$$(H_{\min})_o = \frac{(h_{\min})_o}{R_{x,o}} = 3.63 U_o^{0.68} G^{0.49} W^{-0.073} (1 - e^{-0.68k_o})$$

= 3.63 × 2.087 × 10⁻⁷ × 65.29 × 1.785 × 0.9919
= 0.876 × 10⁻⁴ (21.156)

Thus

$$(h_{\min})_{a} = 0.876 \times 10^{-4} R_{ra} = 0.665 \ \mu m$$

In this case, the lubrication factor Λ is given by

$$\Lambda_o = \frac{0.665 \times 10^{-6}}{[(0.175)^2 + (0.0625)^2]^{1/2} \times 10^{-6}} = 3.58$$
(21.157)

Once again, it is evident that the smaller minimum film thickness occurs between the most heavily loaded ball and the inner race. However, in this case the minimum elastohydrodynamic film thickness is about three times the composite surface roughness, and the bearing lubrication can be deemed to be entirely satisfactory. Indeed, it is clear from Fig. 21.97 that very little improvement in the lubrication factor \tilde{F} and thus in the fatigue life of the bearing could be achieved by further improving the minimum film thickness and hence Λ .

21.4 BOUNDARY LUBRICATION

If the pressures in fluid-film-lubricated machine elements are too high, the running speeds are too low, or the surface roughness is too great, penetration of the lubricant film will occur. Contact will take place between asperities, leading to a rise in friction and wear rate. Figure 21.99 (obtained from Bowden and Tabor⁵⁶) shows the behavior of the coefficient of friction in the different lubrication regimes. It is to be noted in this figure that in boundary lubrication, although the friction is much higher than in the hydrodynamic regime, it is still much lower than for unlubricated surfaces. As the running conditions are made more severe, the amount of lubricant breakdown increases, until the system scores or seizes so badly that the machine element can no longer operate successfully.

Figure 21.100 shows the wear rate in the different lubrication regimes as determined by the operating load. In the hydrodynamic and elastohydrodynamic lubrication regimes, since there is no asperity contact, there is little or no wear. In the boundary lubrication regime the degree of asperity interaction and wear rate increases as the load increases. The transition from boundary lubrication to an unlubricated condition is marked by a drastic change in wear rate. Machine elements cannot operate successfully in the unlubricated region. Together Figs. 21.99 and 21.100 show that both friction and wear can be greatly decreased by providing a boundary lubricant to unlubricated surfaces.

Understanding boundary lubrication depends first on recognizing that bearing surfaces have asperities that are large compared with molecular dimensions. On the smoothest machined surfaces these asperities may be 25 nm (0.025 μ m) high; on rougher surfaces they may be ten to several hundred times higher. Figure 21.101 illustrates typical surface roughness as a random distribution of



Fig. 21.99 Schematic drawing showing how type of lubrication shifts from hydrodynamic to elastohydrodynamic to boundary lubrication as the severity of running conditions is increased. (From Ref. 56.)



Fig. 21.100 Chart for determining wear rate for various lubrication regimes. (From Ref. 57.)

hills and valleys with varying heights, spacing, and slopes. In the absence of hydrodynamic or elastohydrodynamic pressures these hills or asperities must support all of the load between the bearing surfaces. Understanding boundary lubrication also depends on recognizing that bearing surfaces are often covered by boundary lubricant films such as are idealized in Fig. 21.101. These films separate the bearing materials and, by shearing preferentially, provide some control of friction, wear, and surface damage.

Many mechanism, such as door hinges, operate totally under conditions (high load, low speed) of boundary lubrication. Others are designed to operate under full hydrodynamic or elastohydrodynamic lubrication. However, as the oil film thickness is a function of speed, the film will be unable to provide complete separation of the surfaces during startup and rundown, and the condition of boundary lubrication will exist. The problem from the boundary lubrication standpoint is to provide a boundary film with the proper physical characteristics to control friction and wear. The work of Bowden and Tabor,⁵⁶ Godfrey,⁵⁹ and Jones⁶⁰ was relied upon in writing the sections that follow.



Fig. 21.101 Lubricated bearing surfaces. (From Ref. 58.)

21.4.1 Formation of Films

The most important aspect of boundary lubrication is the formation of surface films that will protect the contacting surfaces. There are three ways of forming a boundary lubricant film; physical adsorption, chemisorption, and chemical reaction. The surface action that determines the behavior of boundary lubricant films is the energy binding the film molecules to the surface, a measure of the film strength. The formation of films is presented in the order of such a film strength, the weakest being presented first.

Physical Adsorption

Physical adsorption involves intermolecular forces analogous to those involved in condensation of vapors to liquids. A layer of lubricant one or more molecules thick becomes attached to the surfaces of the solids, and this provides a modest protection against wear. Physical adsorption is usually rapid, reversible, and nonspecific. Energies involved in physical adsorption are in the range of heats of condensations. Physical adsorption may be monomolecular or multilayer. There is no electron transfer in this process. An idealized example of physical adsorption of hexadecanol on an unreactive metal is shown in Fig. 21.102. Because of the weak bonding energies involved, physically adsorbed species are usually not very effective boundary lubricants.

Chemical Adsorption

Chemically adsorbed films are generally produced by adding animal and vegetable fats and oils to the base oils. These additives contain long-chain fatty acid molecules, which exhibit great affinity for metals at their active ends. The usual configuration of these polar molecules resembles that of a carpet pile with the molecules standing perpendicular to the surface. Such fatty acid molecules form metal soaps that are low-shear-strength materials with coefficients of friction in the range 0.10-0.15. The soap film is dense because of the preferred orientation of the molecules. For example, on a steel surface stearic acid will form a monomolecular layer of iron stearate, a soap containing 10^{14} molecules/cm² of surface. The effectiveness of these layers is limited by the melting point of the bearing metals, so that less reactive, inert metals like gold and platinum are not effectively lubricated by fatty acids.

Examples of fatty acid additives are stearic, oleic, and lauric acid. The soap films formed by these acids might reduce the coefficient of friction to 50% of that obtained by a straight mineral oil. They



Fig. 21.102 Physical adsorption of hexadecanol. (From Ref. 59.)

21.4 BOUNDARY LUBRICATION

provide satisfactory boundary lubrication at moderate loads, temperatures, and speeds and are often successful in situations showing evidence of mild surface distress.

Chemisorption of a film on a surface is usually specific, may be rapid or slow, and is not always reversible. Energies involved are large enough to imply that a chemical bond has formed (i.e., electron transfer has taken place). In contrast to physical adsorption, chemisorption may require an activation energy. A film may be physically adsorbed at low temperatures and chemisorbed at higher temperatures. In addition, physical adsorption may occur on top of a chemisorbed film. An example of a film of stearic acid chemisorbed on an iron oxide surface to form iron stearate is shown in Fig. 21.103.

Chemical Reaction

Films formed by chemical reaction provide the greatest film strength and are used in the most severe operating conditions. If the load and sliding speeds are high, significant contact temperatures will be developed. It has already been noted that films formed by physical and chemical adsorption cease to be effective above certain transition temperatures, but some additives start to react and form new high-melting-point inorganic solids at high temperatures. For example, sulfur will start to react at about 100°C to form sulfides with melting points of over 1000°C. Lubricants containing additives like sulfur, chlorine, phosphorous, and zinc are often referred to as extreme-pressure (EP) lubricants, since they are effective in the most arduous conditions.

The formation of a chemical reaction film is specific; may be rapid or slow (depending on temperature, reactivity, and other conditions); and is irreversible. An idealized example of a reacted film of iron sulfide on an iron surface is shown in Fig. 21.104.

21.4.2 Physical Properties of Boundary Films

The two physical properties of boundary films that are most important in determining their effectiveness in protecting surfaces are melting point and shear strength. It is assumed that the film thicknesses involved are sufficient to allow these properties to be well defined.

Melting Point

The melting point of a surface film appears to be one discriminating physical property governing failure temperature for a wide range of materials including inorganic salts. It is based on the observation that only a surface film that is solid can properly interfere with potentially damaging asperity contacts. Conversely, a liquid film allows high friction and wear. Under practical conditions, physically adsorbed additives are known to be effective only at low temperatures, and chemisorbed addi-



Fig. 21.103 Chemisorption of stearic acid on iron surface to form iron stearate. (From Ref. 59.)



Fig. 21.104 Formation of inorganic film by reaction of sulfur with iron to form iron sulfide. (From Ref. 59.)

tives at moderate temperatures. High-melting-point inorganic materials are used for high-temperature lubricants.

The correlation of melting point with failure temperature has been established for a variety of organic films. An illustration is given in Fig. 21.105 (obtained from Russell et $al.^{61}$) showing the friction transition for copper lubricated with pure hydrocarbons. Friction data for two hydrocarbons (mesitylene and dotriacontane) are given in Fig. 21.105 as a function of temperature. In this figure the boundary film failure occurs at the melting point of each hydrocarbon.

In contrast, chemisorption of fatty acids on reactive metals yields failure temperature based on the softening point of the soap rather than the melting point of the parent fatty acid.

Shear Strength

The shear strength of a boundary lubricating film should be directly reflected in the friction coefficient. In general, this is true with low-shear-strength soaps yielding low friction and high-shear-



Fig. 21.105 Chart for determining friction of copper lubricated with hydrocarbons in dry helium. (From Ref. 61.)

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strength salts yielding high friction. However, the important parameter in boundary friction is the ratio of shear strength of the film to that of the substrate. This relationship is shown in Fig. 21.106, where the ratio is plotted on the horizontal axis with a value of 1 at the left and zero at the right. These results are in agreement with experience. For example, on steel an MOS_2 film gives low friction and Fe_2O_3 gives high friction. The results from Fig. 21.106 also indicate how the same friction value can be obtained with various combinations provided that the ratio is the same. It is important to recognize that shear strength is also affected by pressure and temperature.

21.4.3 Film Thickness

Boundary film thickness can vary from a few angstroms (adsorbed gas) to thousands of angstroms (chemical reaction films). In general, as the thickness of a boundary film increases, the coefficient of friction decreases. This effect is shown in Fig. 21.107*a*, which shows the coefficient of friction plotted against oxide film thickness formed on a copper surface. However, continued increases in thickness may result in an increase in friction. This effect is shown in Fig. 21.107*b*, which shows the coefficient of friction plotted against indium film thickness on copper surface. It should also be pointed out that the shear strengths of all boundary films decrease as their thicknesses increase, which may be related to the effect seen in Fig. 21.107*b*.

For physically adsorbed or chemisorbed films, surface protection is usually enhanced by increasing film thickness. The frictional transition temperature of multilayers also increases with increasing number of layers.

For thick chemically reacted films there is an optimum thickness for minimum wear that depends on temperature, concentration, or load conditions. The relationship between wear and lubricant (or additive) reactivity is shown in Fig. 21.108. Here, if reactivity is not great enough to produce a thick enough film, adhesion wear occurs. On the other hand, if the material is too reactive, very thick films are formed and corrosive wear ensues.

21.4.4 Effect of Operating Variables

The effect of load, speed, temperature, and atmosphere can be important for the friction and wear of boundary lubrication films. Such effects are considered in this section.

On Friction

Load. The coefficient of friction is essentially constant with increasing load.

Speed. In general, in the absence of viscosity effects, friction changes little with speed over a sliding speed range of 0.005 to 1.0 cm/sec. When viscosity effects do come into play, two types of behavior are observed, as shown in Fig. 21.109. In this figure relatively nonpolar materials such as mineral oils show a decrease in friction with increasing speed, while polar fatty acids show the opposite trend. At higher speeds viscous effects will be present, and increases in friction are normally observed.







Fig. 21.107 Chart for determining relationship of friction and thickness of films on copper surfaces. (From Ref. 62.)



Fig. 21.108 Relationship between wear and lubricant reactivity. (From Ref. 63.)



Fig. 21.109 Effect of speed on coefficient of friction. (From Ref. 64.)

Temperature. It is difficult to make general comments on the effect of temperature on boundary friction since so much depends on the other conditions and the type of materials present. Temperature can cause disruption, desorption, or decomposition of boundary films. It can also provide activation energy for chemisorption or chemical reactions.

Atmosphere. The presence of oxygen and water vapor in the atmosphere can greatly affect the chemical processes that occur in the boundary layer. These processes can, in turn, affect the friction coefficient.

On Wear

Load. It is generally agreed that wear increases with increasing load, but no simple relationship seems to exist, at least before the transition to severe wear occurs. At this point a discontinuity of wear versus load is often like that illustrated in Fig. 21.100.

Speed. For practical purposes, wear rate in a boundary lubrication regime is essentially independent of speed. This assumes no boundary film failure due to contact temperature rise.

Temperature. As was the case for friction, there is no way to generalize the effect of temperature on wear. The statement that pertains to friction also pertains to wear.

Atmosphere. Oxygen has been shown to be an important ingredient in boundary lubrication experiments involving load-carrying additives. The presence of oxygen or moisture in the test atmosphere has a great effect on the wear properties of lubricants containing aromatic species.

21.4.5 Extreme-Pressure (EP) Lubricants

The best boundary lubricant films cease to be effective above $200-250^{\circ}$ C. At these high temperatures the lubricant film may iodize. For operation under more severe conditions, EP lubricants might be considered.

Extreme-pressure lubricants usually consist of a small quantity of an EP additive dissolved in a lubricating oil, usually referred to as the base oil. The most common additives used for this purpose contain phosphorus, chlorine, or sulfur. In general, these materials function by reacting with the surface to form a surface film that prevents metal-to-metal contact. If, in addition, the surface film formed has a low shear strength, it will not only protect the surface, but it will also give a low coefficient of friction. Chloride films give a lower coefficient of friction ($\mu = 0.2$) than sulfide films ($\mu = 0.5$). Sulfide films, however, are more stable, are unaffected by moisture, and retain their lubricating properties to very high temperatures.

Although EP additives function by reacting with the surface, they must not be too reactive, otherwise chemical corrosion may be more troublesome than frictional wear. They should only react when there is a danger of seizure, usually noted by a sharp rise in local or global temperature. For this reason it is often an advantage to incorporate in a lubricant a small quantity of a fatty acid that can provide effective lubrication at temperatures below those at which the additive becomes reactive.



Fig. 21.110 Graph showing frictional behavior of metal surfaces with various lubricants. (From Ref. 56.)

Bowden and Tabor⁵⁶ describe this behavior in Fig. 21.110, where the coefficient of friction is plotted against temperature. Curve A is for paraffin oil (the base oil) and shows that the friction is initially high and increases as the temperature is raised. Curve B is for a fatty acid dissolved in the base oil: it reacts with the surface to form a metallic soap, which provides good lubrication from room temperature up to the temperature at which the soap begins to soften. Curve C is for a typical EP additive in the base oil; this reacts very slowly below the temperature T_c , so that in this range the lubrication is poor, while above T_c the protective film is formed and effective lubrication is provided to a very high temperature. Curve D is the result obtained when the fatty acid is added to the EP solution. Good lubrication is provided by the fatty acid below T_c , while above this temperature the greater part of the lubrication is due to the additive. At still higher temperatures, a deterioration of lubricating properties will also occur for both curves C and D.

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