

Boundary Lubrication and Lubricants

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1. Introduction

The term tribology has been used for 18 years to refer to the branch of engineering that deals with friction, wear, and lubrication. Tribology is defined as "the science and technology of interacting surfaces moving relative to each other and associated practical problems." Tribology is a major research field in the mechanical industry—indeed, in any field with even the slightest connection to machinery. Especially in the industrial community, the recent rapid progress in machinery and acceleration of machine speeds has increased production rates, but at the significant added cost of machine damage and energy consumption. With the solution of tribological problems anticipated to save some 800 billion to 1 trillion yen per year, tribology is attracting ever-growing attention.

This issue deals specifically with boundary lubrication, which addresses the complex problems arising from contact between friction surfaces. It also discusses fundamental topics related to this issue and reviews the role of lubricants in boundary lubrication.

2. Boundary lubrication mode

Based on friction experiments on bearings, Stribeck expressed the relationship between the friction

coefficient [f], viscosity of the lubricating oil [η], load [F_N], and velocity [V] in the Stribeck curve (Figure 1). This curve brilliantly captures the characteristics of various lubrication regions, including [I] boundary lubrication, [II] elastohydrodynamic lubrication (EHL), and mixed lubrication.

In hydrodynamic lubrication, the fluid completely isolates the friction surfaces [$h \gg R$], and internal fluid friction alone determines tribological characteristics. In elastohydrodynamic lubrication [$h \approx R$], fluid viscosity, the viscosity-pressure coefficient and the elastic coefficient of the solid surface are the most dominant factors. In contrast, the boundary lubrication mode is mainly characterized by the following three points:

- (i) Friction surfaces are in contact at microasperities
- (ii) Hydrodynamic effects of lubricating oil or rheological characteristics of bulk do not significantly influence tribological characteristics
- (iii) Interactions in the contact between friction surfaces and between friction surfaces and the lubricant (including additives) dominate tribological characteristics.

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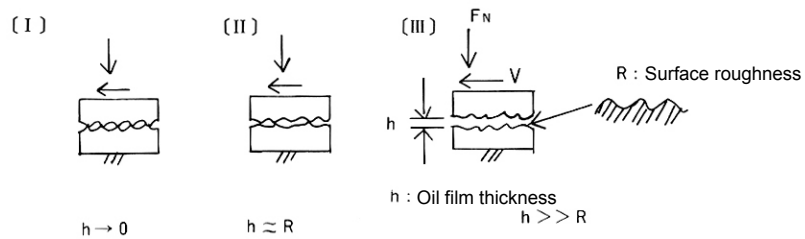
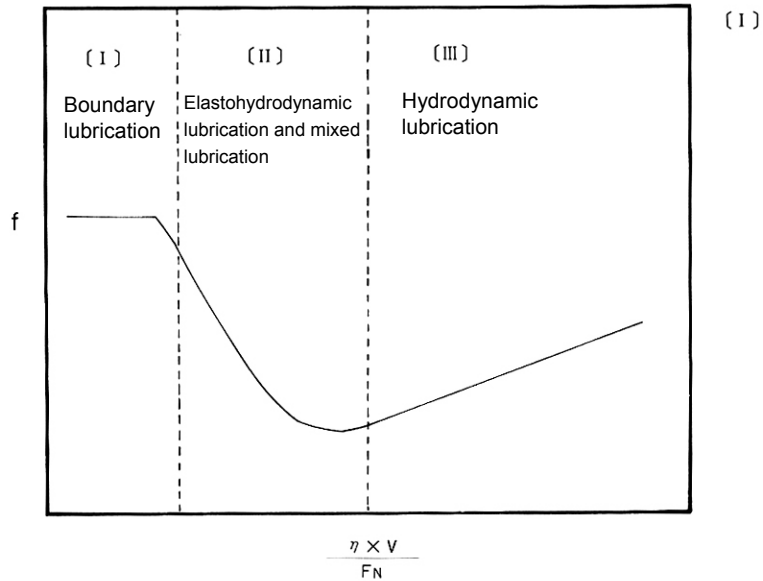


Figure 1: Stribeck curve and lubrication regions

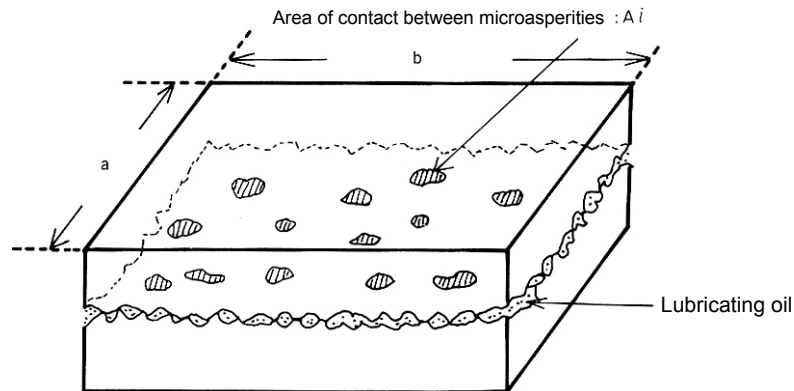


Figure 2: Friction surface contact model (A)

In other words, since the thickness $[h]$ of the oil film between the friction surfaces is smaller than their surface roughness $[R]$ in boundary lubrication, metallic contact occurs across every portion of the surface, as shown in Figure 2. Friction surfaces contact each other over a true contact area ($\sum_{i=1}^n A_i$, n : number of contact points), which is the sum of the contact areas $[A_i]$ between the discontinuous

microasperities, and the load is supported by a much smaller area than the apparent contact area ($a \times b$). Thus, in boundary lubrication where large amounts of friction increase the temperatures of friction surfaces and cause wear and seizure and various resulting problems, it is critical to reduce friction and wear by preventing metallic contact; that is, it is critical to form lubricating films on

friction surfaces by applying lubricants (lubricating oils, additives, and solid lubricants).

As shown in Figure 3 (the cross section of Figure 2), when oil film rupture causes metallic contact, friction force [F] is spent on the shearing not only of the oil film, but of metal bonding. Thus, F is expressed by the following equation:

$$F = A \{ \alpha S_m + (1 - \alpha) S_i \}$$

Where A is load bearing area, α is the ratio of metallic contact, S_m is the shear strength of metal bonding, and S_i is the shear strength of the oil film. Since S_i is significantly smaller than S_m , minimizing α reduces friction.

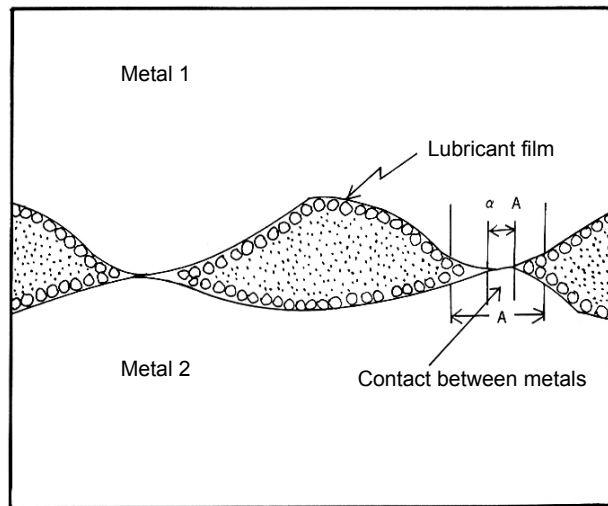


Figure 3: Friction surface contact model (B)

3. Wear in boundary lubrication

The main types of wear in boundary lubrication are as follows.

- (i) Adhesive wear: Caused by adhesion of microasperities to friction surfaces.
- (ii) Abrasive wear: Caused by cutting by hard, foreign particles or abrasive particles in oil.
- (iii) Surface fatigue wear: Caused by surface fatigue resulting from repeated stress and tribological chemical interactions.
- (iv) Chemical wear: Dominated by chemical reactions between friction surfaces and lubricant molecules.

In most cases, these types of wear more or less occur side by side. Mechanical conditions, types of lubricants and metal materials, oil temperatures, atmosphere, generation of friction heat, exo-electron emission, and other factors result in a wide range of complex phenomena on friction surfaces, making boundary lubrication problematic.

As shown in Figure 4, Solid [1] and solid [2] are in relative motion under given mechanical conditions (load and sliding speed). In the area of contact between the two solids, adhesion and

mutual transfer cause adhesive wear, while generated abrasive particles or hard foreign particles cause abrasive wear. In contrast, interactions between solid [1] or solid [2] and lubricant [3] or atmosphere [4] (for example, adsorption and chemical reaction) form a lubricating film that reduces friction and wear and prevents seizure. However, chemical reaction products are sometimes removed into the oil by shearing and dissolution, causing chemical wear.

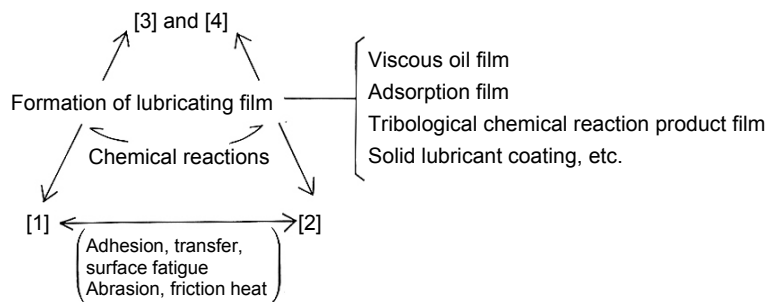
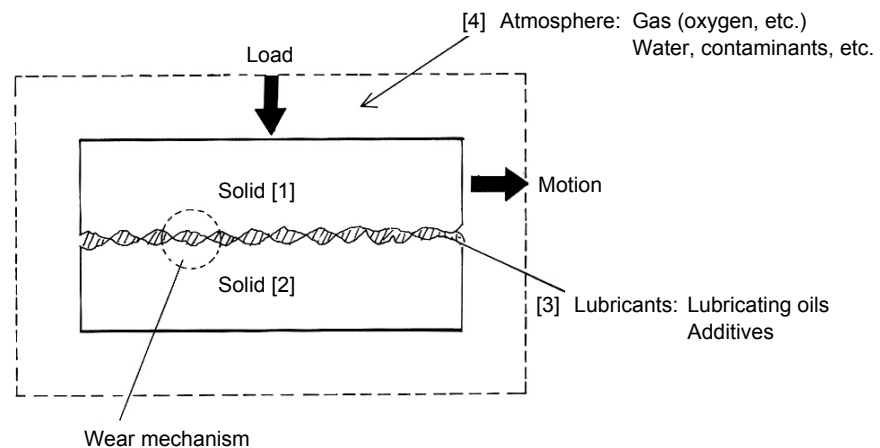


Figure 4: Wear under boundary lubrication

4. Formation of lubricating films

Listed below are factors that dominate film formation for so-called boundary lubricity, in which lubricant forms lubricating films on friction surfaces, reducing friction and wear and preventing seizures.

- (i) Formation of viscous oil films
- (ii) Formation of physical or chemical adsorption films
- (iii) Formation of in situ lubricating films
 - (a) Formation of polymer films (for example, friction polymers) on friction surface spots
 - (b) Formation of solid lubricant films
- (iv) Formation of inorganic reaction product films
- (v) Formation of solid lubricant coatings

These lubricating films vary in range of thicknesses from 20 to 30 Å of adsorbed molecules to micrometer scale reaction films. Oiliness improvers are chemical compounds that have long hydrocarbon chains in molecules terminating in strong acidic groups, which physically or chemically adsorb to friction surfaces to form lubricating films that prevent metallic contact and reduce friction and wear. Long chain fatty acids such as stearic acids, long chain fatty alcohols, and amine are typical oiliness improvers. Oiliness

improvers are suitable for low to medium load conditions but cannot be expected to provide lubrication under severe, high-load, high-temperature conditions. On the other hand, antiwear agents (for example, metal dithiophosphates and phosphoric acid esters) form reaction films that react with friction surfaces to reduce wear under low to medium loads and high-temperature conditions. In high-load conditions, surface asperities penetrate the oil film, causing metallic contact. The subsequent temperature increase at the friction surfaces and strong shear desorb or remove the oil film, increasing friction and wear and eventually resulting in seizures with total loss of lubrication. Extreme pressure agents (EP agents) react with the friction (metal) surfaces under this extreme-pressure lubrication condition to form a reaction coating with less shear strength than the metal to prevent seizure. The films formed under extreme-pressure lubrication conditions are generally inorganic reaction films. Iron sulfide and iron oxide coatings created by organic sulfur compounds are typical examples. Coatings by solid lubricants such as molybdenum disulfide and graphite are also effective.

5. Solid lubricants

Solid lubricants are solids applied to friction surfaces to reduce friction and wear and prevent surface damage. They may be powders, films, or composite materials. Solid lubricants are roughly classified as shown in Table 1. They include substances with layered structures such as molybdenum disulfide and graphite, use of which is particularly widespread. (As a typical example, Figure 5 shows the crystalline structure of graphite.) These solid lubricants are highly anisotropic, with weak bonding between particular crystal planes or molecules. Their self-lubrication properties provide low friction coefficients.

Main methods of application for solid lubricants include the following:

[1] Mixing with fats and fatty oils

- (a) Dispersed in oils or suspension
- (b) Added to grease

[2] Dry coating

- (a) Solid lubricants dispersed in vehicles are coated or sprayed on solid surfaces, and then dried.
- (b) Sputtering: In a vacuum, solid lubricants such as molybdenum disulfide are placed at the cathode and bombarded by inert gas ions to accumulate ejected particles on solid surfaces for coating.
- (c) Ion plating: In a vacuum, the plating material (such as gold or silver) is ionized and accelerated by an electric field to deposit a metal coating.

[3] Composite materials: Used to fill the surface irregularities of resins and ceramics.

[4] Solid lubricants are applied directly to sliding surfaces.

In all these methods, solid lubricants form a

coating on friction surfaces for solid lubrication even when oils are not desired, or when oils with which they are mixed are drained out.

Molybdenum disulfide and graphite are frequently used as thermally stable extreme-pressure agents. (Molybdenum disulfide is stable up to 350°C in air and up to 1,200°C in a vacuum; graphite is stable up to 500°C in air and up to 3,600°C in a vacuum.) These lubricants provide lubricity by physically forming solid films. They do not corrode substrate metals, unlike chemically reactive extreme-pressure agents such as organic sulfur compounds. However, molybdenum disulfide may decompose and release sulfur, causing corrosive wear, depending on conditions, and its lubrication working mechanism may be assumed in terms of iron sulfide coating formation by the released sulfur.

Another application of solid lubricants is reaction-generated coating. The coating may be formed on metal surfaces in advance by chemical reactions or during lubrication by friction heat and other factors (so-called in situ films). One example of the former pretreatment method is formation of iron sulfide films by treatment of metal surfaces with hydrogen sulfide. The resulting surfaces adsorb oiliness improvers such as fatty acids well, and adsorption improves wear resistance. The latter in situ method includes the use of organic molybdenum compounds containing sulfur. This compound decomposes under friction heat and forms a molybdenum disulfide coating on friction surfaces, demonstrating extreme pressure properties.

Table 1: Classification of solid lubricants

Type	Examples
[I] Metals and inorganic compounds (a) Layered structure compounds (b) Non-layered compounds (c) Soft metals	Molybdenum disulfide, graphite, boron nitride PbO, CaF ₂ Pb, Sn, Au, Ag, Cu
[II] Organic compounds (a) Fats, soaps, waxes (b) Polymers (c) Malleable substances	Beef tallow, lithium stearate, bee wax Polytetrafluoroethylene (PTFE), polyimide Phthalocyanine

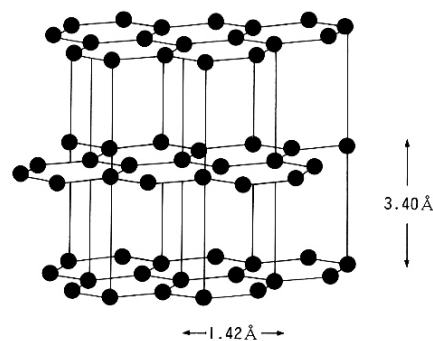


Figure 5: Crystalline structure of graphite

6. Friction modification

Some time has passed since the oil crisis of the 1970s, which focused attention on the importance of resource and energy conservation. With the goal of improving energy efficiency, aspects of lubrication are studied to achieve low friction and low wear by improving lubricants. In automobiles, which consume a particularly large share of petroleum, improved fuel efficiency has become a major concern worldwide. In other words, the goal is to improve engine oil to reduce friction and achieve energy conservation. If a base oil with lower viscosity than conventionally used products is used for the engine oil, the reduced viscous resistance reduces power losses. Reduced capacity to form viscous oil films due to reduced viscosity can be remedied by adding a friction modifier (an additive that adjusts the lubricant for desired friction characteristics). Friction modifiers include oiliness improvers such as fatty acids, extreme

pressure agents, and solid lubricants (for example, molybdenum disulfide and graphite). Improving fuel efficiency by adding molybdenum disulfide and/or graphite to the engine oil and achieving low friction and low wear using fatty acids and organic sulfur compounds together are two examples of friction modification.

Figure 6 shows the relationship between the Stribeck curve and friction modification. When the mechanical conditions of the load and the velocity are kept constant, the friction coefficient decreases in the hydrodynamic lubrication region as viscosity decreases. On the other hand, the capacity to form viscous oil films also decreases, and the system runs the risk of falling into a highly frictional boundary lubrication condition in which friction surfaces are in contact. Friction modification improves this situation, making possible lubrication in the region indicated by the dotted broken curve in the figure, where low friction is maintained.

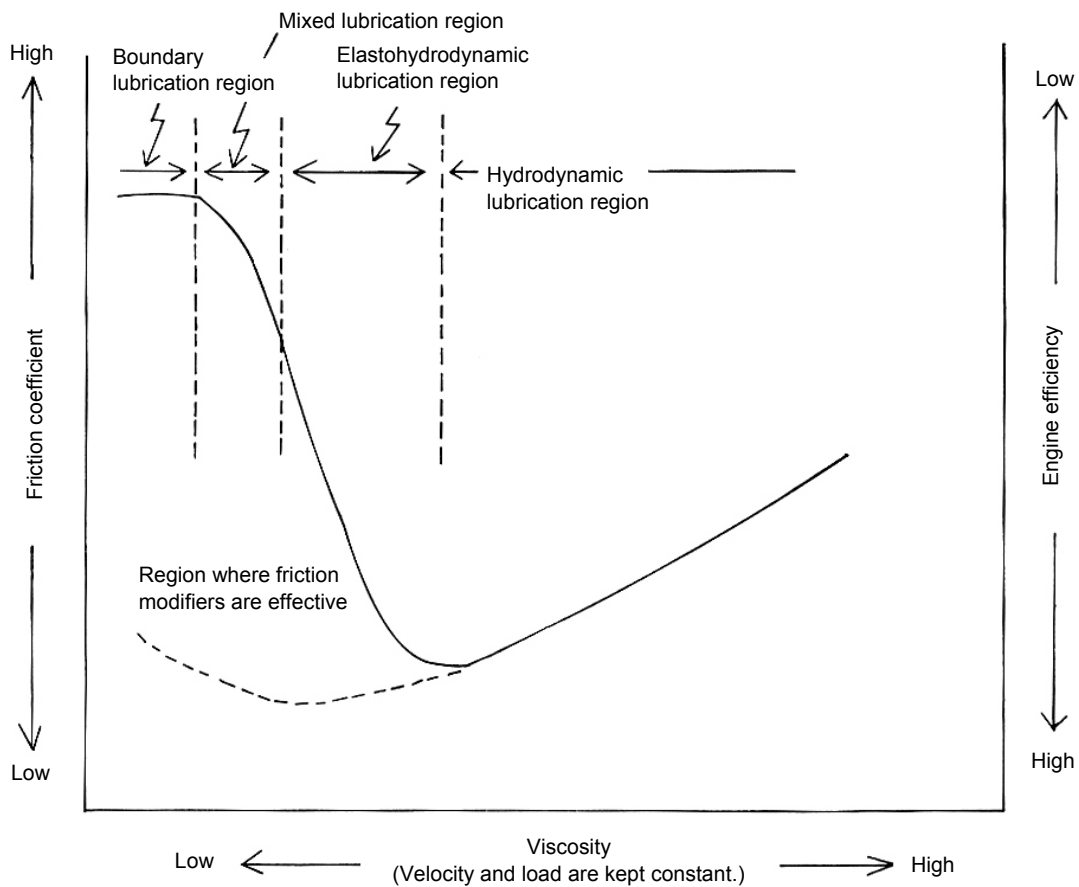


Figure 6: Relationship between Stribeck curve and friction modification

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