

# LUBRICATION AND LUBRICANTS

## 1. Introduction

Lubrication is a process in which a film of lubricant is inserted between rubbing surfaces for the purpose of controlling friction and/or to reduce wear of the surfaces. These films are designed to minimize contact between the rubbing surfaces and to shear easily so that the frictional force opposing the rubbing motion is low. Lubricants may be liquids, solids, gases, or greases. Lubricating oils and greases contain refined or synthesized base oils from animal, vegetable or mineral (petroleum) origin, and a variety of additives to improve their lubricating and other characteristics.

Lubrication is a major component of *tribology*, defined as *the science and technology concerned with interacting surfaces in relative motion, including friction, lubrication, wear and erosion* (1).

Tribology and lubrication are ancient arts. In his splendid *History of Tribology* (2), Professor Dowson traces the development of these arts and sciences, and describes the outstanding artists and scientists responsible, from the paleolithic age to the end of the twentieth century. He reports archeological evidence that bitumen was used to lubricate potters wheels 5000 years ago. Water-lubricated sliding bearings were used in Egypt ~2400 BC to transport large objects. A chariot wheel from ~1400 BC was found with traces of tallow as lubricant, and the Chinese had lubricated metal wheel bearings with leather seals to hold the lubricant in place in the fourth century BC (2).

The word “tribology” first appeared in *Lubrication (Tribology) Education and Research—A Report on the Present Position and Industries Needs*, Department of Education and Science (UK), 1966. This is often called *The Jost Report*, after H. Peter Jost, the chairman of the British Lubrication Engineering Working Group, which prepared the report. The word is derived from the Greek *tribein*, meaning “to rub”, and *logos*, meaning “reading” or “study”. Tribology is literally the study of rubbing. The Working Group defined it more precisely as “the science and technology of interacting surfaces in relative motion and the practices related thereto” (3).

The Jost Report was part of an effort to focus attention on the “scientific, technological, economic and environmental issues” (2) involved in the study and practice of tribology. Another purpose was to bring together the many, and often splintered engineering and scientific disciplines that deal with this technology. Dowson speculates that the dramatic progress in this field in the final third of the twentieth century may have been significantly influenced by these efforts in the 1960s (2).

The 1966 report by the British Lubrication Engineering Working Group demonstrated to industry and government the impact of friction, wear, and lubrication on the nation’s economy, and the value of further research in tribology. That report showed, eg, that the most significant value of better lubrication (91%) comes from increased productivity, lower maintenance and replacement costs, and lower investment cost. Direct energy savings (5%), and savings in the cost of lubrication, in manpower and material (4%), account for the remainder.

Tribology is a multidisciplinary science that embraces lubrication, friction, wear, properties of lubricants, surface characterization, bearing materials, and the selection and design of lubricating systems. The lubrication engineer would add to this list lubricant and coolant selection, plant lubrication and maintenance programs, and machine condition monitoring.

## 2. Fundamentals of Lubrication

Tribology, by definition, is concerned with interacting surfaces in relative motion. It is appropriate, therefore, to begin the discussion of lubrication fundamentals by describing the characteristics of tribological surfaces.

**2.1. The Nature of Interacting Surfaces in Relative Motion.** Tribological surfaces are the load-bearing surfaces on the moving parts of machines. They include surfaces on crankshaft rod and main bearings, radial and thrust bearings on steam and gas turbines, cams and valve lifters, pistons and cylinders, natural and artificial hip joints, ball and roller bearings, machine tool slideways, cutting tools, magnetic information storage devices, and microelectromechanical systems (MEMS). Despite their appearance and finishing efforts, these surfaces are not perfectly smooth. There are microscopic irregularities; gently sloping hills and valleys called asperities on them.

If an imaginary surface is drawn through a real surface, such that the volume of all of the material above the imaginary surface is equal to the volume of voids below that surface, the roughness of the real surface,  $R_a$ , can be defined as

$$R_a = (|y_1| + |y_2| + \cdots + |y_n|)/n \quad (1)$$

Where  $R_a$  is the center line or arithmetic average of the absolute distances,  $y_i$ , from the imaginary surface (mean line) for a given sampling length (usually 0.80 mm).

Roughness ( $R_a$ ) values of machined surfaces range from 0.025  $\mu\text{m}$  for ball bearing surfaces to 25  $\mu\text{m}$  clearance surfaces on rough machine parts (4–6). The roughness of computer hard disk surfaces is measured in angstroms (Å) or nanometers (nm) (7).

The total profile of a surface consists of a “waviness” and a roughness component. The parameter  $R_a$ , although it is the most common measure of surface roughness, is insensitive to the shape or waviness of the profile. A more useful parameter is the root-mean-square (rms) roughness,  $R_q$ .

$$R_q = [(y_1^2 + y_2^2 + \cdots + y_n^2)/n]^{1/2} \quad (2)$$

Where  $R_q$  is the rms deviation of  $y_i$  from the mean line for a given sampling length (4). The rms roughness of computer hard disk surfaces is <2 nm (7).

The most repeatable of the roughness parameters is the 10 points height,  $R_z$ .

$$R_z = [(P_1 + P_2 + \cdots + P_5) - (V_1 + V_2 + \cdots + V_5)]/5 \quad (3)$$

Where  $R_z$  is the average distance between the five highest peaks ( $P_i$ ) and the five deepest valleys ( $V_i$ ) within the sampling length. It is also linked with the machining parameter  $S^2/8r$ , where  $S$  is the feed rate and  $r$  is the tool radius (4).

Another index of roughness is  $R_t$ , the maximum peak-to-valley height.

$$R_t = R_p + R_v \quad (4)$$

Where  $R_p$  is the maximum peak height and  $R_v$  is the maximum valley depth within the sampling length (4).

The description of the test disk used in the ASTM D 6425-02 test method for measuring friction and wear illustrates the impact of surface texture on these quantities (8) and is shown below and used with ASTM's permission.

*Test Disk*, AISI 52100 Steel,  $62 \pm 1$  HRC Hardness. The surfaces of the disk are lapped and free of lapping raw materials. The topography of the disk will be determined by four values:  $0.005 \mu\text{m} < R_z < 0.65 \mu\text{m}$ ;  $0.035 \mu\text{m} < R_a < 0.050 \mu\text{m}$ ;  $0.020 \mu\text{m} < R_p < 0.035 \mu\text{m}$ ;  $0.050 \mu\text{m} < R_v < 0.075 \mu\text{m}$

Four different measures of surface topography are specified for the disk in order to get acceptable reproducibility of the test method (9).

Approximate roughness indexes obtained with various metal-working processes are

Production process	$R_t, \mu\text{m}$	$R_a, \mu\text{m}$
turning	4.00–25.0	0.500–3.0
grinding	2.00–6.0	0.400–0.8
milling	1.50–20.0	0.200–2.0
boring	0.50–20.0	0.050–1.6
honing	0.03–1.0	0.015–0.2
lapping	0.03–0.6	0.015–0.1

Engineering surfaces also differ in composition from the underlying bulk material. A metal bearing, eg, will have a work hardened layer at the surface, over which an oxide layer forms, on top of which is an adsorbed layer of moisture and gases. When two such surfaces come in moving contact, their surface structures, compositions, and the interaction between opposing asperities accounts for a major portion of the friction between them and much of the wear that inevitably occurs (10–12).

For example, without the oxide and adsorbed layers, coefficients of friction  $> 4$  have been measured in a vacuum of 0.133 mPa on surfaces cleaned by abrasive cloth and heated. The coefficient decreased considerably when oxygen was admitted to a pressure of 0.133 Pa (13). The oxide and adsorbed layers on metal surfaces can, therefore, be considered as lubricating films.

**2.2. Friction.** When two of these surfaces are brought together, they initially touch at the highest asperities. The load,  $N$ , normal to the surfaces at

the contact points causes the asperities to deform until the pressure in the resulting contact areas just equals the yield pressure,  $p$ , of the asperities. The sum of these contact areas is the real contact area,  $A_r$ . The yield pressure is equivalent to the Brinell Hardness Number (BHN), in consistent units, measured at the surface of the material (4).

$$A_r = N/p = N/BHN \quad (5)$$

The real area of contact is a minute fraction of the total surface area. For example, with a typical bearing contact stress of 3 MPa and a bronze bearing asperity yield pressure of 500 MPa, <1.0% of the nominal area would involve asperity contact (14).

As the load on the surfaces increases, the asperities continue to deform, the softer surface more than the other. More of the asperities come in contact and the real area of contact grows. The opposing surfaces also tend to adhere or bond to each other in the contact area. The shear strength of these bonds depends on the time of contact and the difference in composition of the two surfaces.

Sliding of one of these nonlubricated surfaces across the other requires a friction force,  $F$ , to displace the contacting asperities. This force includes several components, among them: a shear or adhesion component arising from bonding of the contacting asperities; a plowing or deformation component, arising from the interlocking of asperities; a lifting component to raise asperities over the roughness of the mating surfaces.

The shearing component,  $F_s$ , may account for 90% or more of the total friction force (14). This component is proportional to the shear strength,  $s$ , of the asperity junctions:

$$F_s = A_r s \quad (6)$$

More detailed descriptions of surface texture, surface structure, and composition and the real area of contact will be found in Refs. (4–6,12,13,15,16).

**2.3. Coefficient of Friction.** The coefficient of friction,  $f$ , of a pair of contacting surfaces is defined as the ratio of the total frictional force to the normal force or load. It can also be expressed as the ratio of shear strength,  $s$ , to the yield pressure,  $p$ , at the asperity junctions.

$$f = F/N = s/p \quad (7)$$

If there is a lubricating film on the surfaces, the coefficient of friction is the ratio of the shear strength of the surface film,  $s_f$ , to the yield pressure,  $p_m$  of the substrate or backing material.

$$f = s_f/p_m \quad (8)$$

If a shear force is gradually applied to one of two dry, unlubricated surfaces in contact, the surface will not move until the force is great enough to overcome

the shear strength of the asperity contacts. The ratio of the shear force required to start motion to the normal force on the surfaces is the static coefficient of friction. Once motion starts, less force is needed to keep the surface moving at a constant velocity. The coefficient of friction during sliding is the kinetic or dynamic coefficient.

The static coefficient measured for a hard steel surface on another hard steel surface is 0.78. The dynamic coefficient measured for hard steel on hard steel is 0.42. When a thin film of light mineral oil is applied to these surfaces, the static coefficient drops to 0.23. The dynamic coefficient with a light oil film drops to  $\sim 0.1$ . Adding a friction modifier to the oil can reduce or reverse the difference between the two coefficients. Adding stearic acid to the lubricant, eg, for hard steel on hard steel, reduces the static coefficient to 0.0052, which is lower than the dynamic coefficient, 0.029 (17).

An extensive Friction and Wear Databank is found in Ref. 18. Tables of the coefficient of friction values for a wide variety of material combinations are also available in Refs. 19 and 20 and many other sources. These data, however, should be used with caution. The coefficient of friction varies with changes in humidity, gas pressure, time, temperature, sliding speed, surface quality, the shape of the contact region, the method of testing, and other variables. Where high reliability is needed, the friction should be measured using a prototype device under design conditions (20).

**2.4. Wear.** The principal types of wear in sliding contacts are adhesive, abrasive, and corrosive wear. Fatigue wear occurs in concentrated contacts (ball and roller bearings, gears, cams, and automotive valve lifters) under the combination of sliding and rolling (21).

The Archard equation reported by Rabinowicz (21) gives a simple, quantitative relationship for predicting the adhesive wear rate:

$$V = kNx/p \quad (9)$$

where  $V$  = wear volume,  $k$  = wear coefficient,  $N$  = normal load,  $x$  = sliding distance,  $p$  = yield stress or indentation hardness.

Values of  $k$  for several unlubricated material combinations are shown in Table 1 (14). Others will be found in Ref. 18 and in Refs. (21–24).

Adhesive wear is material separated or transferred during the shearing of asperity contacts. These wear particles, and other particulate surface contaminants that are hard enough to damage the surface, cause abrasive wear. Abrasive wear is the removal of material by ploughing, cutting, or scratching. Its rate generally obeys equation 9 and the wear coefficients tend to be higher than the adhesive coefficients (21). Corrosive wear is the wearing away of the products of galvanic or chemical corrosion of the surface. There is no simple equation that characterizes this type of wear.

Current broader discussions of the friction and wear phenomena are found in Refs. 13, 25, and 26.

**2.5. Viscosity.** Viscosity, or resistance to flow is the most important property of a lubricating oil. It was defined by Newton (27) as the ratio of the

shear stress,  $T$ , divided by the shear rate,  $dU/dh$ , in a fluid during flow. Newton's law of viscosity is given in equation 10 (28).

$$T = F_s/A_s = \mu \cdot dU/dh \quad (10)$$

The fluid in contact with the surface of the moving plate has the same velocity,  $U$ , as the plate. The fluid in contact with the stationary plate has zero velocity. There is, therefore, a shear stress,  $T$ , on the fluid equal to the force,  $F_s$ , required to keep the plate moving divided by the area,  $A_s$ , of the moving plate, and is proportional to the velocity gradient,  $dU/dh$ , of the fluid. The parameter  $F_s$  is a frictional force and the coefficient,  $\mu$ , is the dynamic viscosity of the fluid (29). The unit of dynamic viscosity in the System International (SI) is pascal-second (Pa·s). The customary unit is centipoise (cP), which is  $\text{Pa} \cdot \text{s} \times 10^{-3}$ .

Schoff and Kamarchik (30) describe methods of measuring the viscosity of a wide variety of materials. Standard methods for measuring the dynamic viscosity of lubricating oil can be found in Refs. 31–34.

Generally, however, it is easier to measure the kinematic viscosity,  $\nu$ , of a lubricating oil using a capillary viscometer. Kinematic viscosity is the dynamic viscosity divided by the density,  $d$ , of the fluid at the same temperature.

$$\nu = \mu/d \quad (11)$$

The customary unit for kinematic viscosity is centistoke (cSt), which is equivalent to millimeters squared per second ( $\text{mm}^2/\text{s}$ ). The most common method for accurate measurement of kinematic viscosity over a wide temperature range is ASTM D 445 (35). Older literature may report kinematic viscosities of lubricating oils in Saybolt Universal Seconds (SUS). ASTM D2161-04, has been retained for the purpose of calculating kinematic viscosity in centistokes from SUS or SFS data (36).

**Viscosity–Temperature Relationship.** The MacCoull equation, also called the Walther equation, relates the kinematic viscosity,  $\nu$ , of a liquid to its temperature.

$$\log \log Z = A - B(\log T) \quad (12)$$

Where  $Z = (\nu + 0.7)$  for  $2.00 \text{ cSt} \leq \nu \leq 2 \times 10^7 \text{ cSt}$ ;  $A$  and  $B$  = constants, and  $T$  = absolute temperature,  $^\circ\text{K}$  = temperature,  $^\circ\text{C} + 273.2$ .

It is applicable to homogeneous liquid lubricants with conventionally refined hydrocarbon base oils and is valid between the cloud point at low temperature and the initial boiling point ( $\sim 340^\circ\text{C}$ ) at higher temperatures. (The cloud point is the temperature at which a cloud of wax crystals first appears when it is cooled under conditions prescribed in ASTM D 2500.) This equation is the basis of the viscosity–temperature charts described in ASTM D 341 (37).

Oils with ester, phosphate, silicone, and synthesized hydrocarbon base oils follow the MacCoull (Walther) relationship over the range of  $-18$  to  $175^\circ\text{C}$  to within 5%. Many esters, synthesized hydrocarbons, and low pour point mineral oils exhibit low temperature ( $-40$  to  $-54^\circ\text{C}$ ) viscosities substantially below MacCoull equation predictions (38).

**Viscosity Index.** Another widely used and accepted measure of the variation of viscosity with temperature is the viscosity index (VI). The higher the VI, the lower is the variation of viscosity with temperature. The VIs for oils having values  $< 100$  are calculated by

$$VI = 100[(L - U)/(L - H)] \quad (13)$$

where  $U$  = kinematic viscosity at  $40^\circ\text{C}$  of the oil whose viscosity index is to be calculated;  $L$  = kinematic viscosity at  $40^\circ\text{C}$  of a "0" VI oil with the same viscosity at  $100^\circ\text{C}$  as the unknown;  $H$  = kinematic viscosity at  $40^\circ\text{C}$  of a "100" VI oil with the same viscosity at  $100^\circ\text{C}$  as the unknown.

Values of  $H$  and  $L$  for viscosities of 2 cSt and above are given in ASTM D 2270 (39).

Equation 13 gives confusing results for VI values  $> 100$ . Viscosity indexes of 100 or greater are calculated by the empirical formula (39):

$$VI = [((\text{antilog } N) - 1)/0.00715 + 100] \quad (14)$$

where  $Y^N = H/U$  and  $Y$  = kinematic viscosity at  $100^\circ\text{C}$  of the oil whose viscosity index is to be calculated.

Viscosity index is sometimes used as a measure of the quality of lubricating oil, especially for selecting base stocks for automotive engine oils and automatic transmission fluids. This is not always applicable, however. The role of viscosity index in base stock selection is described later.

Several aromatic type fluids, polyphenyl ethers, aryl phosphate esters, and halogenated aromatic hydrocarbons have negative VIs.

**Effect of Pressure on Viscosity.** The lubricant film pressure in the concentrated contact areas of rolling element bearings, gears, cams, etc, can be as high as 2000–3000 MPa. The viscosity of the film at these pressures could be a million times higher than that of the lubricating oil at atmospheric pressure, as illustrated in Fig. 1, or the lubricant may have solidified (38,40). The rate of viscosity increase with pressure of a liquid lubricant varies with its composition and chemical structure and with temperature and pressure.

Traction drives, found in some industrial machinery and the toroidal drives in some continuously variable transmissions (CVTs) depend on this property of traction fluids to transfer power.

Generalized pressure–temperature–viscosity relationships from extensive data on petroleum and synthetic oils are described in Refs. (14,41,42).

**Newtonian Versus Non-Newtonian Behavior.** If the viscosity of a fluid subjected to shear is independent of the rate of shear or magnitude of the shear stress, it is a Newtonian fluid. Most industrial lubricating and hydraulic oils are Newtonian fluids.

If the viscosity changes with shear stress or shear rate, the fluid is non-Newtonian. This behavior is typical of multigrade engine oils and other oils containing polymeric viscosity improvers.

The rate of decline in viscosity in a non-Newtonian lubricating oil is initially slow, then reaches a maximum, and finally slows again. At very high shear rates, the viscosity tends to level out and approach that of the base oil.

Grease also behaves in a non-Newtonian manner. At low shear rate, it acts like a high viscosity semisolid and “stays in place”. In a bearing, under high shear rate, it acts more like its base oil and supports full fluid lubricating films.

**2.6. Lubrication Regimes.** In the full fluid film regimes, the moving, load-bearing surfaces are completely separated. There is no contact between them. Resistance to motion arises solely from the internal friction of the fluid, a function of its viscosity. Adhesive wear is absent. Wear may occur from surface fatigue or from contamination of the fluid with corrosive or abrasive substances.

The coefficient of friction in a liquid lubricated system is dependent on, among other things, the lubricant viscosity, the relative speed of the surfaces, and the load on the surfaces. In a journal bearing, eg, the lubricant film thickness and the coefficient of friction are functions of the dimensionless Sommerfeld bearing characteristic number  $S$ .

$$S = (R^2/C^2)ZN/P \quad (15)$$

where  $P$  is the average pressure on the bearing surface,  $W/2RL$ ;  $Z$  is the dynamic viscosity,  $\mu$ , of the fluid; and  $N$  is the rotational speed of the journal,  $U/2\pi R$ .

The relationship between the kinetic coefficient of friction and the dimensionless quantity,  $ZN/P$ , is illustrated in Fig. 2 (10). This is known as a Stribeck curve.

At values of  $ZN/P$  greater than  $\sim 30$ , lubrication is in the full fluid film regime. Friction increases with increasing  $ZN/P$  because of increasing resistance to flow. As  $ZN/P$  is reduced, by reductions in the speed or viscosity, or by increases in load, the coefficient will reach a minimum value. Further reduction in  $ZN/P$  leads to partial breakdown in the fluid film and lubrication is in the mixed-film regime. Friction increases as  $ZN/P$  decreases in this regime, as more and more of the load is carried by asperity contact and less by fluid-film pressure. Finally, a point is reached, as  $ZN/P$  gets smaller, where there is no fluid pressure, the rate of increase in the coefficient of friction starts to level out, and lubrication is in the thin-film boundary regime (43). Ideally, a bearing is designed to operate where the coefficient of friction is at its minimum.

**Hydrodynamic Lubrication Regime.** Rohde (44) and Dowson (45) remind us that the basic mechanism of fluid-film lubrication was explained by Reynolds (46) in 1886, based on the earlier work of Petrov (47), and Tower (48).

The fundamental requirements of lubrication in the hydrodynamic regime are the formation of a wedge-shaped film; and generation of pressure in the film, sufficient to keep the surfaces apart, by the motion of the surfaces themselves.

The pressure distribution in the lubricating film of the sliding bearing illustrated in Fig. 3 (29), moving with velocity  $U$  relative to a slanted stationary pad in a fluid with viscosity  $\mu$ , and assuming no flow out of the sides of the bearing, is (49)

$$p = 6 \mu Ux(h - h_2)/h^2(h_1 + h_2) \quad (16)$$



The total force  $P$  that the bearing will support per unit width is

$$p = [6 \mu UB^2 / (h_1 - h_2)^2] [\ln((h_1/h_2)) - 2[(h_1 - h_2)/(h_1 + h_2)]] \quad (17)$$

and the frictional force  $F$  required to move the slider at speed  $U$  is

$$F = [2 \mu UB / (h_1 - h_2)] [2 \ln(h_1/h_2) - 3(h_1 - h_2)/(h_1 + h_2)] \quad (18)$$

The analysis of hydrodynamic fluid films assumes laminar flow in the film, ie, a Reynolds number,  $Re$ ,  $< 1000$ .

$$Re = U \rho h / \mu = Uh / \nu \quad (19)$$

where  $U$  = velocity,  $\rho$  = density,  $h$  = average film thickness,  $\mu$  = dynamic viscosity,  $\nu$  = kinematic viscosity.

Transition from laminar flow to turbulent flow starts when the  $Re$  is  $\sim 1000$  and the flow is completely turbulent at a  $Re$  of 1600 (50).

In a journal bearing, the wedge is formed because the diameter of the journal is smaller than that of the bearing. As the journal starts to rotate, its centerline moves away from that of the bearing. The rotating journal drags, or pumps the lubricant through the wedge, against the resistance to flow, and increases the pressure in the fluid until the journal is lifted off the bearing surface. The load carrying capacity  $W$  of a journal bearing is (51)

$$W = (\mu UR^2 L / C^2) 12 \pi \varepsilon / (2 + \varepsilon^2)(1 - \varepsilon^2)^{1/2} \quad (20)$$

where  $\mu$  = lubricant viscosity,  $U$  = journal peripheral speed,  $R$  = journal radius,  $C$  = clearance = bearing radius - journal radius,  $L$  = axial length of the bearing,  $\varepsilon$  = eccentricity = center offset distance  $e$ /clearance  $C$ .

Bearings designed for hydrodynamic lubrication include journal and thrust bearings in steam and gas turbines, and main and rod bearings for automotive engine crankshafts.

**Elastohydrodynamic (EHD) Lubrication Regime.** The shapes of sliding surface bearings designed for hydrodynamic lubrication have a high degree of conformity, a relatively large contact area, and low unit loading, such that the effect of pressure on viscosity can be neglected. In contrast, the surfaces in a rolling element bearing and on gear teeth are nonconforming. Surface contact is concentrated at a point in ball bearings or along a line in roller bearings and gears. Contact pressure, therefore, is high enough to cause elastic deformation of the contacting surfaces, forming a small area of contact. The viscosity of liquid lubricants entering the contact area increases exponentially and may solidify. Since the viscosity of the lubricant is affected by the elastic deformation of the surfaces, as well as other fluid properties, this lubrication regime is called elastohydrodynamic or EHD.

The hydrodynamic pressure developed in the lubricant is sufficient to separate the surfaces at the leading edge of the contact area. As the lubricant is

drawn into the contact, its pressure and viscosity increase further, keeping the surfaces apart. During contact, the fluid acts like an elastic solid, so that it cannot escape the contact except in the direction of rolling (52).

As the lubricant comes out of the contact area, there is a sharp pressure spike, followed by a sudden pressure drop so extreme that it causes a bulge in the rolling surfaces. The minimum film thickness is at the location of this bulge. The pressure spike and sudden film restriction directly affect the rolling element fatigue life (53). The Dowson - Higginson equation for minimum film thickness (54,55) is

$$h_{\min}/R = 1.6(\alpha E')^{0.6}(\mu U/E'R)^{0.7}(P/E')^{-0.13} \quad (21)$$

where  $R$  is the effective radius of the contacting surfaces,  $\alpha$  is the viscosity-pressure coefficient,  $E'$  is the effective Young's modulus of the contacting surfaces,  $\mu$  is the dynamic viscosity at the inlet temperature and atmospheric pressure,  $U$  is the effective velocity, and  $P$  is the Hertz pressure at the line contact.

Similar equations for film thickness in point contact are given by Dowson (2) and by Khonsari and Hua (53).

The life of rolling element bearings is related to a film thickness parameter,  $\lambda$ .

$$\lambda = h/\sigma \quad (22)$$

where  $h$  is the calculated EHD film thickness, and  $\sigma$  is the composite surface roughness.

In the absence of chemically active additives in the lubricating oil, damage to the bearing surface occurs, and reduces the life of the bearing, if the film thickness becomes less than the height of the surface asperities ( $\lambda \leq 1$ ). The life of the bearing increases significantly at values of  $\lambda > 1.5$  (56).

**Hydrostatic Lubrication.** In hydrostatic lubrication, fluid is pumped under pressure to the load-carrying bearing. Almost any fluid may be used, including gases (nitrogen, helium, air), water, and liquid metals.

The principle applications of hydrostatic lubrication are gas bearings, moving large masses on relatively small bearing areas and for startup of heavily loaded hydrodynamic bearings.

**Squeeze Films.** Viscous lubricant films do not immediately collapse when sliding stops. During the time it takes for these films to be squeezed out of the contact area, they can support peak loads higher than those supported in steady-state operation. This time delay also provides damping for shock loads and shaft vibration. These squeeze films are important in rod bearings of reciprocating automotive engines, damping in turbomachinery and in the lubrication of skeletal joints (hips etc). Ludema (55) estimates the time delay for a viscous fluid squeezed out of an elliptical contact area as

$$1/h^2 = 1/h_0^2 + \{[2W(a^2 + b^2)t]/3\pi a^3 b^3 \mu\} \quad (23)$$

where  $a$  and  $b$  are dimensions of the ellipse,  $h_0$  is the original film thickness (for small values of  $h_0$  relative to  $a$  or  $b$ ),  $\mu$  is the dynamic viscosity of the fluid, and  $W$  is the load that produces a film of thickness  $h$  after time  $t$ .

**Boundary Film Lubrication Regimes.** At lower values of the Sommerfeld number (eq. 15), ie, when unit loads,  $P$ , are very high or when sliding speed,  $N$ , or viscosity,  $Z$ , are low, a full-fluid film cannot be generated. The film thickness is smaller than the height of asperities on the surfaces and the surfaces come in contact with each other. When there is no fluid pressure, and only a thin film of lubricant on the surfaces, lubrication is said to be in the boundary regime. Except in the case of starved lubrication, ie, inadequate or blocked lubricant supply, lubricating oils and greases usually provide lubrication in the mixed or partial film regime, where the load is supported by a combination of surface asperity contact and fluid film pressure, at lower Sommerfeld numbers.

Lubricants designed to operate in the mixed- or partial-film regime may contain additives that form lubricating films on the bearing surface by adsorption, chemisorption, or tribochemical reaction. The additives may be friction modifiers, antiwear additives, EP additives, or multifunctional additives. These films are discussed later under lubricant films.

**2.7. Micro- or Nanotribology.** Micro- or nanotribology began with the ability to study tribological phenomena at the molecular or atomic level. A key tool is the atomic force microscope. With this tool a probe, the tip of which has a radius  $<10$  nm ( $<10^{-9}$  m), can be moved over a surface to measure frictional resistance and other phenomena. At this level, the apparent surface interactions do not obey the same "laws" as those observed on a macroscopic scale (57,58). Topics in micro- or nanotribology are discussed in Refs. 59 and 60.

A principal application for micro- or nanotribology is computer hard disk drives. The rms roughness,  $R_q$ , of the disk surface is  $<2$  nm. The surface is covered with a 1–2-nm film of a perfluoropolyether-based lubricant, and, as a desired goal, a hydrodynamic air film thickness (flying height) of 1–3 nm. Flying height is the distance between the disk and the read-write head–slider assembly (7).

**2.8. Lubricant Films.** Layers of lubricating material, deposited on the rubbing surfaces, control friction, and wear in the boundary portion of the mixed-film regime. This material is initially dissolved or dispersed in the oil, and is deposited on the surface by adsorption, chemisorption, or tribochemical reaction. As portions of these films are rubbed off, they are replaced by additional material in the oil.

A film of paraffin oil adsorbed on rubbing steel surfaces can reduce the coefficient of friction from 0.78 to 0.23 (17). Such a film will not, however, support much load or high temperature.

A better strategy for friction modification is to add a surface-active polar molecule, with a long, nonpolar tail to the paraffin oil. These molecules, known as "friction modifiers" or "boundary lubricity additives" can be naturally occurring substances derived from animal fats, like lard oil, neatsfoot oil, tallow and, in time past, sperm whale oil; vegetable oils, like olive oil, palm oil, rapeseed oil and soybean oil, or they may be synthesized molecules designed to have a particular structure and chain length.

Typical structures are fatty alcohols, esters, amines, and acids with chain lengths of 16–22 carbon atoms. These additives are adsorbed or chemisorbed out of the nonpolar base oil and condense on the surface. The polar end sticks to the surface, and the nonpolar tails pack in as closely as possible and, because of the lateral cohesive forces (London forces) between them, form a strong solid film. This film resists the penetration of asperities and inhibits metal-to-metal contact (61).

Fatty acids are chemisorbed on a metal surface, forming a metal soap without removing the metal atoms from the lattice structure of the surface. With stearic acid, eg, the length of each soap molecule is  $\sim 19 \text{ \AA}$ , and there can be little over four such molecules on each  $100 \text{ \AA}^2$  of surface (61).

Adsorbed films and soaps are temperature sensitive. As surface temperature increases, it reaches the point where the film desorbs, gets disoriented, or melts. For this reason, some lubricants contain EP or antiwear additives, which are activated by the heat of friction at points of metal-to-metal contact during sliding. They react with the surface to form protective layers of solid compounds that prevent welding and catastrophic destruction of the metal surface. Both antiwear and EP additives usually contain one or more of the elements chlorine, phosphorus, or sulfur.

These tribochemical reactions involve the controlled corrosion of the metal surface to prevent more serious damage under extreme loads and temperatures. This regime is often called the Extreme Pressure or EP lubrication regime. Examples of the type of chemicals used include (1) Zinc dialkyl or diaryl thiophosphate (ZDDP), an effective antiwear additive used in engine oils and hydraulic fluids. It has a relatively high activation temperature ( $\sim 150^\circ\text{C}$ ) and forms a tough, wear-resistant surface layer. It is not an effective friction modifier. (2) Mild EP additives with intermediate activation temperatures, such as the sulfur–phosphorous compounds used in automotive hypoid and industrial gear systems. (3) Highly sulfurized or halogenated compounds used in some metal cutting fluids that are activated at relatively low temperature, in some cases at room temperature.

### 3. Lubricating Oil Base Stocks

The most important component of a lubricating oil or grease is its base oil. Although often supplemented by additives, the base oil determines the flow characteristics of the lubricant, its oxidation stability (sludge and deposit-forming tendency), its volatility, and its corrosion potential.

Most lubricant base oils are mixtures of paraffins (straight- or branched-chain hydrocarbons), naphthenes (cycloparaffins), and aromatics (alkyl benzenes and multiring aromatics), typically containing 20–40 carbon atoms per molecule. If paraffins predominate, the base stock is paraffinic. If naphthenes predominate, it is a naphthenic base stock. Paraffins and naphthenes are saturates, meaning that all of the carbon atoms in the hydrocarbon molecule are singly bonded to another carbon atom or to a hydrogen atom. These lubricant base stocks are manufactured by the distillation of selected crude oils, followed by further refining of the lube oil distillates by conventional separation or modern conversion

processes. When refined by conventional separation processes, the type of base stock is crude specific, meaning that paraffinic base stocks come from paraffinic crude oils, and naphthenic oils from naphthenic crudes. When refined by modern conversion processes, base stocks are less crude specific, since these processes are capable of converting naphthenic and aromatic compounds to paraffins (see also HYDROCARBONS).

**3.1. Base Stock Classification.** The American Petroleum Institute (API) defines a *base stock* as "... a lubricant component that is produced by a single manufacturer to the same specifications (independent of feed source or manufacturer location); that meets the same manufacturer's specification; and that is identified by a unique formula, product identification number, or both. Base Stocks may be manufactured using a variety of different processes including but not limited to distillation, solvent refining, hydrogen processing, oligomerization, esterification, and rerefining. Rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use" (62).

"A *base stock slate* is a product line of base stocks that have different viscosities but are in the same base stock grouping and from the same manufacturer" (62).

"A *base oil* is the base stock or blend of base stocks used in an API-licensed oil" (62).

API has also established five base stock categories, classified according to saturates content, sulfur content, and VI. The classification is shown in Table 2 (62).

Base oils with higher saturates content are generally more resistant to, and easier to protect against, oxidation. They also have higher VIs. Paraffinic oils, at the same saturates level, have higher VIs than naphthenic oils. Sulfur compounds produce corrosive material when oxidized. Base stocks with a wide molecular weight range tend to be more volatile than those with a narrow range.

Base Stocks in API groups I–IV are paraffinic hydrocarbons and are manufactured in several viscosity grades. Naphthenic base stocks are in group V (Refs. 63–70). Typically, the saturates content of group II and III base stocks is >99%, and the sulfur content is <15 ppm (<0.0015%). Group IV stocks are 100% saturates and contain no sulfur. The viscosity indexes of group II stocks are typically 100–115, and those of groups III and IV are 120–140. Group IV base stocks have the best low temperature flow characteristics because they contain no wax. Naphthenic stocks, with minimal wax contents, also have good low temperature flow properties. They also have the lowest viscosity indexes. Oxidation stability of the paraffinic stocks improves with each group number, as do volatility and deposit, sludge, and soot control.

**3.2. Synthetic Base Stocks.** The word "synthetic" is not part of the API classification. It is a marketing term, not a technical term. The application of the word synthetic is the subject of controversy because of the difficulty of defining it. It was originally used to differentiate between base stocks made by conventional crude oil refining processes and those synthesized from other chemicals. Polyalphaolefins in group IV are still called synthetic, as are the diesters, polyol esters, polyglycols, etc, in group V. This definition has been blurred, however, by the availability of base stocks derived from petroleum feed stocks by

modern conversion processes (71). "Synthetic" is an accepted description, eg, for group III oils.

**3.3. Base Stock Manufacturing Processes.** Figure 4 lists some of the refining and conversion processes used to manufacture groups I, II, and III base stocks (72,73). Crude oil is first fractionated in an atmospheric distillation tower to produce light gases and fuel products. The residue, or bottoms, from the atmospheric tower are then fractionated in a vacuum distillation tower to produce gas oil and lube oil fractions. The vacuum residue is separated with propane to produce asphalt and deasphalted cylinder oil.

**Solvent Extraction.** In the solvent extraction process, lube oil feedstock from the vacuum tower flows upward through a treating tower, countercurrent to a stream of solvent. The solvent preferentially removes undesirable tars, resins, asphaltic compounds, and polycyclic naphthenes and aromatics. Solvents used include phenol, furfural, and *N*-methyl-pyrrolidone (NMP). Solvent is then stripped from both the aromatic extract and raffinate streams. Solvent extraction increases the VI and the stability of the raffinate (71,73).

**Hydrofinishing.** Hydrofinishing is catalytic hydrogenation process that converts unstable compounds remaining after solvent extraction to stable ones. It converts some aromatics to naphthenes and removes some sulfur compounds and other trace materials. It is a relatively mild process compared to the modern hydrocracking process that causes major molecular changes (74). It is severe enough, however, to produce naphthenic base oils from unextracted distillates that do not require labeling as carcinogenic under OSHA's Hazardous Substances Communication Standard. This makes them suitable for use as base oils for metalworking fluids, greases, and other industrial lubricating products.

**Dewaxing.** Paraffinic distillates contain some high molecular weight, high melting point paraffin waxes. At temperatures below their melting point, these waxes crystallize and cause the oil to gel. Several methods are used to reduce the wax content of lubricating oil base stocks. In one method, the hydrofined raffinate is mixed at low temperature with a chilled solvent, in which the heaviest waxes are insoluble. The wax crystallizes and is then separated from the mixture by cold filtration. Solvents used include propane, methyl ethyl ketone (MEK), methyl isobutyl ketone, and a mixture of MEK and toluene.

Another method for removing wax from the raffinate is catalytic dewaxing. This method uses a shape-selective dewaxing catalyst to crack straight-chain or slightly branched waxes into naphtha and gas (73) (see also MOLECULAR SIEVES).

Isomerization technology is used in the manufacture of group II and III base stocks. In this process, high melting point straight-chain paraffins are isomerized in a shape-selective catalyst to branched-chain, lower pour-point lube molecules. The process also produces gasoline and diesel fuels (73,75).

**Hydrogen Processing.** Hydrogen reforming, hydrocracking, and wax isomerization are modern refining processes that convert undesirable components of lube oil fractions into desirable components, rather than remove them. They are used instead of solvent extraction on vacuum tower distillates, or on raffinates from the extraction tower, to produce group II and III lubricating oil base stocks with higher saturates content, lower sulfur content and higher viscosity index. The principal reactions taking place in these processes are (71)

saturation, ring opening, reforming (isomerization), cracking, desulfurization, denitrogenation.

Naphthenic and group I paraffinic base stocks are refined by conventional separation processes and are crude specific. Groups II and III paraffinic stocks produced by modern conversion processes, hydrogen reforming, hydrocracking, catalytic dewaxing, and wax isomerization, are less crude specific (See also PETROLEUM REFINING PROCESSES).

**3.4. Polyalphaolefins.** Group IV base stocks are poly( $\alpha$ -olefins) (PAO). They are produced by steam cracking hydrocarbons to produce ethylene; ethylene oligomerization to produce linear  $\alpha$ -olefins (1-decene, 1-dodecene, or 1-tetradecene); oligomerization of linear  $\alpha$ -olefin to form a mixture of dimers, trimers, tetramers, and higher oligomers; hydrogenation of the unsaturated oligomer.

The characteristics of the finished PAO are affected by the chain length of the olefin raw material, temperature, time and pressure, catalyst types, and concentration and distillation of the final product to remove the dimers (76,77) (see also OLEFIN POLYMERS, INTRODUCTION).

**3.5. Polyinternal Olefins and Gas-Liquid Base Stocks.** The Technical Association of the European Lubricants Industry, ATIEL, has established a group VI category for polyinternalolefins (PIO). These are mixtures of linear and cyclic olefin isomers (78,79).

The conversion of natural gas to liquids (GTL) by the Fischer Tropsch process is a promising method for producing high quality lubricating oil base stocks. Table 3 shows the typical properties of a GTL base stock compared to those of current base stocks (80) (see also FUELS, SYNTHETIC, LIQUID FUELS).

**3.6. Organic Esters.** Organic esters synthesized by reacting dibasic acids with monoalcohols (diesters), or by reacting monoacids with polyhydric alcohols (polyol esters), have been used as lubricating oil base stocks for > 50 years. They are branched hydrocarbon molecules with multiple ester linkages, which give them polarity. Their unique structure gives them excellent thermal and oxidation stability, good low temperature flow characteristics, low volatility, lubricity, detergency and dispersancy, and biodegradability. Esters have been used exclusively in aircraft turbine engine oils (jet engine oils) for >40 years. They are also the preferred base stock in refrigerator compressor lube oils used with R-134 refrigerants. Other applications for ester base stocks include rotary screw air and process gas compressors, oven chain lubricants and gas engines. Typical structures of ester base stocks can be found in Refs. 79,81,82 (see also ESTERS, ORGANIC).

**3.7. Polyglycols.** Polyalkylene glycols (PAG) and polyethers are usually copolymers of ethylene oxide and propylene oxide. The oxide monomer sequence can be random or blocked and their solubility can be varied from oil soluble to completely water soluble. Their applications include gear and compressor lubricants, metalworking fluids, fiber lubricants, and fire-resistant hydraulic fluids (79,83) (see also HYDRAULIC FLUIDS).

**3.8. Vegetable Oil Esters.** Triglyceride esters are obtained from renewable sources: olive, soybean, rapeseed, canola, safflower, sunflower, meadowfoam, castor, and other vegetable oils. They are biodegradable and offer specific environmental benefits over hydrocarbon-based lubricants. Lubricating oils made with these base stocks and their derivatives are recommended in

applications where lubricant leaks and spent lubricant can contaminate the environment. Examples include chain bar lubricants, two-cycle oils for outboard marine engines, hydraulic fluids for farm machinery, and rail curve greases.

Most vegetable oil esters have a combination of saturated and unsaturated fatty acids attached to the three alcohol groups in glycerine. Highly saturated oils have good oxidation stability and poor low temperature flow properties. As the amount of saturation decreases, oxidation stability decreases and the low temperature flow properties improve. Advances in breeding technology can change fatty acid profiles and alter the physical properties of vegetable oils (84).

**3.9. Biodegradable Base Stocks.** Lubricant or base stock biodegradability is the extent to which the material can be broken down by living things (microorganisms) into innocuous products such as water, carbon dioxide, inorganic compounds and methane. The least biodegradable of lubricant base stocks are silicone oils, polyphenyl ethers, perfluoro alkyl ethers and alkylated aromatic oils. Naphthenic stocks and base stocks in API groups I–IV also have relatively poor biodegradability. The most biodegradable base stocks are vegetable oil esters, followed by polyalkylene glycols, organic esters, and phosphate esters (85).

**3.10. Other Base Stocks.** Other chemical compounds used as lubricant base stocks include polybutenes (84), hydrocarbons obtained by the alkylation of naphthalene with  $\alpha$ -olefins (70,87), alkylated aromatic hydrocarbons (88), silicones (88,89), phosphate esters (90), chlorotrifluoroethylene (91,92), polyphenylethers (92), perfluoroalkyl polyether (92,93).

**3.11. Rerefined Base Stock.** In its definition of a base stock, the API states “Rerefined stock shall be substantially free from materials introduced through manufacturing, contamination, or previous use” (62).

Products made from rerefined stock are subject to the same stringent refining, compounding and performance standards applied to virgin oil products. Rerefined oil may, in fact, have superior oxidation stability than virgin stocks because the easily oxidized compounds will have been reacted during previous use and then removed during reprocessing (71,94).

In the rerefining process, used oil is preferably segregated by type, collected, and delivered to the reprocessing facility. The oils are then screened and inappropriate feed stocks rejected. Solid and other gross contaminants are then separated by, eg, propane precipitation, alcohol–ketone precipitation, acid–clay filtration, etc. The filtrate is dehydrated and then refracted by vacuum distillation. The distillates are then finished by hydrotreating or clay filtration or both, and then vacuum distilled to obtain the desired viscosity grades (71,94).

## 4. Additives for Lubricating Oil and Grease

Advanced refining and manufacturing technologies have significantly improved the quality of base oils used in the manufacturing of lubricating oils and greases. They are more stable, have better low temperature flow properties, are less volatile, and less corrosive. Alone, however, they do not meet the requirements of modern lubricating oils and greases. Additives are chemical substances added



to the base oil to impart or improve certain properties. They include oxidation inhibitors, rust and corrosion inhibitors, pour point depressants, viscosity (VI) improvers, detergents, dispersants, friction modifiers, EP agents, thickeners, emulsifiers, demulsifiers, bactericides, fungicides, and tackiness additives. Most oils and greases contain several different additives, many of them surface active. They can assist each other, resulting in a synergistic effect, or they can have antagonistic effects. Many additives have several functions (multipurpose additives). These additives and base stocks are the elements used by the lubricant designer to meet the increasingly critical requirements of equipment manufacturers and of the users of lubricating oils and greases (95,96).

**4.1. Oxidation Inhibitors (Antioxidants).** Hydrocarbons and many other components of lubricating oils and greases are subject to oxidation under the operating conditions in which they are used. The products of oxidation may be corrosive, they may be varnish, soot or sludge that cause wear, interfere with proper operation of equipment or plug oil passages, preventing the lubricant from getting to its intended application.

Preventing or delaying the oxidation of lubricating oils and greases extends their operating lives. Oil change intervals for automotive engines have increased 10-fold over the past 50 years, even though engine operating temperatures have increased significantly over the same period. Many machine elements are "lubricated for life". Steam turbine oils remain in use for decades without any oxidation effects. These are major economic benefits for machine operators.

The oxidation process is a chain reaction with several different chemical actions. It is generally initiated by heat or light leading to the formation of free radicals, followed by, in the presence of air, the formation of peroxides, and then a variety of reactions including polymerization. It is catalyzed, or speeded up, by the activity of metal surfaces. Metals employed in soap thickeners have been found to catalyze the oxidation of greases (97). Detailed mechanisms are described in Refs. 98 and 99 (see also HYDROCARBON OXIDATION).

Natural inhibitors (sulfur or nitrogen containing) present in some base stocks, or their oxygen-containing intermediates can impair the formation of free radicals. Molecules with carbon-carbon double bonds and aromatic residues can promote formation of radicals. Refining processes remove easily oxidized components from the base stock and make it more responsive to oxidation inhibitors. They also remove some natural inhibitors. Synthesized base stocks with few impurities (and no natural inhibitors) are less prone to oxidation and more responsive to antioxidants.

A variety of additives are available that terminate the chain reaction in the early stages of oxidation. There are (97) (1) free-radical scavengers, primary antioxidants that function by breaking the propagation step; (2) hydroperoxide decomposers, secondary antioxidants that function by inhibiting the branching step; (3) metal deactivators and corrosion inhibitors that prevent catalysis of the initiation reaction.

High quality lubricants may contain more than one of each type of these oxidation inhibitors. The combination of different antioxidants is synergistic. Each functions via a different mechanism, in a different temperature range, and at different rates. Each stabilizes different species, and one may act to regenerate another (98-100).

There are two types of primary antioxidants or free radical scavengers: Hindered phenols and aromatic amines. Both function by donating a hydrogen atom to the peroxide radical,  $\text{ROO}\bullet$ , to break the propagation step in the oxidation mechanism and form relatively inert products (97,98).

In the presence of active antioxidants, oxidation proceeds very slowly until the inhibitors have no more available hydrogen atoms to contribute. At this point, the rate of oxidation increases dramatically and other measures are necessary to deal with the oxidation products. These include dispersants and detergent additives (discussed later), filtration, reconstitution of the additive package and replacing the oil. Oil quality monitoring is often used to follow the progress of deterioration and determine when an oil change is needed (100,101).

Figure 5 shows the way hindered phenols react with peroxide radicals to terminate the oxidation chain reaction (98,99). Chemicals used in this process include (97,98,102,103) 2,6-di-*tert*-butyl phenol (DTBP), 2,6-di-*tert*-butyl-*p*-cresol (DBPC or BHT), 3,5-di-*tert*-butyl-4-hydroxyanisole (BHA), 4,4'-methylenebis(2,6-di-*tert*-butyl phenol), 3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamic acid, C7–C9 branched alkyl ester, 1,6-hexamethylene bis(3,5-di-*tert*-butyl-4-hydroxy-hydrocinnamate).

Examples of aromatic amine antioxidants include alkylated diphenylamines (ADPA), phenyl alpha diphenyl amine (PANA), alkyl substituted PANA, and trimethyl quinoline derivatives (94,98,99).

A variety of mechanisms is reported for the action of amine-type antioxidants. They act at both the initiation and propagation steps and are effective at lower concentrations and over a wider temperature range than are the hindered phenols (97–99).

There is also evidence that some of the DBPC and PANA in the oil react directly with oxygen and those portions are not contributing to the termination of the chain reaction (100,104).

Secondary antioxidants include sulfur containing and organophosphorus compounds. Typical examples include dialkyl thioesters, metal dithiocarbamates, metal dithio phosphates, and aryl phosphites. They inhibit the branching step by decomposing hydroperoxides. Reyes-Gavilan and Odorisio (97), referring to several earlier works, report that, in general: (1) Thioethers react with hydroperoxides to form sulfoxides, sulfones, and alcohols; (2) zinc dialkyl dithiocarbamates react with hydroperoxides to form sulfur acids that ionically catalyze hydroperoxide decomposition; (3) the reaction of zinc dialkyldithiophosphate (ZDDP) with hydroperoxides occurs through an *O,O'*-dialkyl hydrogen phosphoro dithioate catalyzed ionic mechanism; (4) hydroperoxide decomposition by phosphites is accomplished through a displacement reaction mechanism. The products of this reaction consist of an organic phosphate and an alcohol.

Secondary antioxidants are best used in combination with primary antioxidants. They are not as effective as the latter when used alone. There are some multifunctional additives, in which sulfur is incorporated in the phenolic molecule, that are both primary and secondary antioxidants (97,98).

**4.2. Metal Deactivators.** Metal deactivators passivate the surface, of copper, brass, and bronze alloys, or they chelate ions of copper, iron, manganese, cobalt, and other metals. Passivators, which lay a protective layer over the metal

surface, include benzotriazole, 2-mercaptobenzothiazole, and tolutriazole derivatives. Chelators, which trap metal ions in the bulk of the substrate, include *N,N'*-disalicylidene-1,2-diaminopropane and ethylenediaminetetraacetic acid (EDTA) (95,98). Both types prevent metal catalysis at the oxidation initiation step.

**4.3. Corrosion Inhibitors.** Corrosion inhibitors in lubricating oils and greases form a protective layer on the surface of metals to prevent moisture and oxygen from easily reaching the surface. Natishan and Moran discuss the mechanism of corrosion of metals, mainly caused by electrolytic reactions (see CORROSION AND CORROSION CONTROL). Polyisobutenylsuccinic acid derivatives, amine phosphates, fatty acid amides of sarcosine, imidazoline derivatives, and sulfonates are a few of the chemicals used in lubricating oils as corrosion inhibitors (102,103,105).

**4.4. Detergents and Dispersants.** Detergent and dispersant additives are used principally in gasoline and heavy duty diesel engine oils, automatic transmission fluids, and tractor hydraulic fluids. Their primary function is to keep the engine surfaces clean: they prevent deposits on hot surfaces such as pistons and rings; they neutralize corrosive oxidation products and other contaminants; they suspend insoluble oxidation products and debris in the oil, thus preventing them from clogging vital oil passages. They do *not*, however, remove deposits already on the surfaces.

Detergents are made by reacting metal oxides or hydroxides with long-chain organic acids. The metals include calcium, magnesium, barium, and sodium. Acids include alkylbenzene sulfonic acid, alkylnaphthalene sulfonic acid, alkyl phenol, sulfur, or methylene bridged alkyl phenol, alkyl salicylic acid, and polyisobutenyl phosphonic acid (106).

Detergents may be neutral, basic, or overbased. Basic and overbased detergents have reserve alkalinity to neutralize acidic combustion products (usually formed from sulfur in the fuel) that leak or “blow by” the rings in an internal combustion engine. These are made by using excess metal base in the reaction and then blowing the product with CO<sub>2</sub> to form metal carbonate. The carbonate is held in suspension in a micelle structure (106).

Some detergents, particularly the phenates and salicylates, are detergent inhibitors, meaning that parts of the molecule are able to inhibit oil oxidation and bearing corrosion (107).

Dispersants are metal free and therefore ashless. They are higher in molecular weight than detergents and more effective in suspending oxidation products and debris. Some examples of dispersant chemistry are polyisobutenylsuccinimides, polyisobutenyl succinate esters, polyaminomethylpolyisobutylphenols, and bis(hydroxypropyl polyisobutenylthiophosphonate) (106).

The polar ends of the dispersant molecules surround and attach themselves to the insoluble contaminant particles. Their oil-soluble, nonpolar tails keep the particles in suspension (106,107).

Dispersancy is also built into multifunctional viscosity improvers based on olefin copolymers, polyacrylates, and styrene–maleic anhydride polymers (106).

**4.5. ZDDP: Antiwear Additive, Antioxidant, and Corrosion Inhibitor.** The ZDDP (Zinc Dialkyl DithioPhosphate and Zinc Diaryl DithioPhosphate) compounds have, for > 50 years, been the most effective wear reducing additives in engine lubricating oils, hydraulic oils and other lubricants.

When two steel surfaces rub together, and the metal on one surface is in contact with the metal on the other surface, the frictional heat caused by the rubbing causes the ZDDP to react chemically with the surfaces to form very tough wear-resisting boundary lubricating films. These films do not shear easily, and have little effect on the coefficient of friction. The ZDDP films do rub off, however, and they are constantly being rebuilt by the chemical reaction of the metal with ZDDP. These films are particularly effective in concentrated sliding contacts such as those found in engine valve trains and in vane type hydraulic pumps. Concentrated contacts have a very small contact area which results in extremely high pressure on the contact area. Some friction modifying additives work with ZDDP to reduce both friction and wear of the rubbing surfaces.

The ZDDP compounds are multifunctional. They are secondary oxidation inhibitors, decomposing hydroperoxides in the branching step of hydrocarbon oxidation. They are also effective bearing corrosion inhibitors.

This compound is manufactured by first reacting an alkyl or aryl alcohol with phosphorous pentasulfide ( $P_2S_5$ ), and then neutralizing the resultant acid with zinc oxide. The alkyl alcohol may be primary alkyl, branched chain primary alkyl, secondary alkyl or, rarely, tertiary alkyl. As a rule, the secondary and tertiary alkyl derivatives are more effective as antiwear additives, but are the least stable. The aryl derivatives generally have the best thermal stability and the least potent antiwear activity (108,109).

The ZDDP compounds, particularly those with lower thermal stability, can decompose at temperatures below those of rubbing steel surfaces and become corrosive to copper and copper alloys. This is generally not a problem in internal combustion engines, but it can be a problem in machinery using, eg, bronze bushings, pistons, or clutch plates. However, by the judicious selection of alcohols, and careful control of the manufacturing process, ZDDP compounds are made that perform well in machines such as automatic transmissions and piston type hydraulic pumps that contain parts made with copper alloys.

Despite its effectiveness as a wear, oxidation and corrosion inhibitor, and its relatively low cost, there are serious efforts to reduce or eliminate the use of ZDDP additives in engine oils. When the oil gets in the combustion chamber, the additive decomposes at high temperature and, because a metal is present, leaves ash, a solid residue, and other deposits in the chamber. These deposits interfere with engine efficiency and emissions control. There is also evidence that ZDDP decomposition products poison the catalysts used to convert  $CO$ ,  $NO_x$ , unburned hydrocarbons and volatile organic compounds to less harmful emissions. Zinc oxide, phosphorus pentasulfide, and a zinc pyrophosphate glaze have been found on catalyst surfaces that prevent passage of exhaust gases into the porous structure of the catalyst (110). (see also EMISSION CONTROL, AUTOMOTIVE). Lacking an acceptable emission systems protection test, the International Lubricant Standardization and Approval Committee (ILSAC) places maximum phosphorus and sulfur limits on the GF-4 engine oil specification. These limits are expected to be reduced further in the next generation specification.

**4.6. EP and Antiwear Additives.** There is very little distinction between so-called EP and antiwear additives. Both react with rubbing metal surfaces to form lubricating films, and they both inhibit wear. ZDDP additives

have relatively high activation energy and are not effective until the surface temperature gets  $>150^{\circ}\text{C}$ . The EP additives are used in relatively high load, slow speed applications to prevent catastrophic failure of the surface. Mild EP additives used in automotive and industrial gear oils have lower activation temperatures than ZDDP. "Active" EP additives used in metal cutting oils, like elemental sulfur, chlorinated hydrocarbons and some sulfurized esters, can react at room temperature. Table 4 lists some of the many compounds used as EP and antiwear additives in lubricating oils (103,111,112).

**4.7. Friction Modifiers (Boundary Lubricity Additives).** Friction is a force that resists sliding, or slipping, of one surface across another. *Static* friction prevents sliding or causes the surfaces to move together, with no relative motion between the surfaces. When a shearing force high enough to overcome the static force is applied, the surfaces move relative to each other and the friction is *kinetic*. On unlubricated surfaces, and on surfaces lubricated with fluids that do not contain friction modifying additives, static friction is higher than kinetic friction. Friction modifiers added to the oil tend to reduce both the static and kinetic friction forces and to make the static friction lower than the dynamic friction.

Friction modifiers have two functions; to reduce energy consumption by machinery by lowering the kinetic friction; or to eliminate shudder in automatic transmission torque converter clutches, chatter in limited slip automotive differential gear systems, and stick-slip in machine tool slideways. Shudder, chatter, and stick-slip are all the same phenomena, frictional vibration caused by oscillation between static and kinetic friction forces. The oscillation occurs at low relative speeds between surfaces in contact and when the static friction is higher than the kinetic friction. Inherent resilience in the applied shearing force also contributes to stick-slip. With a friction modified lubricant, kinetic friction is higher than static friction and the frictional vibration is eliminated (113–115).

Like many lubricating oil additive molecules, organic friction modifiers have a polar end that attaches to the rubbing surface and a long-chain hydrocarbon tail. Sulfurized fats, phosphoric and thiophosphoric acid derivatives form boundary lubricating film layers by chemical reaction with the surface material. The latter three also function as EP additives. Other friction modifiers, eg, fatty acids, carboxylic acid derivatives, esters, ethers, amines, amides, and imides form layers of boundary lubricating films by chemisorption. The polar heads on the surface are attracted to each other by hydrogen bonding and dipole–dipole interactions and the hydrocarbon tails are lined up perpendicular to the surface by van der Waals (London) forces.

Another class is friction polymers formed at the asperities under the influence of contact temperature and load. These include partial complex esters, methacrylates, unsaturated fatty acids, and sulfurized olefins.

Finally, there are metalloorganic types like molybdenum dialkyldithiophosphate and molybdenum dialkyldithiocarbamate and solid lubricants like graphite, molybdenum disulfide, and PTFE (116).

**4.8. Pour Depressants.** The pour point is the lowest temperature at which an oil is observed to flow, when cooled as prescribed in ASTM D97. At this point, wax crystals that have previously precipitated as solid needles and platelets agglomerate and cause the oil to gel, preventing its flow. Dewaxing

and hydroisomerization processes remove most, but not all of the waxes (high molecular weight *n*-paraffins) from groups I–III base stocks. The resultant pour points of the base stocks vary from about  $-15$  to about  $-25^{\circ}\text{C}$ . Adding a pour depressant can further reduce the pour point another  $30$ – $40^{\circ}\text{C}$ . Pour point depressants are branched-chain polymeric additives that coprecipitate with the wax crystals and prevent them from agglomerating. The side chains on these polymers, often called wax crystal modifiers, are about the same length as the wax molecules (117).

The first pour depressants were alkylated naphthalenes. Phthalic acid dialkylaryl esters followed, and then long-chain alkyl acrylates and methacrylates. Polymethacrylates are probably the most widely used pour depressants today. Many other polymeric additives can be tailored to provide pour depressant properties in addition to their other functions (117–119).

**4.9. Viscosity Improvers.** Viscosity improvers are polymeric additives that are more soluble in oil at high temperature than at low temperature. The dissolved molecules expand or stretch out and considerably increase the viscosity of the oil at high temperatures. These molecules shrivel up and shrink, contributing very little to the viscosity of the oil at low temperature. Viscosity improvers are added to low viscosity base oils, which have the necessary low temperature flow characteristics, to increase their viscosity and resultant lubricating ability at operating temperatures.

Multigrade oils, oils containing viscosity improvers, are non-Newtonian oils. The high temperature viscosity of the oil undergoing high shear rates is lower than its viscosity at very low shear rates. This viscosity loss may be temporary and the oil will recover its original viscosity when the shear stress is relieved. Permanent viscosity loss occurs when the polymer itself is sheared. Automotive engine oil specifications control both temporary and permanent viscosity loss caused by shear stress.

Viscosity improving polymers include olefin copolymers from ethylene, propylene, and butylene monomers; polymethacrylates; styrene–butadiene copolymers; and hydrogenated polyisoprene.

Many of these polymers can be modified to make them multifunctional, giving them pour depressing and/or dispersant properties in addition to viscosity improvement (117,120) (see also METHACRYLIC POLYMERS).

**4.10. Foam Inhibitors.** Foam in lubricating oils consists of bubbles of air on the liquid surface whose walls are thin liquid films. Strong foaming affects the lubricating properties of oils and enhances their oxidation. Foam is generated on mixing air with the oil during agitation and then separation of the air at the oil surface. Foam stability is a function of oil viscosity and surface tension at the oil–air interface. It is strongly affected by surface active substances such as detergents, friction modifiers, EP additives, and corrosion inhibitors.

Finely dispersed polydimethylsiloxane, which is insoluble or has borderline solubility in hydrocarbon oils, forms a monolayer on the liquid surface, lowering the surface tension and breaking the foam. Antifoam additives based on this silicone oil are widely used in automotive engine, transmission, and gear oils.

Silicone oils, however, tend to stabilize air emulsions, where the air bubbles do not separate from the oil or separate very slowly. Entrained air in an oil circulating system is compressible and leads to spongy response in hydraulic

systems and severe cavitation damage in bearings. Alkylacrylate and alkylmethacrylate copolymers, while not as effective as silicones for foam suppression, are preferred where air entrainment is a problem (121–123).

**4.11. Demulsifiers.** Steam turbine oil, paper machine oil, industrial gear oils, hydraulic oils, and oils for many other applications are subject to contamination by water. It is important that this water separates easily from the oil and drops to the bottom of the oil reservoir, where it can be drained off. If it does not, it can mix with and circulate with the oil, seriously degrading the oils lubricating capability. Demulsifiers are sometimes added to the oil formulation to facilitate water separation. They concentrate at the oil–water interface and promote coalescence of the water droplets. Chemicals used include anion-active compounds such as dinonylnaphthalene sulfonates and polyalkoxylated phenols, polyols, and polyamines (124,125).

**4.12. Emulsifiers.** Water-in-oil emulsions are used as coolants–lubricants in metalworking applications and as hydraulic fluids. Medium molecular weight sodium sulfonates (derived from natural and synthetic raw materials) are the most widely used emulsifiers in these fluids. Nonionic emulsifiers based on polyethylene oxide are also used, as are long-chain alkylammonium salts (126).

## 5. Lubricating Oils

Lubricating oils are specifically formulated for virtually every type of machine and manufacturing process. The base stocks and the type and concentration of additives used for these oils are selected based on the requirements of the machinery or process being lubricated, by the quality required by the builders and the users of the machinery, and by government regulation. Table 5 is a partial list of the principal applications for which lubricating oils are specifically formulated:

Each of these oils has a unique set of performance requirements. In addition to proper lubrication of the machine or process, these requirements include maintenance of the quality of the lubricant itself, as well as the effect of the lubricant's use and disposal on energy use, the quality of the environment and on the health of the user. The performance requirements of a few of these lubricating oils are discussed below.

### 5.1. Gasoline Engine Oils for Passenger Cars and Light Trucks.

Internal combustion engines provide the best example of performance requirements dictating the formulation and quality of the engine oil. These engines have lubrication requirements in nearly every regime: hydrodynamic, elastohydrodynamic, squeeze film, EP, boundary, and mixed film. They operate at high oil and surface temperatures, must start up at very low temperatures, are subject to contamination (by fuels, combustion products, oxidation products, and dirt), and they must meet stringent fuel economy and exhaust emission standards. Their lubricating oils contain a wide variety of additives and their base oil requirements determine the type and quality of base stocks produced in lube refineries and chemical manufacturing plants. The performance requirements of gasoline engine oils for use in automobiles are a good example of the

relationship between the performance requirements and the formulation of lubricating oils for a specific application.

Gasoline engine oils for use in automobiles in the United States are licensed and certified to assure that they meet the minimum performance standards established by industry technical specifications. The Engine Oil Licensing and Certification System (EOLCS), administered by the API, is a voluntary program that authorizes oil marketers to use the API Engine Oil Quality Marks—the API Service Symbol “Donut” and Certification Mark “Starburst” (127). This program is a cooperative effort between the oil industry and vehicle and engine manufacturers—Ford, General Motors and Daimler Chrysler; the Japan Automobile Manufacturers Association (JAMA); and the Engine Manufacturers Association (EMA).

Performance requirements, test methods, and limits are cooperatively established by vehicle and engine manufacturers, technical societies, [eg, the Society of Automotive Engineers (SAE) and the American Society of Testing and Materials (ASTM)], and industry associations (such as the American Chemistry Council and API). An ongoing monitoring and enforcement program to ensure licensees adhere to industry technical specifications backs API's Engine Oil Program (128).

The API Service Symbol “Donut” is divided into three parts: (1) The top of the Donut shows the oil's performance level for gasoline and/or diesel engines. The letter “S” followed by another letter (eg, “SM”) refers to oil suitable for gasoline engines. The letter “C” followed by another letter and/or number (eg, CI-4) refers to oil suitable for diesel engines. (2) The center identifies the oil's viscosity characteristics. The numbers and the letter “W” indicate the SAE viscosity grade. These grades are defined in SAE J300, May 2004 (129). The low temperature “W” grades indicate how quickly an engine will crank and how well the oil will flow to lubricate critical engine parts at low temperatures. The grades without the “W” indicate the oil's operating temperature flow properties. A multi-grade oil (eg, 5W-30) provides good flow capability for low temperatures and adequate viscosity characteristics for high temperature lubrication. It meets the viscosity requirements of both the “W” grade and the other grade indicated (129). (3) The bottom of the Donut tells whether the oil has demonstrated energy conserving properties in a standard test in comparison with reference oil. It may also include a supplemental category description (eg, CI-4 PLUS).

The API Certification Mark “Starburst” (Fig. 6) is designed to identify engine oils recommended for a specific application (such as gasoline engine service). An oil may be licensed to display the Starburst only if the oil satisfies the most current requirements of the International Lubricant Standardization and Approval Committee (ILSAC) minimum performance standard for this application. Members of ILSAC include representatives of the Japanese Automobile Manufacturers Association, DaimlerChrysler Corporation, Ford Motor Company and General Motors Corporation.

An engine oil meeting the latest API service category may or may not meet all of the requirements of the latest ILSAC category. When it does meet both requirements, its container may display both symbols.

The current ILSAC minimum performance standard, suitable for use in the current and all earlier model year automobiles, is ILSAC GF-4 Standard



for Passenger Car Motor Oils (130). The corresponding API Service Category is API Service SM. Both were issued in 2004 and superceded the 2001 standards, ILSAC GF-3 (131) and API Service SL. Those, in turn, superceded ILSAC GF-2 and API Service SJ, issued in 1996 and API Service SH, issued in 1992 and now obsolete. After April 2005, the Starburst can no longer be used for GF-3 oils.

The performance required by ILSAC for GF-4 Engine Lubricating Oils is measured in a battery of full scale engine tests and laboratory bench tests conducted by qualified independent laboratories. Tables 6–11 describe these engine and bench test requirements for ILSAC GF- 4, GF-3, and GF-2 and for API Service SM, SL, SJ, and SH (130,131).

Engine test requirements in the ILSAC GF-4 Standard include (1) The ASTM Sequence IIIG test measures viscosity increase, piston deposits at high operating temperature and valve train wear. At the end of the test, the low temperature pumping viscosity of the oil is measured. It is run in a 1996/1997 3800 cc series II General Motors V-6 fuel-injected gasoline engine. After a 25-min break-in, it operates at 125 bhp, 3600 rpm, 150°C oil temperature for 100 hours (130,132). (2) The ASTM Sequence VG test (ASTM D 6593-04) evaluates the oil's ability to prevent sludge and varnish formation. It is run in a 1994 Ford V-8, 4.6 liter fuel injected gasoline engine. The procedure involves 54 cycles in 216 h, each cycle consisting of three different sets of operating conditions (130,132,133). (3) The ASTM Sequence IVA test (ASTM D 6891-03) measures the average camshaft lobe wear in a 100 hour test in a KA24E Nissan 2.4 liter, 4-cylinder engine (130,132,134). (4) The ASTM Sequence VIII test (ASTM D 6709-03a) evaluates a lubricant's performance in combating copper, lead and tin bearing corrosion and measures viscous shear stability at high operating temperature. A 42 C.I.D. single cylinder engine runs for 40 hours at 3150 rpm. The oil temperature is raised to 143°C using an external oil heater (130,132,135). (5) The ASTM Sequence VIB test (ASTM D 6837-04) measures the effects of multi-grade engine oils on the fuel economy of passenger cars and light duty trucks. It is run in a 1993 Ford 4.6 liter V-8 engine on a dynamometer test stand (130,132,136).

Maximum phosphorus and sulfur contents are specified in GF-4 for catalyst compatibility (130,137,138). Minimum phosphorus is specified for wear protection (132,137). Bench tests are specified for minimum volatility, maximum high temperature deposits, filterability, engine rusting and foaming characteristics (132,139–145).

Many of the engine test results are visual merit ratings. These are made by experts trained in the rating process using standards published in Coordinating Research Council (CRC) Manuals (146,147).

**5.2. Heavy Duty Diesel Engine Oils for Trucks, Agricultural, and Construction Vehicles.** The driving forces for diesel engine oil development are engine durability, reduction of NO<sub>x</sub>, and soot emissions and compatibility with exhaust aftertreatment systems. As with gasoline engine oils, the performance of diesel engine oils is continually being upgraded to meet engine manufacturers' needs, consumer requirements and government regulations. Diesel engine oils are licensed and certified by the API in its Engine Oil Licensing and Certification System (EOLCS) (130). Performance Requirements, test methods, and limits are cooperatively established by the ASTM Heavy Duty Engine

Oil Classification Panel (HDEOCP) and the Diesel Engine Oil Advisory Panel (DEOAP). Both of these groups are made up of members of the Engine Manufacturers Association (EMA) and oil and additive company members of API (148).

Table 12 is an example of the performance criteria and the engine and bench tests used to measure them, for the API “C” category diesel engine oils. This table illustrates the increasingly rapid growth of new performance requirements (categories), the number of tests and the number of new engines required for certification of heavy-duty diesel engine oils (149–153). Detailed performance requirements and engine test details for European diesel oil categories are in reference (150).

**5.3. Gas Turbine Oils.** The performance requirements for aircraft jet engines are described in the military specifications MIL-PRF-7808L and MIL-PRF-23699F. These specifications require bench tests for physical, chemical, and performance characteristics, an accelerated endurance test in a turboshaft engine and, if these requirements are met, a 150-h test on two different models of aviation gas turbines conducted in a test cell and a 500-h flight evaluation test (154,155).

Critical bench test performance requirements in MIL-PRF-23699F include oxidation and corrosion stability tests (OCS) for 72 h each at temperatures of 175, 204, and, 218°C, a thermal stability and corrosivity test at 274°C, a test for gear load carrying ability, and tests for bearing deposits and bearing corrosion. The maximum pour point specified is  $-54^{\circ}\text{C}$  (155).

The wide operating temperature range needed in this application is the reason that neopentyl polyol ester base stocks are used for aircraft jet engine oils. MIL-PRF-23699F fluids have a nominal viscosity of 5 cSt at  $100^{\circ}\text{C}$ . The nominal viscosity of MIL-PRF-7808L fluids is 3 cSt at  $100^{\circ}\text{C}$ .

**5.4. Automatic Transmission Fluids.** Automatic Transmission Fluids (ATFs) are highly complex fluids that perform many essential functions in an automatic transmission (156). They transfer power in the torque converter; provide hydraulic pressure to operate clutches and shift gears; lubricate bearings, gears and bushings; remove heat from the transmission; and provide the right friction profile for proper operation of plate, band, and torque converter clutches.

Automatic transmissions normally operate at temperatures of  $75\text{--}95^{\circ}\text{C}$  and start up at temperatures as low as  $-40^{\circ}\text{C}$ . The ATFs must flow easily at low temperatures, be highly resistant to thermal and oxidative degradation at high temperatures, be noncorrosive towards all transmission components, be resistant to foaming and have specialized friction and wear properties. They may contain as many as 15 different additives and a mixture of base stocks in API groups I–IV (114).

The major automobile and truck manufacturers each develop their own specifications for automatic transmission fluids, often using proprietary test methods and test materials consistent with their own transmission designs. Current examples include General Motors Dexron III fluid, version H; Ford’s Mercon V and Mercon SP; Daimler Chrysler’s MS-9602 (ATF+4); Toyota’s Fuel Saving WS ATF, and Detroit Diesel Allison’s TES-295 (157). These fluids are not necessarily interchangeable. Performance requirements specified by all manufacturers include friction characteristics, oxidation stability, low temperature flow, shear stability, EP and wear protection, antishudder, and friction durability.

Fluids designed for use in continuously variable transmissions (CVTs) require special frictional characteristics. There are two types of CVT used in modern production vehicles: (1) Belt-drive CVTs using a Van Doorne Type steel push-belt or a link-plate chain running in hydraulically adjustable, variable width sheaves or pulleys. Torque is transferred between the sheaves and the belt by the frictional force provided by metal-metal contact. (2) Traction-drive CVTs using a movable roller between two disks with toroid-shaped cavities. Torque is transferred between the roller and disks by a fluid film in the elastic-plastic (EHD) flow regime.

Fluids with high traction coefficients, two to three times higher than those of conventional ATFs, are required for efficient operation of the toroidal traction drive. Fluids that have been evaluated as base stocks for traction fluids include derivatives of the  $\alpha$ -methyl styrene dimer, of isomerized tricyclopentadiene and other multiring naphthenic structures (158,159).

Transmission fluids for belt-drive CVTs require high metal-metal friction coefficients to provide adequate torque transfer between the belt and sheaves. They must also provide good antiwear and antipitting protection. Since CVTs use controlled slip torque converters and wet clutches for starting and reverse, these properties must be provided without sacrificing the antishudder and wet clutch performance of modern ATFs. They must also have the proper viscosity characteristics over the entire operating temperature range, excellent thermal and oxidation stability and compatibility with other transmission components.

**5.5. Automotive Gear Oils.** Automotive and industrial gear systems are the principal applications for mild EP lubricants. These lubricants are formulated to prevent wear, fatigue pitting, and catastrophic failure (spalling, scoring, scuffing) of gear tooth surfaces. They are also formulated to protect against thermal and oxidative degradation, rust, cuprous alloy corrosion, foaming, and oil seal deterioration (160).

Automotive gear lubricants in API category GL-5 are designed for use in final drive axles (differential gears) in moderate to severe service. Gear oils in API category MT-1 are intended for use in nonsynchronized manual transmissions in heavy-duty trucks and buses (161). Test requirements for GL-5 gear lubricants include

CRC L-37 24-h dynamometer test, operated at high torque, low speed conditions, to measure gear scoring and wear (162).

CRC L-42 2-h dynamometer test, operated at high speed with occasional shock loading, to measure gear scoring (162).

CRC L-60-1 48-hour oxidation test with motored gears to measure viscosity increase and insolubles (162).

CRC L-33 7 days in humidity cabinet after initial motoring phase to rate rusting (162).

ASTM D 130 to measure copper strip corrosion (163).

ASTM D 892 to measure foam tendency (164).

Gear Oil viscosity grades are defined by the SAE J306 Automotive Gear Oil Viscosity Classification (160,161,165).

The MT-1 requirements include additional CRC L-60-1 ratings, ASTM D 5662-99 seal compatibility tests (166), ASTM D 5579-04 high temperature cyclic durability test (167), a more severe copper corrosion requirement, and ASTM D 4998-95(2003)e FZG tractor hydraulic fluid wear test (161,162,168).

SAE J2360 and MIL-PRF-2105E, which have identical performance requirements, combine the requirements of GL-5 and MT-1 gear oils (160).

Limited slip differentials contain friction clutches that operate to apply equal torque to each driving wheel under slippery conditions. Lubricants for these units require a supplemental friction modifier added to the GL-5 lubricant to prevent chatter and noise when the clutches engage (161).

**5.6. Industrial Oil Viscosity Classification and Guide Recommendations.** The ISO viscosity classification system for industrial oils, based on kinematic viscosity at 40°C, is shown in Table 13 (169,170). Other viscosity classification systems include ASTM D 6080 (171), and ANSI/AGMA 9005 (172).

Recommended ISO viscosity grades for hydrodynamic bearings operating between 15 and 60°C are given in Table 14 (173). Table 15 shows viscosity grade recommendations for industrial enclosed gears (174). The recommended viscosity grade for rolling bearing lubricants as a function of temperature and dN number are given in Ref. 175. dN number is the product of the bore diameter and rotational speed.

The lubrication of gears, hydrodynamic thrust and radial bearings, rolling-contact bearings and other machine elements, such as sintered metal sliding bearings, screws, wire ropes, seals, valves, springs, and pneumatic components, is discussed at length in Ref. 176 (for an excellent discussion of hydraulic fluids see HYDRAULIC FLUIDS).

**5.7. Turbine Oils for Industrial Steam and Gas Turbines.** Steam and gas turbines are prime movers for electric power generation, for large ocean-going vessels, for pumps and compressors, for processing sugar cane, for rolling steel, and in many other industrial processes. Lubricating oils for the thrust and radial shaft bearings on these turbines may also be used for the generators, reduction gears, compressors, and other machines that the turbines are driving.

Compared to internal combustion engine oils, turbine oils have a relatively small number and concentration of additives. Their lives, however, are measured not in miles or hours, but in decades. A popular advertisement several years ago showed a young engineer next to a large turbine with the caption The oil in this turbine was put there before this engineer was born. Steam and gas turbine bearings are lubricated by an oil circulation system, which includes the oil, a pump, driven by the turbine shaft, an oil reservoir, a filter, an oil cooler, the bearings, and auxiliary equipment.

Turbine oils must have excellent thermal and oxidation stability, protect bearing surfaces from corrosion, separate easily from water, and they may not entrain air or foam excessively. Some may also require load carrying capacity beyond that afforded by a hydrodynamic lubricating film.

Typical specifications for an ISO 32 grade steam turbine oil and an ISO 32 grade gas and steam turbine oil are shown in Table 16. Specifications for oils requiring additional load carrying capacity have a minimum ASTM D 5182 FZG failure load stage of 8 or 9 (177–181).

Premium turbine oils can be formulated for >10,000 h D 943 oxidation lives, RPVOT lives of >1000 min, D 1401 demulsibility of 41/39/0 in 3 min and an FZG failure load stage of 12 (178).

## 6. Metalworking Fluids

Metalworking fluids are lubricants and coolants for metalworking processes. There are metal cutting or machining processes, which include drilling, turning, grinding, honing, lapping, milling, broaching, and other metal removal operations; and deformation processes such as rolling, drawing, extrusion, forging, stamping, and spinning (see METAL TREATMENTS).

**6.1. Types of Metalworking Fluids.** Types of metalworking fluids are found in the following sections (175).

**Straight Oils.** Blends of lubricity and EP additives in naphthenic base oils from API group V stocks and, increasingly, paraffinic oils from Groups I–IV stocks. Additives include sulfur, chlorine, fatty oils, sulfurized, chlorinated or sulfo-chlorinated fatty oils, phosphorus, metal salts, and solid lubricants (182).

**Soluble Oils.** A misnomer; They are milky macroemulsions of naphthenic or paraffinic hydrocarbon oil and additives in water. Emulsifiers include petroleum sulfonates and naphthenates, alkanolamides, amine salts of fatty acids, and other surfactants. Particle sizes range from 2 to 5  $\mu\text{m}$  and lubricating additives are the same as those used in straight oils (183–185).

**Synthetics.** The word “synthetic” has a somewhat different meaning for metalworking fluids. Here it means an aqueous metalworking fluid that contains no mineral oil. Synthetic metalworking fluids are solutions of totally water-soluble chemicals or they are emulsions of synthesized base oils from group V stocks. Base oils include polyglycols, amides, and organic esters. Particle sizes are  $<10^{-3}$   $\mu\text{m}$ . Synthetics may contain borates, molybdates, phosphates, amines and amides for corrosion protection, surface active agents to promote wetting, and water soluble lubricity and EP additives (183–185).

**Semisynthetics.** Microemulsions of oil and additives in water. Emulsifiers include petroleum sulfonates, ethoxylated alcohols, fatty amines and amides, sulfonamide compounds, and other surfactants. Particle sizes are between  $10^{-3}$  and 1  $\mu\text{m}$ . Lubricity and EP additives include polyol esters, phosphate esters, dithiophosphates and carbamates, and others (183–185).

All of the water-based fluids will contain biocides, or the biocide may be added to the cutting fluid reservoir, or both. Biocides are used to prevent the growth of bacteria and fungi in the reservoir (186). A list of commonly used chemicals registered by the U. S. Environmental Protection Agency (EPA) for use as metalworking fluid preservatives is included in reference (187).

Polymers may be added to all types of fluid to reduce the amount of mist generated during use.

In general, for high speed cutting operations where cooling is critical, water-based fluids are preferred. For heavy duty, slow speed cutting, where lubrication is more important, straight oils are used. However, there are a multitude of factors involved in cutting fluid selection. They include machinability of the metal, the mix of cutting operations, recovery and disposal of the spent fluid, plant size, water quality, type of filtration, and cost (183).

**6.2. Metal Cutting and Grinding Applications.** Lubrication in metal cutting and grinding operations differs from lubrication in bearings and gears in several important ways: (1) The relative motion of the chip and workpiece surfaces on the rake face and clearance face of the cutting tool (Fig. 7) tends to move fluid away from the contact zone rather than into it. Lubrication, therefore, is always in the boundary regime. Cutting fluid enters the contact zone through a labyrinth of capillaries formed by asperities on the surfaces. It is drawn in by the pressure difference between the contact zone and the atmosphere. (2) As the chip shears off the workpiece, nascent metal surfaces are formed, which rub on the rake and clearance faces of the cutting tool. Without an oxide coating, these surfaces are very reactive. Pieces of this active metal weld together to form a “built-up edge”, which causes poor quality of the machined surface and wear of the clearance face. Wear of the rake face occurs behind the built-up edge and shows up as a crater some distance from the tool tip. Lubricating additives in the cutting fluid must react with the nascent metal surfaces, at the temperature on the surfaces, to minimize formation of the built-up edge and prevent wear of the cutting tool. (3) The additives must also reduce friction force on the chip. The higher the friction force on the chip, the smaller the shear angle, the longer the shear plane and the more force it takes to shear the metal and form the chip. About one-quarter of the work in metal cutting is done to overcome friction and about three-quarters is done to form the chip. (4) Finally, cooling is extremely important to prevent distortion of the machined surface and to extend the life of the tool. Tool life decreases exponentially as the temperature at the tool–chip interface increases (188):

$$T\theta^n = K \quad (24)$$

where  $T$  is the tool life (min);  $\theta$  is temperature at the tool–chip Interface ( $^{\circ}\text{C}$ ); and  $n$  is an exponent dependent on type of tool, with value usually between 20 and 30; and  $K$  is a constant dependent on tool and workpiece material.

The other function of the cutting fluid is to flush chips and metal fines, called swarf, from the cutting area. This prevents the swarf from damaging the finished surface.

**6.3. Metal-Forming Operations.** Metal forming is the process of changing the shape or size of a piece of metal without removing any material. Operations include blanking, drawing, extrusion, forming, forging, rolling, spinning, and stamping.

For example, soluble oil emulsions are sprayed on the backup rolls in aluminum hot rolling mills to cool the rolls and lubricate the process. Its principle purpose is to prevent pickup of aluminum by the work roll surfaces. Friction

control is critical to provide traction to bring the work into the rolls, and to prevent slippage of the rolls on the surface being rolled.

In cold rolling aluminum sheet and foil, narrow boiling, paraffinic distillate oils fortified with fatty acids or alcohols or fatty esters such as lanolin and butylstearate. Normal paraffins, made by passing an atmospheric distillate like kerosene through a molecular sieve, and then hydrotreating and fractionating the *n*-paraffins, are widely used base stocks for aluminum cold rolling oils (184,189–192).

## 7. Lubricating Grease

Lubricating grease is a mixture of a fluid lubricant and a thickener that is dispersed in oil. It is a non-Newtonian fluid that acts like a sticky solid when there is no shear stress on it and that flows when a shear force is applied. It is widely used in ball and roller bearings and other machine elements where liquid lubricants cannot be retained. Automotive applications include wheel bearings, alternator bearings, constant velocity driveshaft joints (CVJ), mechanical clutch mechanisms, and gear-box bearings. Steel mills have central lubricating systems filled with multipurpose EP greases that are pumped long distances and applied through complex dispensing systems. Electric motor bearings, couplings, and roll neck bearings are some of the applications for grease in this industry (193,194).

Greases are classified by their consistency and by the type of thickener. The consistency of a grease is measured by cone penetration, ie, the distance, in mm/10 (penetration number), that a standard cone, acting under the influence of gravity, will penetrate a grease sample at 25°C under test conditions described in ASTM D 217-02 (195). The National Lubricating Grease Institute (NLGI) classification system for greases, based on worked penetration, is: (193)

Worked penetration is the penetration of a sample immediately after it has

NLGI Consistency number	Worked penetration, mm/10 at 25°C
000	445–475
00	400–430
0	355–385
1	310–340
2	265–295
3	220–250
4	175–205
5	130–160
6	85–115

been subjected to 60 double strokes in a standard grease worker.

The thickener in a grease may play as important a role as the oil in lubrication. The first greases were lime soap greases, made by saponifying a fatty oil with an slurry of hydrated lime,  $\text{Ca}(\text{OH})_2$ , and then dispersing the soap in oil and heating to drive off excess water. These greases are highly resistant to water, but unstable at high temperatures. Soda soap greases, made with

NaOH, are stable at high temperatures, but wash out in moist conditions. Lithium soap greases resist both heat and moisture. A mixed-base soap is a combination of soaps, offering some of the advantages of each type (196).

A complex soap is formed by the simultaneous reaction of an alkali with a high molecular weight fat or fatty acid and with a low molecular weight organic or inorganic acid. Non-soap thickeners include clays, silica gels, carbon black, and synthesized organic materials such as substituted ureas and polyureas (193,194,196).

Lithium soap and lithium complex greases are the most widely used multi-purpose greases. The fatty acid portion is most often 12-hydroxystearic acid, made from hydrogenated castor oil. Dimethyl azelate and sebacate have been used as complexing agents. The dropping point of lithium soap greases is in the range 180–190°C; of lithium complex greases, 260–300°C. Dropping point is the lowest temperature at which a grease is sufficiently fluid to drip, as determined by test method ASTM D 566-02 or D 2265-00. It is an indication of whether a grease will stay in a bearing at operating temperatures (197,198).

Polyurea greases are made by reacting amines with isocyanates or diisocyanates in base oil. Because they have superior high temperature durability, water resistance, structural stability and low torque performance, polyurea greases are used in sealed-for-life bearings in electric motors and alternators and water pumps, and in constant velocity joints (CVJ).

Bentonite clay (sodium montmorillonite and hectorite) is used as a grease thickener after being coated with quaternary alkyl ammonium cations (see CLAYS, USES). Clay thickened greases have good oxidation, excellent thermal, and mechanical stability. They have been successfully used in applications where ambient temperatures >260°C. An example is roller bearings on conveyor belts in glass factories.

The effect of shear rate on the apparent viscosity of three greases is shown in Fig. 8 (199,200). Grease has a yield point or yield stress, and does not flow until that stress is exceeded. Given the high shear rates in most rolling bearings, the apparent viscosity of grease is nearly the same as the viscosity of its base oil (193,199,200).

Table 17 is a grease application guide, comparing the properties of the several grease thickener systems (193).

ASTM D4950-01 (2004)e (201) covers lubricating greases suitable for the periodic relubrication of chassis systems and wheel bearings of passenger cars, trucks, and other vehicles. It includes specifications for two chassis lubricants, LA and LB, and three wheel bearing lubricants, GA, GB, and GC. To facilitate easy and accurate identification of greases in these categories, NLGI has made available the “NLGI Certification Mark” to be displayed on grease packaging. These specifications and the certification marks are also described in the January 2000 revision of SAE recommended practice J310 (194).

## 8. Solid-Film Lubrication

There are several applications where liquids do not provide adequate lubrication. In aerospace applications, eg, wide temperature ranges (–240 to 900°C) are



encountered accompanied by high vacuum. The manufacture of glass products requires lubricants that work at the temperature of molten glass. Lubricants are also needed that can withstand chemical attack in a corrosive atmosphere and are resistant to acids, aggressive gases, liquid oxygen, fuels, and solvents. Electrical contacts and precision machinery that require low start-up friction and cannot tolerate contamination by lubricating oils and greases are further examples (202). For these applications, solid lubricating films are applied to the rubbing surfaces.

The wide range of solid lubricants can generally be classified as either inorganic compounds or organic polymers (both commonly used in a bonded coating on a matching substrate), chemical conversion coatings, and metal films. Since solid-film lubricants often suffer from poor wear resistance and inability to self-heal any breaks in the film, the search continues for improved compositions (200).

**8.1. Inorganic Compounds.** The most important inorganic materials are layer–lattice solids in which the bonding between atoms in an individual layer is by strong covalent or ionic forces and those between layers are relatively weak van der Waal's forces. Because of their high melting points, high thermal stabilities, low evaporation rates, good radiation resistance, and effective friction lowering ability, molybdenum disulfide ( $\text{MoS}_2$ ) [1317-33-5], and graphite [7782-42-5] are the preferred choices in this group. Hexagonal boron nitride and boric acid also provide excellent lubrication (203). Among other layer–lattice solids that find occasional use are tungsten disulfide ( $\text{WS}_2$ ) [12138-09-9], tungsten diselenide ( $\text{WeS}_2$ ) [12067-46-8], niobium diselenide ( $\text{NbSe}_2$ ) [12034-77-4], calcium chloride [10108-64-2]; cadmium iodide ( $\text{CdI}$ ) [7790-80-9], and graphite fluoride [11113-63-6] (Table 18) (200,204).

Graphite is widely used as a dry powder or as a colloidal dispersion in water, petroleum oil, castor oil, mineral spirits, or other solvents. The water dispersions are used for lubricating dies, tools, metalworking molds, oxygen equipment, and wire drawing. Graphite dispersed in solvents is used for drawing, extruding, and forming aluminum and magnesium, as a high temperature lubricant for conveyors, and for a variety of industrial applications. Graphite alone is ineffective in vacuum since adsorbed water normally plays a decisive role in its lubricating ability. Its film-forming ability can be restored, however, by mixing with cadmium oxide or  $\text{MoS}_2$  and most organic materials, so that graphite may offer effective lubricating action when bonded to the surface with organics. Air oxidation commonly sets a use limit of  $\sim 550^\circ\text{C}$ , and high friction may occur in air with water desorption  $> 100^\circ\text{C}$  (205).

Molybdenum disulfide has increasingly supplanted graphite for three reasons: consistent properties in rigid specifications, independence from need for adsorbed vapors in providing lubrication, and superior load capacity (205). Like graphite,  $\text{MoS}_2$  has a layer–lattice structure in which weak sulfur–sulfur bonds allow easy sliding between each sulfur–molybdenum–sulfur layer. Molybdenum disulfide covered by MIL-M-7866 is the most common lubricant grade: It is purified from molybdenite ore and is essentially free of abrasive constituents (204).

Petroleum oil and grease dispersions of  $\text{MoS}_2$  are used extensively in automotive and truck chassis lubrication and in general industrial use. Dispersions

are also made with 2-propanol, polyalkylene glycols, other synthetic oils, and water for airframe lubrication, in wire drawing, and for splines, fastenings, gears, and fittings. Above 400°C, the  $\text{MoS}_2$  is oxidized to molybdenum trioxide, which has a significantly higher coefficient of friction. There are indications that, as rubbed films, both  $\text{MoS}_2$  and graphite may accelerate corrosion:  $\text{MoS}_2$  by hydrolysis to form corrosive acids and graphite by galvanic action.

Various other soft materials without the layer-lattice structure are used as solid lubricants (209), eg, basic white lead or lead carbonate [598-63-0] used in thread compounds, lime [1305-78-8] as a carrier in wire drawing, talc [14807-96-6] and bentonite [1302-78-9] as fillers for grease for cable pulling, and zinc oxide [1314-13-2] in high load capacity greases. Graphite fluoride is effective as a thin-film lubricant up to 400°C and is especially useful with a suitable binder such as polyimide varnish (206). Boric acid has been shown to have promise as a self-replenishing solid composite (203,207).

**8.2. Organic Polymers.** These self-lubricating polymers are used primarily in three ways: as thin films, as self-lubricating materials (see BEARING MATERIALS), or as binders for lamellar solids (203,205,208). Coatings are typically applied in powder or dispersion form with thickness ranging upward from 25  $\mu\text{m}$ . The polymer is then fused to the surface as a coating that provides lubricity, abrasion and chemical resistance, or release properties.

PTFE is outstanding in this group. In thin films it provides the lowest coefficient of friction (0.03–0.1) of any polymer, is effective from –200 to 250°C, and is generally unreactive chemically. The low friction is attributed to the smooth molecular profile of PTFE chains that allows easy sliding (203,205). Typical applications include chemical and food processing equipment, electrical components, and as a component to provide improved friction and wear in other resin systems.

Other polymers finding self-lubricating use are fluorinated ethylene-propylene copolymer (FEP), perfluoroalkoxy resin (PFA), ethylene-chlorotrifluoroethylene alternating copolymer (ECTFE), and poly(vinylidene fluoride) (PVDF) (208). With a useful temperature range up to 200°C, outstanding weatherability, and low friction, FEP finds use in chemical process equipment, roll covers, wire and cable, and as powder in resin bonded products. Perfluoroalkoxy resin provides somewhat better mechanical properties than PTFE and FEP at temperatures up to 250°C. The ECTFE provides superior strength, wear resistance, and creep resistance from cryogenic temperatures to ~165°C. Although fairly expensive, it is effective in its common use as a corrosion-resistant coating. Also having superior mechanical properties, PVDF is more commonly used for lining chemical piping and reactor vessels than as a lubricant.

**8.3. Bonded Solid-Film Lubricants.** Although a thin film of solid lubricant that is burnished onto a wearing surface often is useful for break-in operations, >95% are resin bonded for improved life and performance (210). Use of adhesive binders permits applications of coatings 5–20  $\mu\text{m}$  thick by spraying, dipping, or brushing as dispersions in a volatile solvent. The performance properties of some commonly used bonded lubricant films are listed in Table 19 (208,210).

For many moderate-duty films for operating temperatures <80–120°C,  $\text{MoS}_2$  is used in combination with acrylics, alkyds, vinyls, and acetate room

temperature curing resins. For improved wear life and temperatures up to 150–300°C, baked coatings are commonly used with thermosetting resins, eg, phenolics, epoxies, alkyds, silicones, polyimides, and urethanes. Of these, the MIL-L-8937 phenolic type is widely used (204).

Inorganic binders are used, usually with graphite or  $\text{MoS}_2$ , for extreme conditions such as high vacuum, liquid oxygen, radiation resistance, and high temperatures (208). The most common binder systems are silicates, phosphates, and aluminates. Some silicon and titanate metalloorganics used for high temperature binders become inorganic on curing. An emerging class of ceramic bonded materials for aerospace applications use either graphite, a  $\text{CaF}_2$ – $\text{BaF}_2$  eutectic, or proprietary systems, often with a glass frit binder that is fused into a continuous film (203,208). Plasma spray coating avoids overheating damage to the substrate metal while achieving the melting point of at least one component in high temperature film compositions (203,205,210).

The solid lubricant/binder ratio is a principal performance factor. High lubricant content usually gives minimum friction, while high binder content tends to give better corrosion resistance, hardness, durability, and a glossy finish (210). With commonly used  $\text{MoS}_2$ –graphite and organic resin binders, the optimum lubricant/binder ratio usually is from 1:1–4:1. With inorganic binding agents, the ratio is from 4:1 to as high as 20:1 and increases with high temperatures.

**Substrate Properties.** It is clear from equation 8 that higher hardness of the substrate lowers friction. Wear rate of the film also is generally lower. Phosphate undercoats on steel considerably improve wear life of bonded coatings by providing a porous surface that holds reserve lubricant. The same is true for surfaces that are vapor- or sandblasted prior to application of the solid-film lubricant. A number of typical surface pretreatments are given in Table 20 to prepare a surface for solid-film bonding (208).

Optimum surface roughness usually is 0.05–0.5  $\mu\text{m}$ ; a very smooth surface contains very little lubricant within its depressions, whereas rough peaks penetrate the lubricant to promote wear. Improved corrosion resistance may be obtained with a suitable subcoating surface conversion treatment or by inclusion of inhibitors in the coating.

**Plasma-Applied Coatings.** Composite coatings consisting of, eg, NiCr as a binder,  $\text{Cr}_2\text{O}_3$  as hardener,  $\text{BaF}_2/\text{CaF}_2$  as high temperature lubricant, and silver as low temperature lubricant have been developed by NASA (211,212). Applied as a plasma spray, these coatings provide lubrication at temperatures from –85 up to 1000°C (203,212).

Plasma enhanced chemical vapor deposition (PECVD) is used to produce diamond-like carbon and near-frictionless carbon coatings on steel substrates. Thin-film carbon coatings applied by this technique are described as “nanosmooth”, and have excellent friction modifying, wear reduction and antiscuffing characteristics (213–215).

Vacuum deposition techniques, such as sputtering, ion plating, physical vapor deposition, pulse laser deposition, ion beam assisted deposition, and plasma enhanced chemical vapor deposition, produce solid lubricant films that strongly adhere to the substrate. When these advanced methods are combined

with surface texturing and micropatterning, the films achieve much improved tribological properties (216).

**8.4. Chemical Conversion Coatings.** These involve inorganic surface compounds developed by chemical or electrochemical action (see METAL SURFACE CONVERSION TREATMENTS). One of the best known treatments for steel is phosphating to coat the surface with a layer of mixed zinc, iron, and manganese phosphates. Other films are anodized oxide coatings on aluminum, oxalate on copper alloys, and various sulfides, chlorides, and fluorides. Although many of these films are not strictly solid lubricants, they are often effective for short-term wear resistance. For long-term effectiveness, they often provide a porous reservoir for liquid lubricants and increased life of organically bonded coatings.

Diffusion provides an alternative procedure for generating a chemically modified surface, eg, sulfide surface films can be formed by immersing steel in molten mixtures of sulfur-containing salts such as sodium thiosulfate or sodium sulfide. Similar processes are employed for carburizing, nitriding, boriding, or siliconizing. Metallizing can introduce a new element into many metal surfaces from a molten fluoride bath. A number of hardening treatments, as well as flame sprayed tungsten and titanium carbides, provide excellent wear resistance. Some of these also provide good bases for low shear strength films.

**8.5. Metal Films.** In many respects, soft metals such as gallium, indium, thallium, lead, tin, gold, and silver are ideal solid lubricants (203,209). They have low shear strength, can be bonded strongly to substrate metal as continuous films, have good lubricity, and have high thermal conductivity. Metal films can be applied by electroplating or by vacuum processes, eg, evaporation, sputtering, and ion plating (see METAL COATINGS, SURVEY).

Melting points of gallium, indium, and tin are too low, and those of thallium and lead are borderline when high surface temperatures are generated by high speeds and loads. Gallium is a special case, ie, it is above its melting point under most conditions and is too reactive with many metals. It is effective, however, when applied in a vacuum with AISI 440C stainless steel and with ceramics (qv) such as boron carbide or aluminum oxide, which can be applied as undercoats (217).

A number of metal films are used industrially. Copper and silver are electroplated on the threads for bolt lubrication. Slurries of powders of nickel, copper, lead, and silver are also used in commercial bolt lubricants. Tin, zinc, copper, and silver coatings are used as lubricants in metalworking, where toxicity has virtually eliminated lead as a lubricating coating (218). Gold and silver find limited use on more expensive workpiece materials such as titanium. Silver films are useful in a variety of other sliding and rolling contacts, in vacuum and at high temperatures, since silver forms no alloys with steels and is soft at high temperatures.

Under severe conditions and at high temperatures, noble metal films may fail by oxidation of the substrate base metal through pores in the film. Improved life may be achieved by first imposing a harder noble metal film, eg, rhodium or platinum-iridium, on the substrate metal. For maximum adhesion, the metal of the intermediate film should alloy both with the substrate metal and the soft noble-metal lubricating film. This sometimes requires more than one intermediate layer. For example, silver does not alloy to steel and tends to lack adhesion. A

flash of hard nickel bonds well to the steel, but the nickel tends to oxidize and should be coated with rhodium before applying silver of 1–5- $\mu\text{m}$  thickness. This triplex film then provides better adhesion and greatly increased corrosion protection.

## 9. Extreme Ambient Conditions

**9.1. Gas Lubrication.** Despite severe limitations, gas lubrication of bearings has received intensive consideration for its resistance to radiation, for high speeds, temperature extremes, and use of the working fluid (gas) in a machine as its lubricant. A primary limitation is, however, the very low viscosity of gases (219) that leads to a limiting load of only 15–30 kPa (2.2–4.4 psi) for most self-acting (hydrodynamic) gas bearings and up to 70 kPa (10 psi) for operation with external gas-lifting pressure in hydrostatic operation.

Gases that have been used for bearing lubrication include air, hydrogen, helium, nitrogen, oxygen, uranium hexafluoride [7783-81-5], carbon dioxide, and argon [7440-37-1]. A useful property of gases is that their viscosity, and hence their capacity to generate hydrodynamic pressure  $P$ , increases with temperature whereas the opposite is true for liquids. Gas viscosity is usually independent of pressure up to  $\sim 1$  MPa (10 atm).

Hydrodynamic principles for gas bearings are similar to those involved with liquid lubricants except that gas compressibility usually is a significant factor (220,221). With gas employed as a lubricant at high speeds, start–stop wear is minimized by selection of wear-resistant materials for the journal and bearing. This may involve hard coatings, such as tungsten carbide or chromium oxide flame plate, or solid lubricants, eg, PTFE and  $\text{MoS}_2$ .

Because of the very small bearing clearances in gas bearings, dust particles, moisture, and wear debris (from starting and stopping) should be kept to a minimum. Gas bearings have been used in precision spindles, gyroscopes, motor and turbine-driven circulators, compressors, fans, Brayton cycle turbomachinery, environmental simulation tables, and memory drums.

**9.2. Liquid Metals.** If operating temperatures rise  $>250$ – $300^\circ\text{C}$ , where many organic fluids decompose and water exerts high vapor pressure, liquid metals have found some use, eg, mercury for limited application in turbines; sodium, especially its low melting eutectic with 23 wt % potassium, as a hydraulic fluid and coolant in nuclear reactors; and potassium, rubidium, cesium, and gallium in some special uses.

Liquid metal selection is usually limited to the lower melting point metals such as those mentioned above. Liquid metal viscosity generally is similar to water at room temperature and approaches the viscosities of gases at high temperature (Fig. 9). Hydrodynamic load capacity with both liquid metals and water in a bearing is about one-tenth of that with oil, as indicated in Table 21.

The sodium–potassium eutectic is commercially available for use as a liquid over a wide temperature range. Because of its excessive oxidizing tendency in air, however, its handling and disposal is hazardous; it can be used only in closed vacuum or in an inert gas atmosphere of helium, argon, or nitrogen. In addition to the oxidation problem, bearing material selection is critical for liquid metal

bearings. Tungsten carbide cermet with 10–20 wt% cobalt binder gave superior performance when running against molybdenum under heavy loads at low speeds at temperatures up to 815°C (222).

A low melting (5°C) gallium–indium–tin alloy has been the choice for small spiral-groove bearings in vacuum for X-ray tubes at speeds up to 7000 rpm (223). Surface tension 30 times that of oil avoids leakage of the gallium alloy from the ends of the bearings.

**9.3. Cryogenic Bearing Lubrication.** Cryogenic fluids, such as liquid oxygen, hydrogen, or nitrogen, are used as lubricants in liquid rocket propulsion systems, turbine expanders in liquefaction and refrigeration, and pumps to transfer large quantities of liquefied gases. (see CRYOGENIC TECHNOLOGY). Bearings operating in cryogenic fluids are amply cooled from the standpoint of dissipating the heat generated from friction. Unfortunately, the low viscosity of the fluids leads to marginal lubrication.

For wear resistance and low friction, coatings of PTFE or MoS<sub>2</sub> generally have been satisfactory. Use of low thermal expansion filler in PTFE helps minimize cracking and loss of adhesion from metal substrates with their lower coefficients of expansion.

Because of the low viscosities of cryogenic liquids, rolling element bearings seem better suited than hydrodynamic bearings for turbo pumps. The AISI 440C stainless balls and rings generally are preferred for their corrosion resistance over the more commonly used AISI 52100 steel.

**9.4. Nuclear Radiation Effects.** Components of a nuclear reactor system that are exposed to radiation and that require lubrication include control-rod drives, coolant circulating pumps or compressors, motor-operated valves, and fuel handling devices, and, of course, are exposed to varying amounts of ionizing (224).

Degree of damage suffered by a lubricant depends primarily on the total radioactive energy absorbed, whether it is from neutron bombardment or from gamma radiation. The common energy unit for absorbed dosage, the gray (Gy), is equal to 10<sup>-5</sup> J (100 ergs) absorbed per gram of material, or 0.01 Gy = 1 rad. The first changes observed with petroleum oils (at ~10<sup>4</sup> Gy dosage) is evolution of hydrogen and light hydrocarbon gas as fragments from the original molecule. Unsaturation results in decreased oxidation stability, cross-linking, polymerization, or scission (225).

The trend is for increasing viscosity with increased dose for several petroleum oils (225). For many lubricant applications, a dose that gives a 25% increase in 40°C viscosity can be taken as a tolerance limit. Lower radiation absorption seldom changes the lubricant sufficiently to interfere with its performance. Greater dosage results in more rapid thickening, sludging, and operating trouble (226).

The general range of tolerance limit of 1–4 × 10<sup>5</sup> Gy (1–4 × 10<sup>8</sup> rad) for petroleum oils in Table 22 tends to be somewhat higher than for synthetic oils (227). This is surprising in view of the excellent thermal and oxidative stability of methyl silicones, diesters, silicates, and some other synthetics. An exception is the high order of stability with synthetic oils consisting of aromatic hydrocarbons in which much of the absorbed energy appears to be transferred into harmless resonance in the aromatic ring structure. This reduces the degree of

damaging ionization and free-radical formation that occurs on a more general basis with the chain-like structures in paraffinic oils or in the saturated ring structure of alicyclic oils. Oil life is reduced by both the radiation dose and by oxidation if oxygen (air) is present at high temperature.

Conventional greases consisting of petroleum oils thickened with lithium, sodium, calcium, or other soaps suffer significant breakdown of the soap gel structure at doses above  $\sim 10^5$ – $10^6$  Gy ( $10^7$ – $10^8$  rad). Initial breakdown commonly involves increased softening of the grease to the point, where it may become fluid. At even higher doses, polymerization of the oil phase eventually leads to overall grease hardening. Some greases with radiation-resistant components, eg, polyphenyl ether oil and nonsoap thickeners, maintain satisfactory consistency for lubrication purposes up to  $10^7$  Gy ( $10^9$  rad).

**9.5. Lubrication with Glass.** Softening glass is used as a lubricant for extrusion, forming, and other hot working processes with steel- and nickel-base alloys up to  $\sim 1000^\circ\text{C}$ ; for extrusion and forming titanium and zirconium alloys; and less frequently for extruding copper alloys (218). Principal types of glasses used are pure fused silica [7631-86-9], 96% silica–soda–lime, borosilicates, and aluminosilicates [1327-36-2]. The glass composition is selected for proper viscosity, typically  $10$ – $100$  Pa  $\cdot$  s ( $1000$ – $10,000$  P) at the mean temperature of the die and workpiece, to serve as a true hydrodynamic lubricant. Glass may be applied as fibers or powder to the die or hot workpiece, or as a slurry with a polymeric bonding agent to the workpiece before heating. Another method involves rolling heated steel billets across glass sheets, where the glass then wraps itself around the billet before passing to a die extrusion chamber.

The U.S. Bureau of Mines has employed glass for forming ceramic materials at high temperatures (228).

**9.6. Ionic Liquids.** Ionic liquids are organic salts that remain liquid at room temperature. They have virtually no vapor pressure and, in applications like aluminum cold rolling, can significantly reduce air emissions if used in place of hydrocarbon-based lubricants. Forces holding the molecules together are Coulombic or electrostatic, as opposed to the weaker van der Waals forces holding most liquids together. A variety of anions such as  $\text{Cl}^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ , to name a few, may be used. The properties of two of these liquids, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide and 1-butyl-3-methylimidazolium hexafluorophosphate are described in Ref. 229 (see also MICROWAVE TECHNOLOGY).

**9.7. Solid and Liquid Lubricants for Extreme Environments.** A compilation of papers presented at a Symposium on Lubricants for Extreme Environments is given in Ref. 230.

## 10. The Lubricants Market

The National Petrochemical and Refiners Association (NPRA) reports lubricating oil sales of 2.4 billion gallons in the United States in 2002. Grease sales in 2002, according to NLGI International, were 500 million lb. Worldwide Lubricant demand in 2003, without marine oils, was  $\sim 36$  million metric tons. Lubricating oil base stock production in North America was  $\sim 71$  million barrels in 2003.

These numbers are broken down by region and product type in Table 23 (231,232).

The sales of automotive oils and greases have been fairly level in the period 1998–2002. Sales of industrial oils have declined in this period. The number of base stock refineries in the United States and Canada has fallen from ~40 in 1989–23 in 2004. United State and Canadian base stock capacity has dropped from 250,000 barrels/day in 2001 to 217,000 barrels/day in 2004. Production of groups II and III base stocks has grown over the past 10 years, however, from 4 to 42% (231).

## 11. Environmental and Health Factors (Toxicology)

Conservation, health, safety, and environmental pollution concerns have led to the creation of wide-reaching legislation such as the U.S. Congress Energy Policy and Conservation Act, Toxic Substances Control Act of 1976 (233), Resources Conservation and Recovery Act of 1976, the Oil Recycling Act of 1980, and subsequent implementation of many rules and regulations such as the OSHA Hazard Communication Standard. Continuing publications of new and proposed rules and regulations are available from the EPA (Washington, D.C.) and from the National Technical Information Service of the U.S. Department of Commerce (Springfield, Virginia) (234).

Regulations generally prohibit disposal of lubricants in streams, chemical dumps, or other environmental channels. Over one-half of disposed lubricants are burned as fuel, usually mixed with virgin residual, and distillate fuels (235).

Waste aqueous metalworking fluids may be successfully treated by conventional means for removal of tramp oil, surfactants, and other chemical agents to provide suitable effluent water quality (236).

**11.1. Lubricant Recycling.** Considerable effort is underway to improve and expand recycling of lubricating oils. Although typical processes result in 80–90% yield, questions remain regarding initial collection and the separation of used oil from water and other contaminants. Recycling treatment varies from simple cleaning to essentially the complete refining process used with virgin oil. Typical steps involved in purifying used petroleum lubricating oil are indicated schematically in Fig. 10 (237).

**11.2. Reclamation.** Reclamation involves simple separation of contaminants by gravity settling of water and dirt, centrifuging, filtering, and membrane techniques. With water-soluble cutting oils containing only a few percent oil, chemical emulsion breakers are first added that consist of sulfuric acid and then aluminum sulfate as a coagulant. Polymers are sometimes added to speed the process. The separated oil then is decanted, skimmed, or centrifuged and commonly is burned. Generally, 1–5% reprocessed waste oil may be added to fuel and still meet EPA industrial furnace limits, ie, <5 ppm arsenic by mass, <2 ppm cadmium, <10 ppm chromium, <100 ppm lead, and <4000 ppm halogens and a flash point >18°C (234).

**11.3. Reprocessing.** The simplest operation involves flash distillation in an evaporator at ~100–200°C in partial vacuum to remove water and low boiling contaminants, eg, gasoline and solvents. This is followed by treatment with



fuller's earth or other activated clay for removing oxidation products and most additives to produce a purified, light-colored oil which, with suitable additives, is satisfactory for use as fuel, metalworking base stocks, noncritical lubricants, and concrete form oil. Some used oils, eg, hydraulic and transformer oils, can be reprocessed with a portable unit of capacity to their original oil quality directly at the equipment in which they are being used.

**11.4. Rerefining.** The technology currently attracting most attention for producing original quality lubricating oil depends on distillation in thin-film evaporators (TFE) (231). Thin-film evaporator processes usually involve a scheme similar to that shown at the bottom of Fig. 10. The preliminary removal of water, solvents, and fuel is done in the same fashion as in most other recycling. Coking and fouling during distillation is avoided because the maximum temperature is maintained for only 2–5 s as the oil flows down the TFE wall under the influence of moving wiper blades; this is a small fraction of residence time in the packing or plates of a more traditional distillation tower. These variations involve batch operation with a single unit, or sequential distillation in multiple units to produce several lube fractions.

Older rerefining units used 2–5 kg/L of activated clay at 40–70°C and higher temperatures in place of TFE to clean the oil (238). More elaborate chemical and hydrotreating of used engine oils without a distillation step has been developed by Phillips Petroleum for processing 40,000 m<sup>3</sup>/year (10 × 10<sup>6</sup> gal/year). Establishment of a reliable feedstock supply is a critical consideration for larger rerefining plants.

**11.5. Toxic and Hazardous Constituents.** Questionable constituents of lubricating oils are polycyclic aromatics in the base oil plus various additives (239). Of refining steps used in preparing lubricating oil base stocks from toxic distillates, only effective solvent extraction, severe hydrogenation, or exhaustive fuming sulfuric acid treatment appear adequate to eliminate carcinogenicity. Mild hydrofinishing or light solvent extraction reduces carcinogenic potential, but does not necessarily eliminate it. Increasing the severity of hydrofinishing can eliminate carcinogenic compounds. Group IV base stocks, polyalphaolefins, are not expected to be carcinogenic since no polycyclic aromatics are present.

Most additives for lubricants present little risk, but the following involve significant hazards: lead compounds, phenyl 2-naphthylamine, sodium nitrite plus amines, tricresylphosphate high in the *o*-cresol isomer, and chlorinated naphthalenes. A number of sulfur compounds used as additives cause skin irritation; however, properly refined base oils containing usual concentrations of these additives have a low degree of toxicity. Used motor oil has displayed increased carcinogenic activity over its new counterpart (234,239). Users should also avoid contact with lubricants, metalworking oils, and quench oils that are highly degraded, were in service at extremely high temperatures, or are contaminated with toxic metals or bacteria.

The latest government regulations set forth under the Toxic Substances Control Act and in Public Health Service publications should be checked before formulating new lubricants. Users of lubricants should request Material Safety Data Sheets for each substance involved plus certification of compliance from vendors. Lubricant compounders should insist on similar information from

their suppliers for any additive packages. Manufacturers of both additives and lubricants commonly make toxicity checks on commercial products.

**11.6. Food Processing.** Prior to September, 1998, the U.S. Department of Agriculture (USDA), Food Safety Inspection Service (FSIS), working with the Food and Drug Administration (FDA) maintained a system to assure minimal risk to the consumer from incidental or unintended contact with lubricants used in the food and beverage industries (see FOOD PROCESSING) (240).

Upon satisfactory determination of nontoxicity, the USDA issued one of three ratings (241): H1 Lubricants: Food-grade lubricants used in the food processing environment, where there is a possibility of incidental food contact, eg, as by splashing or dripping from machinery above an edible product. H2 Lubricants: Nonfood-grade lubricants used on equipment and machine parts in locations where there is no possibility of food contact, eg, as in sealed gear boxes or machinery below a product line. H3 Lubricants: Food-grade lubricants, typically edible oils, used to prevent rust on hooks, trolleys and similar equipment. These classes include a number of petroleum and nonpetroleum oils and greases.

In September, 1998, the USDA issued the Hazard Analysis and Critical Control Point (HACCP) protocol and eliminated the approval program. This action shifted the burden of assessing the risk and approval of lubricants to the food processor or manufacturer. Under the HACCP system, food processing facilities must show the FSIS inspectors "documentation substantiating the safety of a chemical's (lubricant's) use in a food processing environment" (240,241).

In order to minimize disclosure of proprietary formulation details, lubricant manufacturers, with the approval of food processors, equipment builders and the USDA, have developed a system whereby third party certifiers assume the role previously handled by USDA. This includes preauthorization of nonfood compounds, screening of product formulations, product registration, and the issuance of approval documents (242,243).

The rating system used by USDA for lubricants will continue to be used. Food-grade lubricants rated H1 or H3 for incidental contact must be generally regarded as safe (GRAS); used in accordance with the provisions of a prior sanction or approval; or listed under 21 CFR 178.3570. Lubricants rated H2 for no allowable contact must not contain poisons, toxins, or other materials that can cause a health risk.

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Table 1. **Wear Coefficients for Various Sliding Combinations**<sup>a</sup>

Material combination	Wear coefficient, <i>k</i>
zinc on zinc	$53 \times 10^{-3}$
low carbon steel on low carbon steel	$7 \times 10^{-3}$
copper on copper	$11 \times 10^{-3}$
stainless steel on stainless steel	$7 \times 10^{-3}$
copper on mild steel	$5 \times 10^{-4}$
mild steel on copper	$17 \times 10^{-5}$
phenolic resin on phenolic resin	$7 \times 10^{-6}$

<sup>a</sup> For equation 9, from Ref. 14.

Table 2. API Base Stock Categories

API group	Saturates content, mass % by ASTM D 2007		Sulfur content, mass % <sup>a</sup>	VI by ASTM D 2270
I	< 90	and/ or	> 0.03	80 ≤ VI < 120
II	≥ 90	and	≤ 0.03	80 ≤ VI < 120
III	≥ 90	and	≤ 0.03	VI ≥ 120
IV	polyalphaolefins (PAO)			
V	All other base stocks not included in group I, II, III, or IV <sup>b</sup>			

<sup>a</sup> Measure sulfur content by the most recent version of one of the following test methods: ASTM D 1522, ASTM D 2622, ASTM D 3120, ASTM D 4294, ASTM D 4927.

<sup>b</sup> Group V includes naphthenic hydrocarbon and re-refined base stocks.

Table 3. **Typical Properties of GTL Base Stock**<sup>a, b</sup>

Base stock properties	ASTM	GTL-5, typical properties	Industry range, min-max	Value
viscosity at 100°C, cSt	D445	4.5	4.0–5.0	—
viscosity index	D2270	144	120–141	high
pour point, °C	D97	–21	–24 to –12	low
cold-cranking simulator at –25°C, cP	D5293	816	729–2239	low
NOACK wt%	D5800	7.8	10.4–14.8	low
composition, mass%				
iso-paraffins		100	47.3–80.9	high
monocycloparaffins		0	18.7–28.8	low
polycycloparaffins		0	5.3–22.2	low
aromatics		0	00–1.2	low

<sup>a</sup> See Ref. 79.<sup>b</sup> Reprinted with permission.

Table 4. EP and Antiwear Additives

zinc dialkyl and diaryl dithiophosphates	antiwear, antioxidant, corrosion inhibitor
zinc dialkyldithiocarbamate	antiwear, antioxidant, corrosion inhibitor, metal deactivator, color stabilizer
molybdenum dialkyldithiophosphate	antiwear, antioxidant, friction modifier, EP
molybdenum di- <i>n</i> -butyldithiocarbamate	antiwear, antioxidant, friction modifier, EP
antimony dialkyldithiophosphate	antiwear, antioxidant, friction modifier, EP
antimony tris(dialkyldithiocarbamate)	EP, antiscuff, antioxidant
ethyl acrylate dialkyldithiophosphate	ashless antiwear, EP
methylene bis(dibutyldithiocarbamate)	ashless EP, antioxidant
2,5-dimercapto-1,3,4-thiadiazol, alkyl polycarboxylate	ashless antiwear, antioxidant
amine phosphate and thiophosphates	ashless antiwear, rust inhibition
tricresyl phosphate	ashless antiwear, EP
trialkyl phosphates	ashless antiwear, EP
alkyl monoacid and diacid phosphates	ashless antiwear, EP
tertiarybutylphenyl phosphate	ashless antiwear, EP
dialkyl, trialkyl and triaryl phosphites	ashless antiwear, EP
sulfurized olefins	EP
sulfurized oils and esters	EP
Esters of thio and dithio phosphoric acid	EP
chlorinated paraffins	EP



Table 5. **Principal Applications for Lubrication Oils**

Automotive lubricating oils	Industrial lubricating oils
gasoline engine oils	industrial gear oils
for passenger cars and light trucks	pneumatic tool lubricating oil
for heavy duty automotive and industrial service	high temperature oils
for piston engines in general aviation service	air and gas compressor oils
small 2-stroke and 4-stroke gasoline engines	for reciprocating compressors
for outboard motors	for rotary vane compressors
for scooters, mopeds, and motorcycles	for rotary screw compressors
for lawnmowers and small tractors	for refrigeration compressors
for chain saws and similar portable equipment	machine tool way oils
diesel engine oils	textile oils
for heavy duty trucks, agricultural and construction vehicles	steam turbine oils
for industrial cross-head and trunk piston diesel engines	hydraulic fluids
for railroad diesel engines	paper machine oils
for marine cross-head and trunk piston diesel engines	food machinery oils
gas engine oils	steam cylinder oils
gas turbine oils	<b>Metalworking fluids</b>
for aircraft jet engines in commercial aviation service	for metal cutting
for industrial gas turbine engines	for metal rolling
automatic transmission fluids	for metal drawing, forging, stamping, etc
gear oils	
for automotive manual transmissions	
for automotive differentials	

Table 6. Engine Test Requirements, ASTM Sequence IIIG, IIIF, IIIE for Wear, Piston deposits, and High Temperature Oxidation

ILSAC	ILSAC GF-4	ILSAC GF-3	ILSAC GF-2	
CLASSIFICATION:				
API SERVICE CATEGORY:	Proposed API SM	API SL	API SJ	API SH
ISSUE DATE:	2004	2001	1996	1992
ASTM Engine Test Sequence	SEQUENCE IIIG	SEQUENCE IIIF	SEQUENCE IIIE	SEQUENCE IIIE
ASTM Test Procedure:			ASTM D 5533	ASTM D 5533
kinematic viscosity increase at 40°C, %	150 max	275 max	375 max	375 max
average weighted piston deposits, merits	3.5 min	4		
hot stuck rings	none	none	none	none
cam plus lifter wear, average, $\mu\text{m}$	60 max	20 max	30 max	30 max
maximum per position, $\mu\text{m}$			64	64
piston skirt varnish		9.0 min	8.9 min	8.9 min
oil consumption, L		5.2 max	5.1 max	5.1 max
avg. oil ring land deposits			3.5 min	3.5 min
avg. engine sludge rating			9.2 min	9.2 min
lifter sticking			none	none
cam + lifter scuffing			none	none
low temperature	stay in grade or			
pumping viscosity at end of test by ASTM D 4684 (MRV TP-1)	next higher grade	rate & report		

Table 7. **Engine Test Requirements, ASTM Sequence VG and VE for Wear, Sludge and Varnish**

ILSAC CLASSIFICATION:	ILSAC GF-4	ILSAC GF-3	ILSAC GF-2	
API SERVICE CATEGORY:	Proposed API SM	API SL	API SJ	API SH
ISSUE DATE:	2004	2001	1996	1992
ASTM ENGINE TEST SEQUENCE	SEQUENCE VG	SEQUENCE VG	SEQUENCE VE	SEQUENCE VE
ASTM Test Procedure:	ASTM D 6593	ASTM D 6593	ASTM D 5302	ASTM D 5302
average engine sludge, merits	7.8 min	7.8 min	9.0 min	9.0 min
average rocker cover sludge, merits	8.0 min	8.0 min	7.0 min	7.0 min
average engine varnish, merits	8.9 min	8.9 min	5.0 min	5.0 min
average piston skirt varnish, merits	7.5 min	7.5 min	6.5 min	6.5 min
oil screen sludge (clogging), % area	20 max	20 max	20 max	20 max
oil screen debris, % area	rate and report	rate and report		
hot stuck compression rings	none	none	none	none
cold stuck rings	rate and report	rate and report	—	—
oil ring clogging, % area	rate and report	rate and report	rate and report	15
cam lobe wear, average, $\mu\text{m}$			127 max	130 max
maximum per position, $\mu\text{m}$			380 max	380 max
cam follower pin wear, cyl #8, avg, $\mu\text{m}$	rate and report	rate and report	—	—
ring gap increase, cyl #1 & #8, avg, $\mu\text{m}$	rate and report		—	—
cylinder bore wear		rate and report	—	—
ring wear		rate and report	—	—

**Table 8. Engine Test Requirements, ASTM Sequence IVA, VIII, IID and CRC-L-38 For Valve Train Wear, Bearing Corrosion, Shear Stability and Engine Rusting**

ILSAC CLASSIFICATION:	ILSAC GF-4	ILSAC GF-3	ILSAC GF-2	
API SERVICE CATEGORY:	Proposed API SM	API SL		
ISSUE DATE:	2004	2001		
ASTM ENGINE TEST SEQUENCE	SEQUENCE IVA	SEQUENCE IVA	API SJ	API SH
ASTM Test Procedure:	ASTM D 6891	ASTM D 6891	1996	1992
average cam wear (7 position average) $\mu\text{m}$	90 max	120 max	—	—
ENGINE TEST SEQUENCE	SEQUENCE VIII	SEQUENCE VIII	CRC L-38	CRC L-38
ASTM Test Procedure:	ASTM D 6709	ASTM D 6709	ASTM D 5119	ASTM D 5119
bearing weight loss, mg	26 max	26.4 max	40 max	40 max
shear stability (10 hour stripped viscosity)	stay in grade	stay in grade	stay in grade	stay in grade
piston skirt varnish				9 min
ASTM ENGINE TEST SEQUENCE:		(See Ball rust bench test)	SEQUENCE IID	SEQUENCE IID
ASTM Procedure:			ASTM D 5844	ASTM D 5844
avg. engine rust rating			8.5 min	8.5 min
lifter sticking			none	none

Table 9. **Engine Test Requirements, ASTM Sequence VIB and VIA for Fuel Economy**

ILSAC CLASSIFICATION:	ILSAC GF-4	ILSAC GF-3	ILSAC GF-2
API SERVICE CATEGORY:	Proposed API SM	API SL	API SJ
ISSUE DATE:	2004	2001	1996
ASTM ENGINE TEST SEQUENCE	SEQUENCE VIB	SEQUENCE VIB	SEQUENCE VIA
ASTM Test Procedure:	ASTM D 6837 <sup>a</sup>	ASTM D 6837 <sup>a</sup>	ASTM D 6202 <sup>a</sup>
SAE 0W-20 and 5W-20 viscosity grades			
% fuel economy improvement, Phase 1	2.3 min	2.0 min	
% fuel economy improvement, Phase 2	2.0 min	1.7 min	1.4 min
SAE 0W-30 and 5W-30 viscosity grades			
% fuel economy improvement, Phase 1	1.8 min	1.6 min	
% fuel economy improvement, Phase 2	1.5 min	1.3 min	1.1 min
% total fuel economy improvement		3.0 min	
SAE 10W-30 and all other grades not listed above			
% fuel economy improvement, Phase 1	1.1 min	0.9 min	
% fuel economy improvement, Phase 2	0.8 min	0.6 min	0.5 min
% total fuel economy improvement		1.6 min	

<sup>a</sup> All fuel economy values, Phases 1 and 2, are determined relative to ASTM Reference Oil BC.

Table 10. **Bench Test Requirements for Catalyst Compatibility, Wear and Volatility**

ILSAC CLASSIFICATION:	ILSAC GF-4	ILSAC GF-3	ILSAC GF-2	
API SERVICE CATEGORY:	Proposed API SM	API SL	API SJ	API SH
ISSUE DATE:	2004	2001	1996	1992
<i>Catalyst compatibility</i>				
phosphorus content, mass %, ASTM D 4951	0.08 max	0.1 max		
SAE 0W-20, 5W-20, 5W-30, and 10W-30 only			0.1 max	
SAE 5W-30 and 10W-30 only				0.12 max
sulfur content, mass %, ASTM D 4951 or D 2622				
SAE 0W and 5W multigrades	0.5 max			
SAE 10W multigrades	0.7 max			
<i>Wear</i>				
phosphorus content, mass %, ASTM D 4951	0.06 min			
<i>NOACK Volatility, ASTM D 5800</i>				
evaporation Loss after 1 h at 250°C, %	15 max	15 max		
SAE 0W-XX			22 max	NR
SAE 5W-XX			22 max	25 max
SAE 10W-30			22 max	20 max
SAE 15W-40			20 max	18 max
<i>Volatility, Simulated Distillation, ASTM D 6417</i>				
% volatilized to 371°C	10 max	10 max		
SAE 0W-XX			17 max	NR
SAE 5W-XX			17 max	20 max
SAE 10W-30			17 max	17 max
SAE 15W-40			15 max	15 max

Table 11. **Bench Test Requirements for High Temperature Deposits, Filterability, Foam Tendency and Stability, Engine Rusting and Flash Point**

ILSAC CLASSIFICATION:	ILSAC GF-4	ILSAC GF-3	ILSAC GF-2	
API SERVICE CATEGORY:	Proposed API SM	API SL	API SJ	API SH
ISSUE DATE:	2004	2001	1996	1992
<i>High temperature deposits,</i>				
<i>TEOST, ASTM D 6335</i>				
Total Deposits, mg	35 max	45 max		
<i>Filterability</i>				
Engine Oil Water Tolerance				
Test, ASTM D 6794				
% flow reduction with 0.6% water	50 max	50 max		
% flow reduction with 1.0% water	50 max	50 max		
% flow reduction with 2.0% water	50 max	50 max		
% flow reduction with 3.0% water	50 max	50 max		
Engine Oil Filterability Test, ASTM D 6795				
% flow reduction	50 max	50 max	50 max	50 max
<i>Foam tendency/stability, ASTM D 892 (Option A)</i>				
sequence I	Oct-00	Oct-00	Oct-00	Oct-00
sequence II	50/0	50/0	50/0	50/0
sequence III	Oct-00	Oct-00	Oct-00	Oct-00
high temperature	100/0	100/0	200/50	NR
<i>Engine rusting, Ball Rust Test, ASTM D 6557</i>			(See Engine Test Sequence IID)	
Avg Gray Value	100 min	100 min		
<i>Flash point, ASTM D 92, °C</i>				
0W-XX			200 min	NR
5W-XX			200 min	200 min
10W-30			200 min	200 min
15W-40			215 min	NR

Table 12. Performance Requirements of 4-Stroke Diesel Engines

API service category	CG-4	CH-4	CI-4	PC-10
Foaming Characteristics (ASTM D892)				
foaming/settling, mL, max,				
sequence I	10/0	10/0	10/0	10/0
sequence II	20/0	20/0	20/0	20/0
sequence III	10/0	10/0	10/0	10/0
ASTM corrosion test	D5968	D5968	D6594	
copper increase, ppm, max	20	20	20	
lead increase, ppm, max	60	120	120	
tin increase, ppm,	report	50	50	
copper Corrosion by ASTM D130, max rating	3	3	3	
NOACK volatility(ASTM D5800) or distillation (ASTM D2887)				X
Evaporative loss at 250°C, % max			15	
SAE 10W-30, % volatility loss at 250°C, max		20		
SAE 15W-40, % volatility loss at 250°C, max		18		
or		or		
volatility by capillary gas chromatography(ASTM D6417)				
SAE 10W-30, % volatility loss at 371°C, max		9.3		
SAE 15W-40, % volatility loss at 371°C, max		12.5		
shear stability(ASTM D6278)				
kinematic viscosity after shearing				
SAE XW-30, cSt min		9.3	9.3	X
SAE XW-40, cSt min		12.5	12.5	X
shear stability -90 cycles(ASTM ASTM D3945)				X
low temperature pumpability with sooted oils				
ASTM D4684 (MRV TP-1)Viscosity of 75 h used				
oil sample from T-10 test at -20°C, mPa-s, max			25,000	X
high temperature/high shear viscosity, mPa-s, min			3.5	X
elastomer compatibility limits				X
nitrile				
volume change			+5/-3	X
hardness			+7/-5	X
tensile strength			+10/-TMC 1006	X
elongation			+10/-TMC 1006	X
silicone				
volume change			+TMC 1006/-3	X
hardness			+5/-TMC 1006	X
tensile strength			+10/-45	X
elongation			+20/-30	



Table 12 (Continued)

API service category	CG-4	CH-4	CI-4	PC-10
polyacrylate				
volume change			+5/−3	X
hardness			+8/−5	X
tensile strength			+18/−15	X
elongation			+20/−30	X
FKM				
volume change			+5/−2	X
hardness			+7/−5	X
tensile strength			+10/−TMC 1006	X
elongation			+10/−TMC 1006	X

Table 13. **Viscosity System for Industrial Fluid Lubricants<sup>a</sup>**

Viscosity grade	Midpoint viscosity, cSt at 40°C	Kinematic viscosity limits, cSt at 40°C	
		min	max
ISO VG 2	2.2	1.98	2.4
ISO VG 3	3.2	2.88	3.52
ISO VG 5	4.6	4.14	5.06
ISO VG 7	6.8	6.12	7.48
ISO VG 10	10	9.00	11.0
ISO VG 15	15	13.5	16.5
ISO VG 22	22	19.8	24.2
ISO VG 32	32	28.8	35.2
ISO VG 46	46	41.4	50.6
ISO VG 68	68	61.2	74.8
ISO VG 100	100	90.0	110
ISO VG 150	150	135	165
ISO VG 220	220	198	242
ISO VG 320	320	288	352
ISO VG 460	460	414	506
ISO VG 680	680	612	748
ISO VG 1000	1000	900	1100
ISO VG 1500	1500	1350	1650
ISO VG 2200	2200	1980	2420
ISO VG 3200	3200	2880	3520

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Table 14. **Suggested Viscosity Grade of Oil for Plain Bearings Operating between 15 and 60°C**

Speed Range, rpm	Loading on projected bearing area		
	Light, Up to 700 kPa	Medium, 700–1700 kPa	Heavy, >1700 kPa
5,000–10,000	10		
2,000–5,000	15		
1,000–2,000	22	32, 46	
500–1000	32, 46	68, 100	
300–500	68, 100	100,150	
100–300	100, 150	220, 320	320, 460
50–100	150, 220	220, 320	460, 680, 1000
< 50	220, 320	320, 460	460, 680, 1000

Table 15. ISO Viscosity Grade Guide Recommendations for Enclosed Gears

Type of gear	Ambient temperature	
	–10 to 10°C	10 to 50°C
parallel shaft units: input speeds to 3600 rpm		
single reduction: shaft center distance <sup>a</sup>		
up to 20 cm	68, 100	100, 150
20–50 cm	68, 100	150, 220
> 50 cm	100, 150	150, 220
double reduction: shaft center distance		
up to 20 cm	68, 100	100, 150
> 20 cm	100, 150	150, 220
triple reduction: shaft center distance		
up to 20 cm	68, 100	100, 150
20–50 cm	100, 150	150, 220
>50 cm	150, 220	220, 320
input speeds > 3600 rpm: all types and sizes	46	68
planetary units: diameter of housing		
up to 40 cm	68, 100	100, 150
> 40 cm	100, 150	150, 220
bevel gears, spiral or straight: cone distance <sup>b</sup>		
up to 30 cm	68, 100	150, 220
> 30 cm	100, 150	220, 320
gear motors and shaft mounted units	68, 100	150, 220

<sup>a</sup> Shaft center distance = distance between centers of largest gear and its pinion.

<sup>b</sup> Cone distance = one-half the outside diameter of the largest gear.

Table 16. **Typical Turbine Oil Specifications**

Property	Test method	Steam turbine oil	Steam and gas turbine oil
ISO viscosity grade	D 2422	32	
flash point, °C,	D 92	215 min	
pour point, °C	D 97	–12 max	
total acid number, mg KOH/g	D 974	2 max	
air release, separation time, min. at 50°C	D 3427	4 max	
foam tendency/ stability	D 892		
sequence I, mL		10/0	
sequence II, mL		20/0	
sequence III, mL		10/0	
demulsibility	D 1401		
oil/water/emulsion, mL		40/37/3	
separation time, min		20	
copper strip corrosion, 3 h at 100°C	D 130	1 max	
distilled water rust test	D 665	Pass	
oxidation stability, TOST	D 943		
time to 2.0 TAN, h		3000 min	7000 min
oxidation stability, RPVOT	D 2272		
time to 25 psi pressure drop, min		500 min	1000 min

Table 17. **Grease Application Guide**<sup>a,b</sup>

70	Properties	Aluminum	Sodium	Calcium, conven- tional	Calcium, anhydrous	Lithium	Aluminum complex	Calcium complex	Lithium complex	Polyurea	Organo clay
	dropping point, °C	110	163–177	96–104	135–143	177–204	260 +	260 +	260 +	243	260 +
	usable tem- perature, °C	79 max	121 max	93 max	110 max	135 max	177 max	177 max	177 max	177 max	177 max
	water resis- tance	good–excel- lent	poor–fair	good–excel- lent	excellent	good	good–excel- lent	fair–excel- lent	good– excellent	good–excel- lent	fair–excel- lent
	work stabi- lity	poor	fair	fair–good	good–excel- lent	good–excel- lent	good–excel- lent	fair–good	good– excellent	poor–good	fair–good
	oxidation stability	excellent	poor–good	poor–excel- lent	fair–excel- lent	fair–excel- lent	fair–excel- lent	poor–good	fair– excellent	good–excel- lent	good
	rust protec- tion	good–excel- lent	good– excel- lent	poor–excel- lent	poor–excel- lent	poor–excel- lent	good–excel- lent	fair–excel- lent	fair– excellent	fair–excel- lent	poor–excel- lent
	pumpability	poor	poor–fair	good–excel- lent	fair–excel- lent	fair–excel- lent	fair–good	poor–fair	good– excellent	good–excel- lent	good
	(in cen- tralized systems)										
	oil separa- tion	good to	fair–good	poor–good	good	good–excel- lent	good–excel- lent	good–excel- lent	good–excel- lent	good–excel- lent	good–excel- lent
	appearance	smooth and clear	smooth– fibrous	smooth and buttery	smooth and buttery	smooth and buttery	smooth and buttery	smooth and buttery	smooth and buttery	smooth and buttery	smooth and buttery
	other prop- erties		adhesive and cohe- sive	EP grades available	EP grades available	EP grades available	EP grades available	inherent EP and anti- wear	EP grades available	EP grades available	
	principal uses	thread lubri- cants	rolling con- tact bear- ings	general uses for econ- omy	military multiser- vice	multiservice automo- tive and industrial	multiservice industrial	multiservice automo- tive and industrial	multiservice automo- tive and industrial	multiservice automo- tive and industrial	high tem- perature (frequent relube)

<sup>a</sup> Multiservice includes rolling contact bearings, plain bearings and others. Reversibility is the ability of a grease to return to its normal grease-like consistency after temporary exposure to temperatures near or above its dropping point.

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Table 18. Common Solid Lubricants<sup>a</sup>

Material	Acceptable usage temperature, °C						Remarks
	Minimum		Maximum		Avg friction coefficient, $f$		
	In air	In N <sub>2</sub> or vacuum	In air	In N <sub>2</sub> or vacuum	In air	In N <sub>2</sub> or vacuum	
molybdenum disulfide (MoS <sub>2</sub> )	−240	−240	370	820	0.10–0.25	0.05–0.10	low $f$ , carries high load, good overall lubricant, Can promote metal corrosion
polytetrafluoroethylene (PTFE)	−70	−70	290	290	0.02–0.15	0.02–0.15	lowest $f$ of solid lubricants, load capacity moderate and decreases at elevated temperature
fluoroethylene-propylene copolymer (FEP)	−70	−70	200	200	0.02–0.15	0.02	low $f$ , lower load capacity than PTFE
graphite	−240		540	unstable in vacuum	0.10–0.30	0.02–0.45	low $f$ and high load capacity in air, high $f$ and wear in vacuum, conducts electricity
niobium diselenide (NbSe <sub>2</sub> )			370	1,320	0.12–0.40	0.07	low $f$ , high load capacity, conducts electricity (in air or vacuum)
tungsten disulfide (WS <sub>2</sub> )	−240	−240	430	820	0.10–0.20		$f$ not as low as MoS <sub>2</sub> , temp capability in air a little higher
tungsten diselenide (WSe <sub>2</sub> )			370	1320			same as for WS <sub>2</sub>
lead sulfide (PbS)			480		0.10–0.30		very high load capacity, used primarily as additive with other solid lunricants
lead oxide (PbO)			650		0.10–0.30		same as for PbS
calcium fluoride–barium fluoride eutectic (CaF <sub>2</sub> –BaF <sub>2</sub> )	430	430	820	820	0.10–0.25 above 540°C 0.25–0.40 above 540°C		can be used at higher temp than other solid lubricants, high $f$ < 540°C
antimony trioxide (Sb <sub>2</sub> O <sub>2</sub> )							high load capacity, used as corrosion inhibitor in MoS <sub>2</sub> lubricants

<sup>a</sup> See Ref. 204.

Table 19. Performance Properties of Typical Solid-Film Lubricants<sup>a</sup>

Specification:	Organic <sup>b</sup>					Inorganic <sup>b</sup>			
	Thermo set				Air dry				
	MIL-L-8937	MIL-L-46010			MIL-L-23398	MIL-L-46009	MIL-L-81329	AMS2525A	AMS2526A
composition: lubricant	MoS <sub>2</sub>	MoS <sub>2</sub> /metal- lic	MoS <sub>2</sub> /gra- phite	PTFE	MoS <sub>2</sub>	MoS <sub>2</sub> /gra- phite	MoS <sub>2</sub> /gra- phite	graphite	MoS <sub>2</sub>
binder application:	phenolic spray	epoxy spray	silicone spray	phenolic spray	spray	aerosol	silicate spray		impinge- ment
cure:	149°C	204°C	260°C	204°C	ambient	ambient	204°C	149°C	149°F
compatibility:									
LOX	N/A	N/A	N/A	N/A	N/A	N/A	X	X	X
OZ	N/A	N/A	N/A	N/A	N/A	N/A	X	X	X
rocket fuel	X	N/A	L	N/A	N/A	N/A	L	X	X
jet fuel	X	X	X	X	X	L	X	X	X
hydrocarbons	X	X	X	X	X	L	X	X	X
solvents	X	X	X	X	X	L	X	X	X
radiation:	Fair	N/A	N/A	N/A	N/A		V.G.	V.G.	V.G.
operating temp.									
air (high)	260°C	260°C	371°C	260°C	176°C	204°C	649°C	+1093°C	400°C
air (low)	-220°C	-220°C	-157°F	-220°C	-220°C	-185°C	-240°C	-240°C	-220°C
vacuum	10 <sup>-4</sup> Pa	10 <sup>-7</sup> Pa	10 <sup>-7</sup> Pa	N/A	N/A	N/A	10 <sup>-3</sup> Pa	10 <sup>-7</sup> Pa	10 <sup>-7</sup> Pa
load capacity <sup>c</sup> force test	2500 lb gage Falex	2500 lb gage Falex	2500 lb gage Falex	150 lb LFW-1	2500 lb gage Falex	2500 lb gage Falex			
wear life <sup>c</sup> load	1000 lb gage Falex	1000 lb gage Falex	1000 lb gage Falex	150 lb LFW-1	1000 lb gage Falex		1000 lb gage Falex	50 Falex	50 Falex
test time	60 min	450 min	60 min	120,000	120 min		70 min	2 min	5 min
coefficient of friction	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
corrosion resistance	G.	V.G.	F	E	G	—	F	—	—

<sup>a</sup> See Ref. 210.<sup>b</sup> X = Compatible; L = Low; N/A = Not Applicable.<sup>c</sup> Falex tests are all designed for English units and are, therefore, reported as such.



Table 20. **Typical Pretreatments for Various Substrates<sup>a</sup>**

Substrate	Pretreatment
aluminum	vapor degrease plus anodize light abrasive blast plus chromate conversion
copper and its alloys	vapor degrease light abrasive blast plus chromate conversion
iron and steel	vapor degrease abrasive blast plus phosphate
stainless steel	vapor degrease sandblast passivation
titanium	alkaline cleaning abrasive blast fluoride phosphate or alkaline anodize

<sup>a</sup> See Ref. 208.

Table 21. **Typical Design Limits for Fluid-Film Hydrodynamic Bearings**

Item	Load on projected area, MPa <sup>a</sup>
oil lubrication	
steady load	
electric motors	1.4
steam turbines	2.1
railroad car axles	2.4
dynamic load	
automobile engine main bearings	24
automobile connecting-rod bearings	34
steel-mill roll necks	34
water lubrication	0.2
gas bearings	0.02

<sup>a</sup> To convert MPa to psi, multiply by 145.

Table 22. **Radiation Tolerance Limits of Several Oil Types**

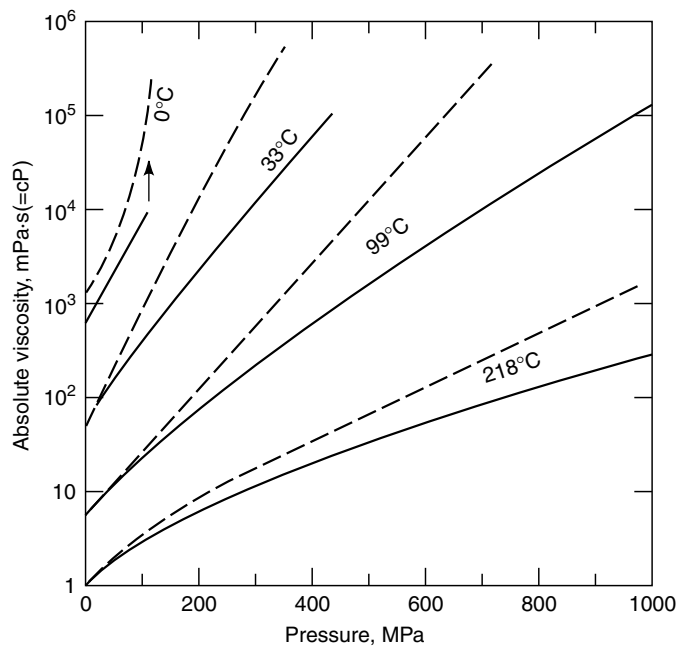
Oil	Tolerance limit, $10^6 \text{Gy}^a$ for 25% increase in 40°C viscosity
petroleum	1–4
synthetic	
diester MIL-L-6085	1.1
synthetic	2.5–4.5
hydrocarbon	
phosphate ester	0.4–0.6
poly(propylene oxide)	1.0
alkylbenzene	5
dimethyl silicone	<1
methyl phenyl	1
silicone	
tetraaryl silicate	0.6

<sup>a</sup>To convert Gy to rad, multiply by 100.

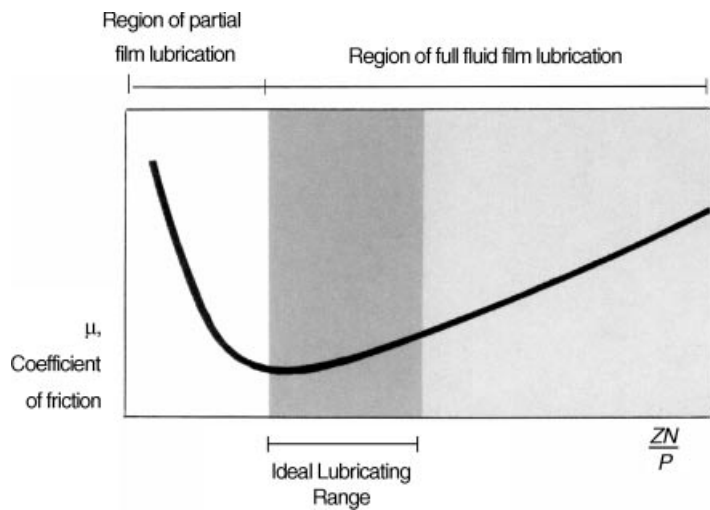
Table 23. **The Lubricants Market**<sup>a</sup>

Worldwide lubricant demand(without marine oils)	2003	%
Asia-Pacific	11.2	31.2
North America	8.4	23.2
Western Europe	4.8	13.4
Central & Eastern Europe	4.8	13.4
Latin America	3.1	8.7
Near and Middle East	1.8	4.9
Africa	1.9	5.2
<i>total</i> worldwide lubricant demand, millions of metric tons	<i>36.0</i>	<i>100.0</i>
U. S. lubricating oil sales,	2002	
multigrade crankcase oils	1,008	42
monograde crankcase oils	96	4
automotive transmission and hydraulic oils	264	11
other automotive oils	48	2
<i>total</i> automotive oils, millions of gallons	<i>1,416</i>	<i>59</i>
general industrial oils	312	13
industrial engine oils	144	6
<i>total</i> industrial lubricating oils, millions of gallons	<i>456</i>	<i>19</i>
process oils	480	20
metalworking oils	48	2
<i>total</i> U. S. lubricating oil sales, millions of gallons	<i>2,400</i>	<i>100</i>
North America lubricating grease production,	2002	
conventional lithium grease	180	36
lithium complex grease	160	32
polyurea grease	35	7
aluminum soap grease	45	9
calcium soap grease	30	6
sodium and other metallic soap grease	5	1
organo-clay grease	35	7
other non-soap grease	10	2
<i>total</i> North American grease production, millions of pounds	<i>500</i>	<i>100</i>
U. S. refinery base stock production,	2003	
paraffinic base stocks	51.0	84
naphthenic base stocks	9.6	16
<i>total</i> U. S. refinery base stock production, million of barrels	<i>60.6</i>	<i>100</i>
Estimated North American base stock production,	2003	
paraffinic group I	30.8	43.4
paraffinic group II	28.0	39.4
paraffinic group III	1.4	2.0
polyalphaolefin group IV	1.0	1.4
naphthenic and other group V	9.8	13.8
<i>total</i> estimated North American base stock production, millions of barrels	<i>71.0</i>	<i>100.0</i>

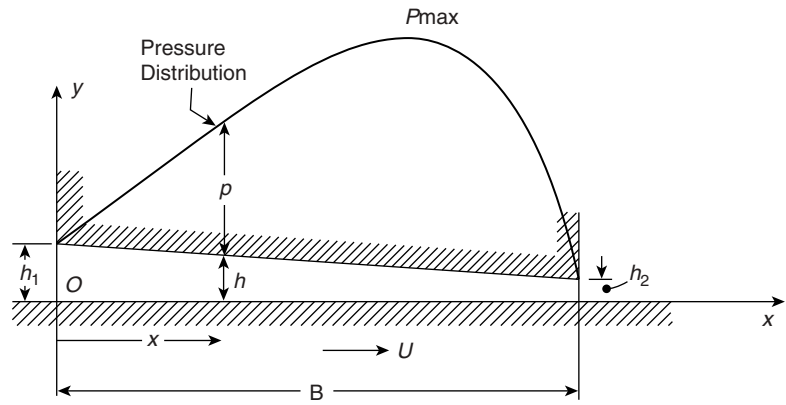
<sup>a</sup> See Refs. 231,232.



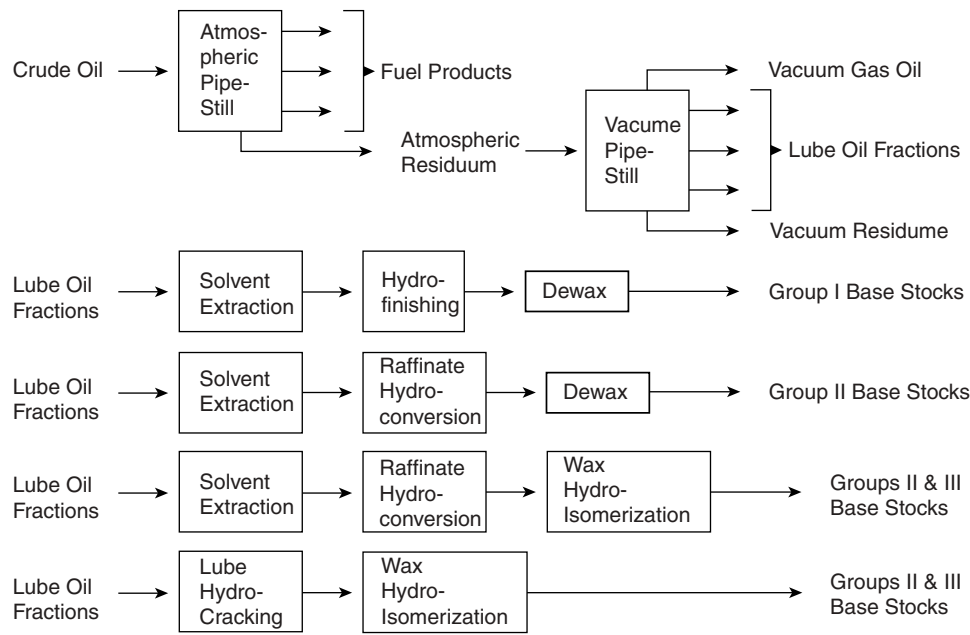
**Fig. 1.** Viscosity pressure curve for typical petroleum oils, where — = Paraffinic, - - - = Alicyclic, ↑ = Solid.



**Fig. 2.** Variation of coefficient of friction with  $\frac{ZN}{P}$ .



**Fig. 3.** Pressure distribution in a hydrodynamic film. Reprinted with permission from Ref. 29.



**Fig. 4.** Base stock refining options. Used with permission.

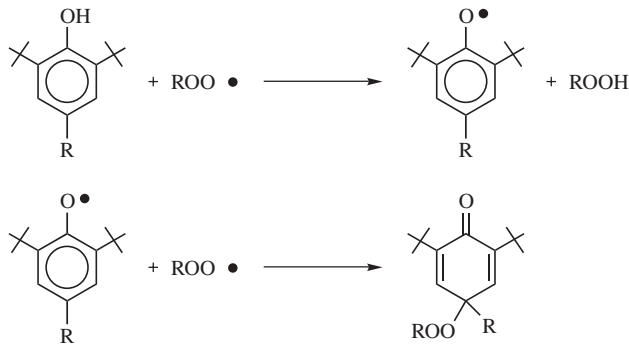


Fig. 5. Radical scavenging with hindered phenols. Reprinted with permission.



Fig. 6. API certification mark.

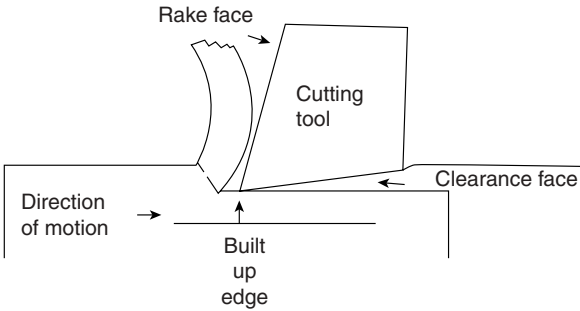
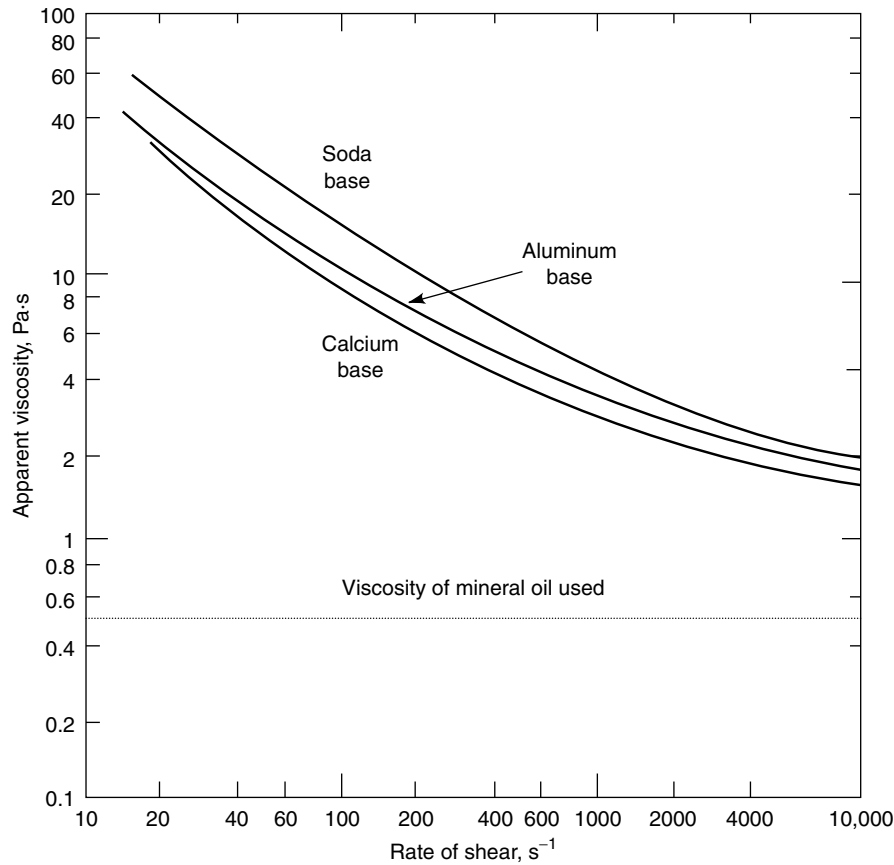


Fig. 7. Chip formation in metal cutting.



**Fig. 8.** Effect of shear rate on the apparent viscosity of three NLGI grade 1 Greases at 25°C.



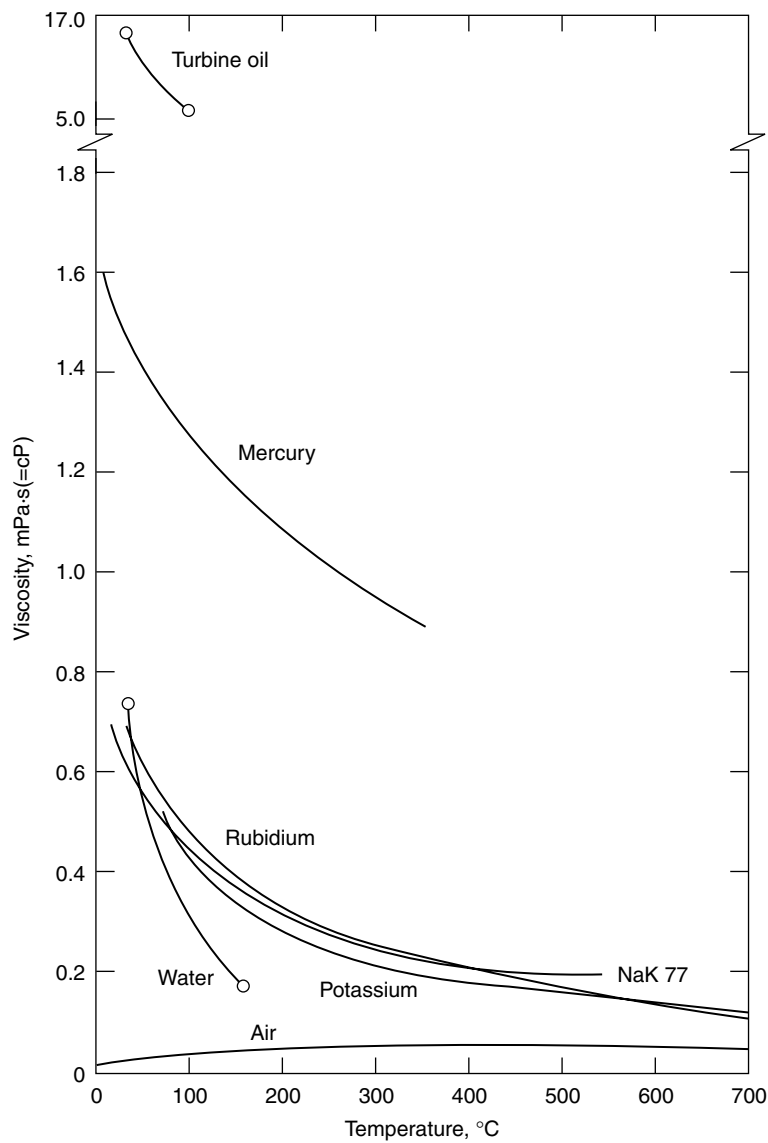
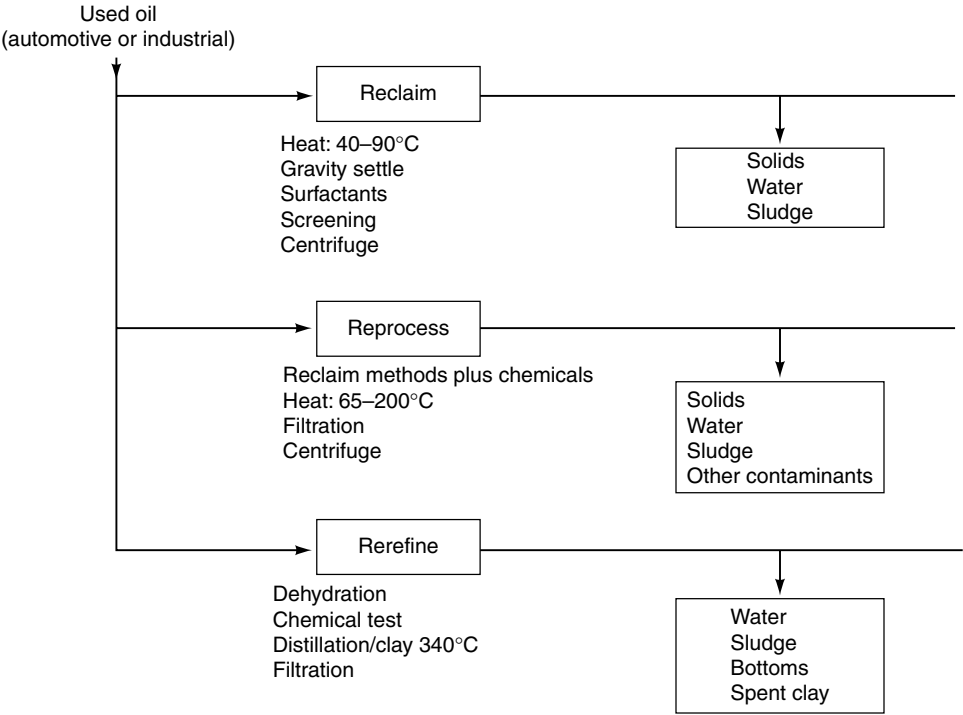


Fig. 9. Viscosity versus temperature.



**Fig. 10.** Oil recycling flow diagram.