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Biodegradable and Water-soluble PAG-based Base Material

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Lubricants are essential for the smooth operation of various machines; therefore, they are often referred to as the "blood" of mechanical devices. With the recent advances in mechanical technology, the demand for environmental load reduction and performance improvement has increased considerably. This article introduces a biodegradable and water-soluble poly alkylene glycol (PAG)-based base material "EXCEBIOL", developed by our company to reduce the environmental load.

Lubricants

Many types of machinery such as automobiles, ships, aircraft, boilers, and pumps have metal parts that often move in contact with one another. This produces friction between the metal parts, resulting in energy loss and wear of the parts, which in turn, reduces the lifespan of the machine. Lubricants reduce such energy losses and wastes caused by friction.

A lubricant is composed of a base oil or base material and various additives. Its basic performance, such as solubility in water, is determined by the base oil (base). There are different types of base oils such as mineral oil, synthetic ester, and polyalphaolefin (PAO), and base materials such as PAG. Mineral-oil-based lubricants, which are inexpensive and exhibit excellent compatibility with various additives, are widely used. Here, PAG is distinguished from base oils, as a "base material," because it often acts as a surfactant and performs other functions.

Reduction in environmental load of lubricants

Lubricants are classified according to their application, into the ones used in open systems (e.g., lubricants for motor bikes, lawn mowers, outboard engines, chainsaw oil, etc.,) and the ones used in closed systems (hydraulic oil, grease, etc.,). In open systems, the environmental load is high because most of the lubricant leaks into the environment. On the other hand, the environmental impact during use is small in closed systems. However, environmental pollution will become a concern if such lubricants accidentally leak into the natural environment. Therefore, it has been recommended or mandated to use lubricants with low environmental load (biodegradable lubricants) in case there is leakage into the natural environment **(Table 1)**. Mineral-oil-based lubricants, which are currently the mainstream, do not degrade easily

Table 1 Examples of regulations/certifications for lubricants[1)]

Area	Country	Name of regulation/ certification	Description	Subject lubricants
Asia	Japan	ECO Mark	The Eco Mark Secretariat has established certification standards for biodegradable lubricants that comply with the Eco Mark. In addition to the biodegradability being 60% or higher, other parameters such as the acute fish toxicity, are evaluated with respect to the restriction on the use of toxic substances and the impact on the ecosystem.	Hydraulic oils, 2-cycle engine oils, grease, etc.
Europe	Entire area	EU Ecolabel	Lubricants that have passed the requirements such as "reduction of impact on the aquatic environment and soil during use," "reduction of CO_2 emissions," "high percentage of renewable raw materials," and "restriction in the use of hazardous substances" are certified by EU Ecolabel.	Lubricants in general
North America	United States	Vessel General Permit (VGP)	The U.S. Environmental Protection Agency (EPA) has mandated the use of lubricants and greases defined as EALs (Environmentally Acceptable Lubricants) that satisfy the biodegradability, nontoxicity and nonbioaccumulation in VGP, from the end of 2013.	Lubricants for ships (hydraulic oils (for others), grease, etc.)
		USDA BioPreferred	To promote the use and purchase of highly biodegradable products, federal government agencies and their contractors are mandated to purchase biodegradable hydraulic oils, as identified by the United States Department of Agriculture (USDA).	Hydraulic oils (for others)

in nature and persist for a long time; therefore, the use of highly biodegradable lubricants is desirable. In addition to applications in open systems, biodegradable products have been developed and released for use in construction machinery, agricultural machinery, and ships, which are used in outdoor environments such as forests and oceans. However, their penetration is insufficient, and the development of lubricants with higher performance is required for further penetration.

[Biodegradability of lubricants[2)]]

Biodegradability refers to the property of a substance to be decomposed into carbon dioxide and water by bacteria and other microorganisms present in the natural environment such as soil and marine sand. In general, lubricants whose biodegradability over 28 days is 60% or higher are considered as readily biodegradable lubricants. Methods for measuring the biodegradability of lubricants have been put forward by the OECD Guidelines for the Testing of Chemicals and American Society for Testing Materials (ASTM)[3)].

[Issues with biodegradable lubricants]

The biodegradability of lubricants depends on the properties of the base oil (base material). Base oils such as synthetic esters and natural oils and fats, and base materials such as PAG are used as biodegradable lubricants. Although synthetic-ester-based lubricants have low pour points and high flash points, they easily hydrolyze when mixed with water. In addition, it is difficult to clean up and remove synthetic esters and natural oils and fats in the case of lubricant leaks, because they do not mix readily with water. This can pollute the surrounding environment such as rivers and oceans and cause plants to wither owing to formation of an oil film on the water surface. To solve these issues, our company proposed the development of PAG-based base materials, which are difficult to hydrolyze, have easily controllable lubrication properties and solubility in water, and cause less environmental pollution and damage in the case of leakage.

[PAG-based base material]

PAG is a compound that is obtained through the addition polymerization of a compound with active hydrogen, such as low-grade alcohol (hereafter referred to as the starting substance), with an alkylene oxide (AO) such as ethylene oxide (EO) or propylene oxide (PO). Compounds with various performances can be synthesized depending on the intended use, by changing the structure of the starting substance, type of AO, degree of addition polymerization, ratio, method of addition, etc. In addition to their use as a base material in lubricants, PAGs are useful in a wide range of lubricating applications because they can also be used as surfactants to perform functions such as emulsification, solubilization, and permeation.

PAG-based base materials exhibit features such as (1) excellent lubrication properties, (2) good viscosity characteristics (high viscosity index, easy control of molecular weight), (3) good control of solubility in water (adjustment of hydrophilicity-hydrophobicity ratio), and (4) excellent low-temperature fluidity. However, it is difficult to design a composition that satisfies all these lubrication properties, biodegradability, and water-solubility requirements. Our company utilized AO addition and interface control technologies to develop various PAG-based bases. We then used our accumulated knowledge to develop "EXCEBIOL," a PAG-based base that solves these issues **(Figure 1)**.

Biodegradable and water-soluble PAG-based base material "EXCEBIOL"

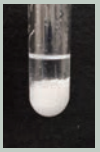
The "EXCEBIOL" series delivers high biodegradability, water solubility, and lubrication properties equivalent or superior to that of the common mineral-oil-based and synthetic-ester-based base oils. As shown in **Tables 2** and **3**, "EXCEBIOL" readily mixes with water and maintains a uniform liquid state without separating over time, as it has excellent water solubility. In contrast, synthetic ester, mineral oil, and PAO-based base oils separate from water over time. Because "EXCEBIOL" is soluble in water, it causes no problems such as environmental pollution, which is a concern with synthetic esters and natural oils and fats, and contributes to the reduction of environmental load, owing to its high biodegradability. Owing to its excellent lubrication properties, it can be used in various applications. Although this study introduces only five types of "EXCEBIOL", its properties such as viscosity and appearance can be customized according to the intended use **(Table 4)**.

Figure 1 Appearance of "EXCEBIOL TE-600"

Application expansion of biodegradable lubricants

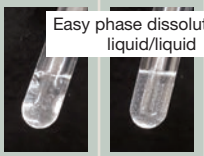
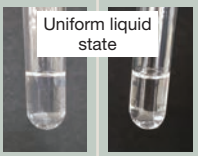
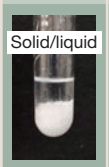
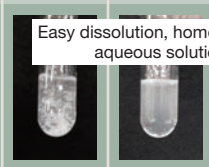
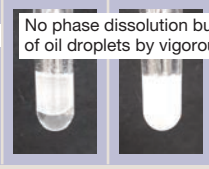
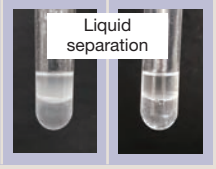
The applications of biodegradable lubricants are expected to expand in the future, and include lubrication and use as bearing oils and gear oils in addition to hydraulic oils. These applications require lubrication properties (load capacity) to facilitate the movement of solid parts such as metals and reduce metal wear. In such applications, the lubricating performance of the base oil alone is insufficient, and it is therefore common to improve the lubrication properties by combining it with

Table 2 Solubility of "EXCEBIOL" and conventional base oils in water

	EXEBIOL MR-260	EXEBIOL MR-660	EXEBIOL TE-600	EXEBIOL DE-300	EXEBIOL DE-1000	Synthetic ester-based base oil	Mineral oil-based base oil	PAO-based base oil
Before agitation								
After letting it stand for 24 h	 Uniform liquid state	 Uniform liquid state	 Uniform liquid state	 Uniform liquid state	 Uniform liquid state	 Liquid separation	 Liquid separation	 Liquid separation

[Test method]
A sample with two layers was prepared by weighing 2 ml of "EXCEBIOL" or base oil in a test tube and gently adding 2 mL of water (3 mL of water per 1 g for DE-1000). The compatibility with water was confirmed by gently agitating the sample first, and then, gradually increasing the vigorousness of agitation.

Table 3 Solubility of "EXCEBIOL" in water (changes over time)

	Before agitation	Gentle agitation	Vigorous agitation	At the start of letting it stand	After letting it stand for 30 minutes	After letting it stand for 24 hours
EXCEBIOL MR-260	 Liquid/liquid	 Easy phase dissolution of liquid/liquid			 Uniform liquid state	
EXCEBIOL DE-1000	 Solid/liquid	 Easy dissolution, homogeneous aqueous solution			 Uniform liquid state	
Synthetic-ester-based base oil	 Liquid/liquid	 No phase dissolution but formation of oil droplets by vigorous agitation			 Liquid separation	

[Test method] The samples that were agitated in Table 2 were allowed to stand, and changes in appearance were observed after 30 min and 24 h.

an extreme-pressure additive. Extreme-pressure additives that can be used with PAG-based base materials have also been identified by our company.

Figure 2 shows the results of the lubrication property evaluation in a system prepared by mixing "EXCEBIOL MR-260," antioxidant, and oil agent, as a model composition for hydraulic oils used in construction machinery to which a specified amount of an extreme-pressure additive is added. The required lubrication performance (load capacity) of the construction hydraulic oil is evaluated using a high-speed shell 4-ball wear tester specified in the Hydraulic Fluids for Construction Machinery standards (JCMAS). In the high-speed shell four-ball test, the steel ball at the top is rotated, and the point where the frictional torque spikes is measured as the seizure load by increasing the load on the test ball in steps. This indicates that the lubricant is more resistant to seizure and that the lubrication properties are better when the antiseizure load value is larger. The model composition satisfies the load-capacity requirements of the JCMAS Standard (1235 N or higher), upon adding 0.2 wt% of an extreme-pressure additive. A higher load capacity is achieved upon increasing the extreme-pressure additive content to 2.0 wt%. In the future, we will continue to develop applications, while balancing the required performance for each application.

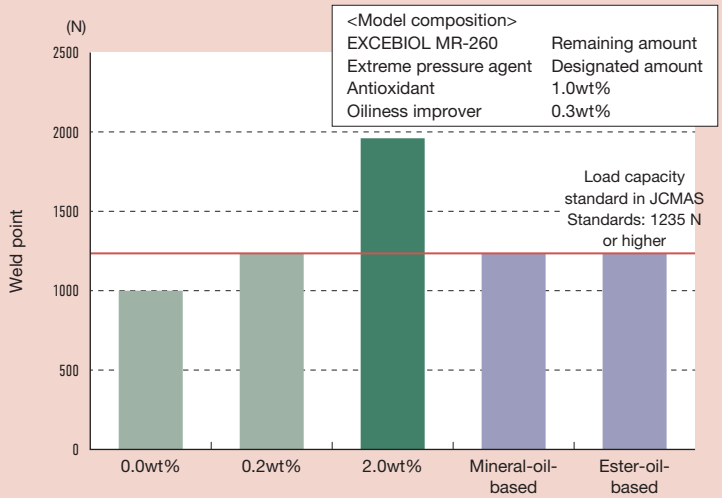
Future developments

Recently, the momentum to achieve Sustainable Development Goals: SDGs and carbon neutrality has increased, and lubricants that can reduce environmental load are in demand. To expand the use of biodegradable lubricants, it is necessary to develop technologies suitable for their intended use, such as the consideration of metal corrosion for lubricants used near water bodies such as rivers and oceans. The environment-friendly "EXCEBIOL" has a wide variety of viscosity grades and a lineup of appearances, allowing selection of grades according to the application. We aim to support the widespread use of biodegradable lubricants and

Table 4 Description and physical properties of "EXCEBIOL" and conventional base oils (base materials)

	Solubility in water Homogeneous dissolution: ○ Insoluble, separation: ×	Biodegradability [OECD301] ≥ 60%: ○	Lubrication property [SRV method*] μ (100 N)	Kinetic viscosity at 40 °C (mm^2/s)	Kinetic viscosity at 100 °C (mm^2/s)	Pour point (°C)
EXCEBIOL MR-260	○	○	0.116	49	11	-40
EXCEBIOL MR-660	○	○	0.116	141	26	-34
EXCEBIOL TE-600	○	○	0.153	91	12	-61
EXCEBIOL DE-300	○	○	0.156	34	6	-13
EXCEBIOL DE-1000	○	○	0.147	–	17	37
NEWPOL PE-61	×	×	0.136	140	–	-30
BLEMBER LUB-90	×	×	0.127	461	–	-5
NEWPOL 75H-90000	○	×	–	19,000	2,700	5
Synthetic ester-based-base oil	×	○	0.137	69	8	-40
Mineral-oil-based base oil	×	×	0.180	37	7	-13
PAO-based base oil	×	×	0.230	30	6	-61

* Lubrication property test conditions [SRV method]: Evaluation of lubrication property (coefficient of friction) using vibration friction wear test (SRV tester).
Test pieces: steel ball (SUJ-2, Φ 10 mm), steel disc (SUJ-2)
Test conditions: Load: 100 N (50 -> 500 N), vibration frequency: 50 Hz, vibration amplitude: 1.0 mm, temperature: 40°C



* Lubrication property test conditions: Evaluation of lubrication property (weld point) using a shell 4-ball wear tester.
Test piece: 1/2 inch steel ball
Test method: ASTM D 2783
Test conditions: Temperature: 18 to 35 °C, number of revolutions: 1760 ± 40 rpm, test period: 10 s

Figure 2 Lubrication property (weld point) evaluation

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contribute to the realization of a sustainable society by developing a high-performance, biodegradable and water-soluble PAG-based base material, "EXCEBIOL."

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