The Reduction of Hazardous Substances

1. Introduction

Believing that coexistence with the global environment is our most important challenge, NTN undertakes eco-conscious management aimed at the reduction of environmental impacts and the realization of a recycling-oriented society. With these goals, NTN is striving to reduce CO₂ emissions, the prevention of air, water and soil pollution, the reduction of wastes, and the promotion of green procurement.

This report describes current and future NTN efforts to reduce hazardous substances in its products. These items would include rolling bearings and constant velocity joints, as well as many other NTN products.

2. Trend in elimination of the use of specific hazardous substances

In 2001, electronic equipment built in Europe contained high amounts of cadmium, a hazardous substance exceeding regulated level standards. This triggered increased consciousness about green procurement.

Consequently, EU issued a series of directives that control or ban the use of hazardous substances in these and other products. These include the ELV (End of Life Vehicle) directive that totally bans the heavy metals lead, mercury, cadmium and hexavalent chromium in cars. The RoHS (Restriction of the use of certain Hazardous Substances in electrical and electronics equipment) directive also imposes a total ban on six hazardous substances, including the heavy metals above and fire retardants for plastics (PBB's and PBDE's), in electrical and electronics equipment, beginning in July, 2006.

In addition, some manufacturers have already started various self-imposed efforts to ban certain organic substances that could harm humans.

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**Research & Development Center  Technical Research Dept.
3. Elimination of controlled substances

3.1 Hexavalent chromium: total ban of use in shields and seal cores

Previously, hexavalent chromium had often been used in NTN product components, including shields and rubber seal cores on bearings. To prevent outward leakage of grease and inward ingress of foreign matter, a shield and a core metal rubber seal are installed on the side faces of sealed rolling bearings. Conventionally, the metal used in shields and cores has been galvanized sheet steel and the surfaces of the pieces have been chromate-treated with a material containing hexavalent chromium.

In 2002, NTN introduced a safe tin-plated sheet steel for shield use with anti-rusting qualities. Two safe materials for seal core metal to ensure good adhesion with rubber were also introduced - galvanized sheet steel with a special electrolytic treatment layer and galvanized sheet steel with a phosphate film.

Photo 1 shows examples of tin-plated sheet steel and conventional chromate-treated (hexavalent chromium) galvanized sheet steel after undergoing a salt spray test. The tin-plated sheet steel samples exhibit higher anti-rusting performance compared to the conventional material.

3.2 Lead: total ban of lead-based extreme pressure agents in grease

Lead naphthenate, lead dithiophosphate and lead dithiocarbamate are excellent extreme pressure agents that have long been used as additives in high-load greases. Constant velocity joints, one of our major products, are used in high surface pressure and rolling-sliding conditions. Therefore, greases containing lead-based extreme pressure additives have often been used on them to prevent wear and achieve low friction. In cooperation with a grease manufacturer, we have developed alternative greases to address this environmental challenge, and started to offer alternative lead-free greases to our customers in 2002.

Our newly developed greases have unique combinations of additives that enhance bearing performance and contain organic molybdenum, molybdenum bisulfide and similar substances instead of lead-based extreme pressure additives.

<table>
<thead>
<tr>
<th>24 hours later</th>
<th>(Conventional) Galvanization + chromating</th>
<th>(Improved) Tin plating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rust occurrence</td>
<td>5/5 parts</td>
<td>0/5 parts</td>
</tr>
</tbody>
</table>

| 48 hours later | 5/5 parts | 5/5 parts |

*Photo 1. Shield appearance after (neutral) salt spray test*

<Saltspray test: in accordance with JIS Z 2371> Sample shield plate: 6203 Z, w/ external rust-preventive oil
Test conditions: 5% salt water, spray rate 1-2 ml/h
Test duration: 24 h and 48 h
Performance data for greases developed for the slidable joint TJ series are summarized in Fig. 1 and Table 1. The results for the 3rd order component of induced cyclic axial load that serves as an index for NVH (Noise, Vibration, Harshness) performance affecting automobile riding comfort, as well as for durability, are better than those of a conventional grease that contains a lead-based extreme pressure additive.

In addition, the bearings used in low-speed, high-load conditions, such as for steel-making and construction machinery, had employed lithium-mineral oil based greases containing lead-based extreme pressure additives. We have already replaced these conventional greases with lead-free greases that we developed in cooperation with a grease manufacturer.

![Fig.1 The 3rd order component of induced cyclic axial load of TJ](image)

**Table 1** Light load durability of TJ

<table>
<thead>
<tr>
<th>Type of grease</th>
<th>T.P</th>
<th>Running time h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>90 125 300</td>
</tr>
<tr>
<td>Newly developed grease A</td>
<td>No.1</td>
<td>○ ○ ○</td>
</tr>
<tr>
<td></td>
<td>No.2</td>
<td>○ ○ ○</td>
</tr>
<tr>
<td>Newly developed grease B</td>
<td>No.1</td>
<td>○ ○ ○</td>
</tr>
<tr>
<td></td>
<td>No.2</td>
<td>○ ○ ○</td>
</tr>
<tr>
<td>Conventional grease</td>
<td>No.1</td>
<td>Δ Δ X</td>
</tr>
<tr>
<td></td>
<td>No.2</td>
<td>Δ Δ △</td>
</tr>
</tbody>
</table>

(○: No problem △: Minor problem X: Severe problem)

![Fig.2 Reaction of secondary amine and nitrite](image)

**3.3 Cadmium: ban of use in resin colorant**

A yellow or red cadmium-based pigment has been used often as a colorant for resins. NTN previously used a cadmium-based pigment in certain resin sliding material BEAREE products and in the band resin for expansion-compensating bearings. The cadmium-based pigment for the former application was replaced with an alternative material by 1993, and for the latter application in 2002.

**4. Efforts to eliminate possible toxic substances**

**4.1 Sodium nitrite: ban of use in greases**

Sodium nitrite has been used often as a rust-preventive agent because of its excellent performance in this role. It also has high performance as an antiseptic and it is a food additive approved by the US Food and Drug Administration (FDA). However, it can generate nitrosamine, a carcinogenic substance, in the presence of a secondary amine (Fig. 2).

During the late 1970’s, NTN totally banned the use of sodium nitrite-containing coolant as a water-soluble grinding coolant because grinding machine operators frequently come into direct contact with such coolants.

Sodium nitrite-containing greases have remained in use because operators directly touch them less frequently, they boast good performance as rust-preventive agents and oxidation inhibitors, and there have been no reliable alternative greases. Recently, however, attempts are being made to regulate this type of grease, especially in Europe. To cope with this trend, we have already switched most outsourced greases to alternative safe greases.

In the 1980’s, peeling phenomenon accompanied by the occurrence of a white structure occasionally appeared on bearings for automotive electrical equipment. This appears to result from hydrogen brittleness caused by the ingress of hydrogen to the bearings due to the decomposition of the base oils in greases.

![Fig.2 Reaction of secondary amine and nitrite](image)

**Table 2** Composition and properties of sodium nitrite free grease

<table>
<thead>
<tr>
<th></th>
<th>Conventional grease</th>
<th>Newly developed grease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base oil</td>
<td>Ether + PAO</td>
<td>Ether</td>
</tr>
<tr>
<td>Base oil viscosity</td>
<td>72</td>
<td>100</td>
</tr>
<tr>
<td>Thickener</td>
<td>Diurea</td>
<td>Diurea</td>
</tr>
<tr>
<td>Consistency</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Life h (at 150°C)</td>
<td>2100</td>
<td>3800</td>
</tr>
<tr>
<td>Resistance against brittleness-induced peeling h</td>
<td>&gt;300 (n=5)</td>
<td>&gt;300 (n=11)</td>
</tr>
<tr>
<td>Rust-preventive performance (rust occurrence %)</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>
We have verified that sodium nitrite helps create a passive condition on steel material surfaces, preventing the ingress of hydrogen. Therefore, sodium nitrite additive is highly effective in preventing this type of peeling phenomenon. NTN had previously developed and been using a high-temperature grease that contained sodium nitrite additives for use in electrical accessories. To cope with the trend toward regulation of sodium nitrite, we have developed a new unique grease. This grease, whose composition and performance are summarized in Table 2, features brittleness-induced peeling resistance and rust prevention qualities comparable to those of the previous grease, with the advantage of longer high-temperature life.

4.2 Phthalates: ban of use in boots and rubber seals for constant velocity joints

Phthalates are often used as plasticizers for plastics and rubbers. In 2003, certain phthalates were added to the EU list of regulated substances (EU directive 2003/36/EC) as CMR substances (Substances classified as Carcinogens, Mutagens or substances toxic to Reproduction). More specifically, sales of dibutyl phthalate (DBP) and diethyl hexyl phthalate (DEHP) and preparations containing these substances were banned in the EU region from the end of 2004.∗

Certain NTN bearing seals and constant velocity joint boots contain phthalates as plasticizers. We are replacing these with phthalate-free components in cooperation with associated component manufacturers with the goal of eliminating phthalates by the end of 2007.

∗Sales of products containing these substances to general consumers are permitted.

4.3 Water-soluble barium compounds

Water-soluble barium compounds are listed as Class 1 designated chemical substances in the Pollutant Release and Transfer Register (PRTR) Law. There is no move toward their regulation in Japan, but in Europe and the USA, attempts are being made to regulate them.

Rust-preventative oils and greases often contain water-insoluble barium sulfonate. Insoluble in water, this substance is not yet regulated by the PRTR Law. However, some researchers suspect that water-insoluble barium sulfonate can generate water-soluble salts. Therefore, we are going to introduce rust-preventive oils and newly developed greases that do not contain barium sulfonate.

5. Conclusion

As stated at the beginning of this report, NTN makes coexistence with in the global environment a top priority and implements eco-conscious management aimed at reducing environmental impacts and realizing a recycling-oriented society. In this report, the authors have introduced NTN’s proactive efforts to reduce the use of regulated substances.

Though not described in this report, NTN wishes to contribute to reducing global environmental impacts and is fully committed to developing eco-friendly products that boast smaller sizes, lower torques, higher efficiency and longer life. Bearings are essentially eco-products that decrease friction and reduce energy loss. NTN will remain dedicated to the development of environmentally friendly products and reduction of substances with environmental impacts - two areas that are crucial to our eco-conscious management activities.

References