the test bearing...
### Table 2—Composition and Properties of Fluorine-Base Test Grease

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>Grease G</th>
<th>Grease H</th>
<th>Grease I</th>
<th>Grease J</th>
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<td>Base Type</td>
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<td>PTFE</td>
<td>PTFE</td>
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<td>Kinematic viscosity mm²/s (40°C)</td>
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<td>Worked penetration (60W)</td>
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<td>280</td>
<td>280</td>
<td>280</td>
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<tr>
<td>Oil separation rate (100°C, 24h)</td>
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<td>2.5</td>
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<td>1.9</td>
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</table>

<table>
<thead>
<tr>
<th>Grease Type</th>
<th>Grease K</th>
<th>Grease L</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Type</td>
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<td>PTFE</td>
<td></td>
</tr>
<tr>
<td>Base oil</td>
<td>Kinematic viscosity mm²/s (40°C)</td>
<td>250</td>
<td>450</td>
</tr>
<tr>
<td>Worked penetration (60W)</td>
<td>265 ~295</td>
<td>235</td>
<td>JIS K2220 5.3</td>
</tr>
<tr>
<td>Oil separation rate (100°C, 24h)</td>
<td>3.0</td>
<td>2.6</td>
<td>JIS K2220 5.7</td>
</tr>
</tbody>
</table>

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**Fig. 1**—Measuring equipment for grease out-particling quantity from bearings.

**Fig. 2**—Measuring equipment for grease out-particling quantity from bearings in vacuum.

ing installed it was placed in a clean chamber kept at 25°C for the normal-temperature test and in a clean thermostatic chamber kept at 70°C for the high-temperature test. The applied radial load was 0.69 N. A value of 3600 rpm for the urea grease and of 500 and 2000 rpm for the fluorine grease was applied, in accordance with the typical operating speeds of these greases. The out-particling quantity was measured with a light scattering type particle counter (AI-Ga-As laser with 780 nm wavelength) and the number of particles with a diameter of 0.11 μm and larger were measured.

**Equipment and Method for Measuring Bearing Out-Particling in Vacuum Conditions**

Figure 2 shows the equipment for measuring the quantity of out-particulates generated by a bearing in vacuum conditions. The driving force from the motor was transferred through the magnetic fluid seal to the test bearing fixed to the spindle in the vacuum chamber. Axial load was applied to the bearing with a coil spring. The test bearing was a stainless steel deep groove ball bearing (608VV) with non-contact rubber seals. It had a bore diameter of 8 mm and an outside diameter of 22 mm. After the bearing was cleaned with an organic solvent and dried, it was filled with 0.1 g of test grease (filling 7 percent of the free internal space in the bearing). The test conditions were as follows: ambient temperature 25°C, vacuum 1 x 10⁻⁵ Pa, and axial load 196 N. Reversing the direction of rotation every 100 revolutions, 5.4 x 10⁶ revolutions were completed at a speed of 600 rpm. The out-particulating quantity was measured with a light scattering type particle counter (Al-Ga-As laser with 780 nm wavelength) that was installed at the lower part of the testing machine. The number of particles 0.21 μm and larger was measured.

**Fig. 3**—Bearing durability test equipment in vacuum.

**Fig. 4**—Effect of urea composition on out-particling performance.

(0.21 μm is the minimum measurable particle size in vacuum conditions).

**EQUIPMENT AND METHOD FOR TESTING BEARING DURABILITY**

Figure 3 shows the equipment used in the bearing durability test. The driving force of the motor was transferred through the magnetic fluid seal to the test bearing installed on the shaft in the vacuum chamber. Axial load was applied by means of the coil spring. Bearing torque could be measured during the test with a load cell installed in the housing. The test bearing was a stainless steel deep groove ball bearing (608VV) with non-contact rubber seals. It had a bore diameter of 8 mm and an outside diameter of 22 mm. After the bearing was cleaned with an organic solvent and dried, it was filled with 0.1 g of test grease (filling 7 percent of the free internal space in the bearing). The test conditions were as follows: ambient temperature 25°C, vacuum 1 x 10⁻⁵ Pa, and axial load 196 N. The direction of rotation was reversed every minute and the rotational speed was 1000 rpm. Bearing life was deemed over when wear in the bearing progressed to the point that bearing torque began to rapidly increase.

**RESULTS AND DISCUSSIONS**

**Effect of Urea Structure on Low Out-Particling Performance**

Figure 4 shows how the number of out-particulates generated by bearings with greases A, B, C, and sample E changed over a period of 300 minutes. Among the urea-based greases, the out-particling of grease A with the alicyclic aliphatic diurea thinnest, was the lowest. The number of out-particulates that it generated was nearly stabilized in the range of 1200 to 1300 about 120 minutes after rotation began. The number of out-particulates for greases B and C was more than 3000, and showed a tendency to continue to increase even after 300 minutes had elapsed. The number of out-particulates of grease A was a little less than that of sample E, which showed the lowest out-particling performance in our previous report. Grease A demonstrated satisfactory low out-particling performance despite the fact that, unlike lithium soap-based grease, the amount of thinnener it contained was low at 13 percent. Grease A also had a worked penetration of 210, harder than NLGI No. 3, and was composed of finer urea structure than greases B and C (Fig. 5).

**Fig. 5**—Urea structure of greases A, B, and C.

**Effect of Kinematic Viscosity of Base Oil on Low Out-Particling Performance**

Figure 6 shows the range between the maximum and minimum values of out-particulates generated by greases B, D, E and F (all of which contained aromatic diurea compound as thinnener) between 120 and 300 minutes of the test. The quantity of out-particulates was high for grease D, whose base oil has kinematic viscosity 30 mm²/s. No significant difference was observed between greases B, E and F with kinematic viscosity ranging from 100 to 400 mm²/s. Grease D had low thinnener yield and its worked penetration of 266 could only be maintained with a urea amount of 27 percent. It also had an oil separation rate of about 2.0 percent after 24 hours at 100°C, and this value was higher in comparison to the other three greases, whose oil separation rates were between 0.3

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Effect of Ambient Temperature on Low Out-Particulating Performance

Bearings with greases A, B, and C were rotated in a clean thermostatic chamber at 70°C. Figure 7 shows the measurement results. The figures in parentheses show the worked penetration of the grease. The out-particulating of all the greases tended to increase as the temperature rose but that of grease B was especially high. Grease B, with an aromatic diurea compound as its thickener, had a lower thickener yield and high worked penetration of 266. This value was higher than both greases A and C, even though the quantity of urea it contained was 22 percent. The extent of softening at 70°C was large, with a penetration of 320. This is considered to be the cause for the increase in out-particulating observed in grease B.

Effect of Worked Penetration on Low Out-Particulating Performance

Because the authors obtained results indicating that grease hardness greatly affects the quantity of out-particles generated, they applied typical shearing to grease A, which generated the fewest out-particles in the test. The shearing was performed with a shell roll tester. Figure 8 shows measurement results at 25°C and 70°C, for regular grease A and grease A with grease J sheared and softened. The numbers in the parentheses are the worked penetration values. At 25°C, the difference observed between the out-particulating of the two greases was not significant as both were within acceptable levels. However, at 70°C, the out-particulating of the grease that was sheared and softened was considerably higher. It is believed that the high-temperature atmosphere decreased the viscosity of the base oil and softened the grease, which further promoted its stirring and shearing and led to the high quantity of out-particles.

LOW OUT-PARTICULATING PERFORMANCE OF FLUORINE-BASED GREASE

Effect of Kinematic Viscosity of Base Oil on Low Out-Particulating Performance

Figure 9 shows the out-particle generation of bearings with greases G, H, J, and K over periods of 60 minutes of rotation at 500 rpm and 2000 rpm, respectively. The base oil of all three of these greases was the same, perfluoralkylpolyether. At 500 rpm, out-particulating was limited and almost no difference was observed between the three greases. However, at 2000 rpm, the quantity of out-particles generated by the bearing containing grease J, whose base oil had higher kinematic viscosity, was considerably higher than the others. With grease J, the generation of fine particles between 0.11 μm and 0.20 μm diameter increased as shown in Fig. 10. The tendency for the greater portion of particles to be fine particles was also observed with the lithium soap-based grease in the authors previous report (1).

Effect of Bearing Rotating Speed on Low Out-Particulating Performance

Figure 11 shows the stabilized out-particle quantities of greases G, H, J, K and L at 500, 1000, 2000 and 3000 rpm. With all the test greases, the quantity of out-particles increased as rotating speed increased, suggesting that the effect of centrifugal force on out-particulating is large, as described in the authors previous report (1). Also discussed in the authors previous report, the degree of out-particulating varies greatly depending on the composition of the fluorine-based greases. Out-particle quantities of straight-chain PPPE base oil (G, H, and J) demonstrated higher out-particulating than greases with branched-chain PFPE base oil (K and L).

Out-Particulating Quantity of Bearing in Vacuum and Durability Performance

A problem with fluorine-based greases is their inferior in terms of the wear protection it provides to bearings. The authors therefore added a perfluoralkylpolyether with a carboxylic acid end-group to grease J and evaluated the grease’s out-particulating performance. Figure 12 compares measurement results on the out-particulating of grease J with the additive, grease J without the additive, and greases K and L. Partly because of the low rotating speed, the quantity of out-particles was very low for all the greases, and no significant difference was observed among them. Figure 13 shows results of the bearing durability test in vacuum. Grease J with the aforementioned additive had wear life of about five times that of grease J without the additive. It also showed a longer life in comparison with greases K and L. By adding the special perfluoralkylpolyether to grease J, the authors increased wear life by approximately five-fold.

CONCLUSION

1. Grease A with the alicyclic aliphatic diurea compound as its thickener, showed a good low out-particulating performance despite the fact that the amount of urea was small. The authors were able to create a low-out-particulating grease containing no metallic elements by using poly-o-olefin as the base oil and selecting an optimum urea structure.
2. It was found that fluorine greases with branched-chain PFPE base oil generated fewer out-particles than greases with straight-chain PFPE base oil.
3. By adding a perfluoroalkyl polyether with a carboxylic acid end-group, the low-out-particle performance of a fluorine-based grease was maintained while wear resistance was improved nearly five-fold.

REFERENCES