

Status of Research on Lubricants, Friction, and Wear

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ABSTRACT

The progress made during the last decade in advancing the knowledge of the science and application of lubricants is reviewed and summarized. Advances have been made during this period in understanding the fundamental mechanisms operable in friction, wear, and lubrication. The adhesion theory of metallic friction has been extended to include high polymers, hard oxides, and brittle materials. The mode of deformation, real area of contact, and the role of junction growth between sliding solids has received more attention. Systematic studies of adhesive and abrasive wear have increased the understanding of the wear process. Considerable progress has been made in the development of solid-film lubricants.

New synthetic liquid lubricants, having unusual physical properties, have been prepared, studied, and evaluated for special applications. Emphasis has been placed on synthesizing lubricants which are stable at increasingly higher temperatures.

Although the mechanism by which additives enhance or impart special properties to liquids is now better understood, much more needs to be learned about the interaction among the many types of additives compounded in a modern lubricating oil. Frequently an additive improves one property at the expense of another. Progress has been made in developing new nonsoap thickeners for the preparation of greases from both petroleum and synthetic oils.

New environmental conditions and more extreme operating requirements have created many new lubrication problems. Lubricants may be subjected to high vacuum, radiation, cryogenic or burning rocket fuel temperatures. Attention is called to areas in research and development where solutions are needed.

PROBLEM STATUS

This is an interim report on the problem; work on this and other phases is continuing.

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STATUS OF RESEARCH ON LUBRICANTS, FRICTION, AND WEAR

I. INTRODUCTION

Since our 1957 review "Trends in Lubricants" (795), considerable progress has been made in understanding the mechanisms operable in friction, wear, and lubrication. Advances have also been made in the synthesis of lubricants having improvements in specific properties and in understanding the mechanisms by which additives enhance (or impart) desirable properties to lubricants. During the past decade new problems in lubrication have arisen because of new environments and more extreme conditions under which lubricants must function. In this review we have tried to summarize and discuss critically the progress made in the past decade in advancing our knowledge of the science and application of lubricants, friction, and wear. Particular attention has been given to discussion of unsolved problems in these areas.

This review was undertaken at the suggestion of Mr. Paul S. Greer and with the support of the U.S. Army Research Office. Although this report was initially intended to assist the Army, its scope has been broadened to include fundamental or applied aspects of interest to the entire Department of Defense.

II. FRICTION AND WEAR

1. HYDRODYNAMIC-HYDROSTATIC LUBRICATION

Two distinct regions of lubrication are recognized: boundary and hydrodynamic or hydrostatic. Under boundary conditions the sliding surfaces are separated only by lubricant films of molecular dimensions, and solid-solid contact frequently occurs through the protective film. At the other extreme, hydrodynamic or hydrostatic lubrication, the bearing solids are completely separated by a continuous fluid film.

In hydrostatic lubrication the film is maintained by a pumping pressure from an external source. The hydrodynamic film is dependent solely upon the motion of the rubbing solids relative to the lubricant. The fluid entering the contact area is subjected to a shearing action which develops pressures in the film. This pressure pushes the surfaces apart. The classical hydrodynamic theory developed by Reynolds in 1866 adequately explains hydrodynamic lubrication behavior where the pressures are relatively low and films relatively thick, for example in a journal bearing where, because of the large area, pressures are small even at high loads. This theory assumes rigid bearing surfaces and constant fluid viscosity for the operating temperature. In highly loaded contacts, such as occur in some gears or ball bearings, these assumptions are not valid. More recently the theory has been modified to include the pressure coefficient of viscosity of the fluid and the elastic deformation of the sliding or rolling surfaces. The term "elasto-hydrodynamic" has been applied to lubricant films in which the pressure is great enough to deform the solids elastically. This factor was first introduced into hydrodynamic theory by Grubin (357) in 1949. It is in this area that the most intense and most fruitful research in

hydrodynamic lubrication has been conducted in recent years (232, 262, 380, 678, 708). As a result of such studies, it is now realized that hydrodynamic films can exist under conditions where it was previously believed that boundary lubrication was operative. Archard and Kirk (39) have shown, for example, that for point contacts (rotating steel cylinders with their axes mutually at right angles) hydrodynamic lubrication persists at speeds below 1 cm/sec with loads of a few kilograms. Tabor and Winer (723) found evidence of hydrodynamic lubrication at a load of three kilograms and a velocity of 2.54 mm/sec with an apparatus which uses a hemispherical slider on a flat surface. The lubricants were trifluoropropylmethyl siloxanes whose rate of viscosity increase with pressure is much greater than that of a dimethyl silicone.

Between the extremes of boundary lubrication (coefficient of friction, $\mu \approx 10^{-1}$) and completely fluid films ($\mu \approx 10^{-3}$ to 10^{-2}) there can occur conditions of mixed lubrication where both types exist simultaneously. This region is variously referred to as "quasi-hydrodynamic," "mixed film," or "partial hydrodynamic." Recently the condition just below that of a fully fluid film has been designated as "metahydrodynamic" (726). Here some solid-solid contacts are commencing, but friction is still determined primarily by the viscosity of the fluid. In some instances hydrodynamic laws apply even though some solid-solid contact is made (649). Since quasi-hydrodynamic lubrication is influenced by many and often complex variables of both hydrodynamic and boundary lubrication, it is less understood than either. The transitions between the extreme types have been the subject of several recent investigations (106, 210, 256, 323, 324, 474). Increasing the sliding velocity and oil viscosity or decreasing the normal load and surface roughness promotes transition from boundary to mixed to fluid film lubrication. Montgomery (548) reported that the reaction product between aliphatic dibasic acids and an aluminum substrate filled in the micro-scratches in the mating steel surface, making it much smoother. This extended the range of conditions for hydrodynamic lubrication. Givens and Tally (335) designed a new apparatus, the tapered spindle top, for studying the transition between hydrodynamic and boundary friction. With this device friction in the transition region can be resolved into hydrodynamic and boundary contributions. The transition region can also be studied with a device developed by Furey (322) which continuously records both friction and extent of metallic contact.

A novel technique, termed magnetohydrodynamic lubrication, uses an electrically conducting lubricant in the presence of a magnetic field (274, 689). The load-carrying capacity of a bearing can be increased by electromagnetic pressurization of the film. This technique appears especially promising for applications where liquid metals have been recommended as lubricants.

Bearing surfaces can be separated by a gas film as well as a liquid. Because of the very low viscosity of gases, the unit loads that can be supported are severely limited. The low viscosity, however, is also the principal advantage, because friction is very low and bearings using a gas film can operate at extremely high speeds. Gaseous films can be used in self-acting, externally pressurized or squeeze-film type bearings. They have been employed in a variety of machines including inertial guidance gyros and computer memory systems. For a complete discussion of the fundamentals of gas-film lubrication, and the design and applications of gas bearings, see Refs. 348, 354, and 355.

Whenever possible it is preferable to design equipment that will operate with fluid film lubrication, because friction is very low and bearing wear is essentially nonexistent. However, hydrostatic lubrication is often impractical and hydrodynamic lubrication at all stages of operation is not always possible, e.g., in starting or stopping or with reciprocating sliding. It is, therefore, necessary to determine the fundamental mechanisms of boundary lubrication and unlubricating sliding. It is toward this goal that this review is directed.

2. UNLUBRICATED SLIDING

The basic concepts of friction were first developed by Leonardo DaVinci. Two entertaining histories which describe the evolution of the early theories to account for frictional behavior and of the men who advanced them have been prepared by Bowden and Tabor (134) and by Courtel and Tichvinsky (218). Although friction and wear have been quantitatively studied for several centuries, only during the last 25 years of intensive investigation have the basic mechanisms begun to be understood.

Metallic Friction

A large and diverse body of experimental evidence strongly suggests that metal-to-metal friction is caused primarily by localized adhesion. This mechanism was first proposed by Tomlison and later effectively supported by Holm. The subject has been developed more extensively and convincingly by Bowden, Tabor, and their coworkers; they have reviewed their work in two well-known and valuable volumes (133, 134).

In applying the adhesion theory it is necessary to distinguish between the real and apparent areas of solid-solid contact. Even highly polished surfaces are in intimate or molecular contact only at the tips of the surface asperities (prominences), which deform under load until the total area is large enough to support the load. This real area of contact is the sum of the many small areas of molecular contact. It is usually much smaller than and independent of the geometric (apparent) area. The major component of friction between sliding solids is the force necessary to shear all of these small junctions. In addition, some energy may be expended by plowing or grooving of the softer material by the harder. Spurr (698) has shown how this plowing term can be calculated for hard steel spheres or wedges sliding on soft metals. With clean metals, except where a hard slider of small radius of curvature traverses a soft platen, the plowing contribution is small compared to the shearing force and may frequently be neglected. If the adhesion between contacting asperities exceeds the force necessary to shear the weaker material, friction (F) will equal the product of the real area of contact (A) and the shear strength (s) of the weaker material.

$$F = As . \quad (1)$$

Based on the thermal aspects, asperity welding is enhanced by lower recrystallization temperature, larger coefficient of sliding friction, larger yield pressures, and smaller thermal conductivity (480). If the asperities deform plastically, the real area of contact will be equal to the quotient of the normal load (W) and the mean yield pressure (P) of the softer material.

$$A = \frac{W}{P} . \quad (2)$$

Therefore, the coefficient of friction (μ) will equal the ratio of the shear strength to the yield pressure of the softer material.

$$\mu = \frac{F}{W} = \frac{As}{AP} = \frac{s}{P} . \quad (3)$$

This relationship is, admittedly, an oversimplification, since the shear strength and yield pressure in the contact region may differ from that of the bulk material (351). Ling and Saibel (479) have modified Equation 3 by multiplying the right-hand side by a factor in which the effects of load, relative velocity, temperature, and other physical properties appear. Nevertheless, most frictional behavior can be explained by this simple quantitative treatment of the adhesion mechanism. Much of the effort in sliding-friction research

during the last ten years has been devoted to expanding, modifying, and refining this theory or in pointing out conditions or circumstances where it is not valid.

The coefficient of friction of most clean metals (clean in the sense that their surfaces are free of organic contaminants but not of the metal oxides or adsorbed atmospheric gases) is between 0.5 and unity. These values are of the same order of magnitude as the ratio of s to P . It is well established that if the surfaces are free of protective oxide films, as is possible in high vacuum, metals will weld on contact and relative sliding will be impossible. It has been adequately demonstrated that this behavior results from the combined effects of the normal load and tangential force in producing a growth of metallic junctions such that the real area of contact increases well beyond the values produced by static loading. The presence of the oxide films on the metal usually effectively limits the growth of junctions and thus prevents seizure. If the metals are ductile the junctions may survive beyond the point when the normal force becomes tensile. This effect results in high sliding friction. With brittle materials junction life is short and friction is lower (349).

Since oxides provide the only protection against seizure in the sliding of unlubricated metals, their role has been intensively investigated. Low-load, high-speed sliding of steel or copper involves the formation and tearing of metallic junctions similar to that observed at low-speed sliding, but it is appreciably inhibited by oxides formed by frictional heating (203, 206). Under high-load, high-speed sliding conditions the amount of metallic contact diminishes, because of increased oxidation, and the coefficient of friction decreases. At high sliding speed and with very high loads, metallic contact is nearly eliminated but severe wear is produced by a process of oxide disintegration. With nickel, oxidation failed to prevent metallic contact even at high loads (206). Peterson et al. (590) reported transition temperatures for iron, copper, nickel, molybdenum, and chromium. The decrease in friction and surface damage above this temperature was associated with the generation of oxide on the metal. Sufficient oxide was formed on cobalt and zirconium at room temperature to permit effective sliding. Possibly the low friction of cobalt at room temperature is related to the adsorption of gases on CoO (306). Johnson et al. (412) demonstrated that oxide films generated on nickel during sliding at high temperatures or high velocities markedly reduced wear. Kingsbury and Rabinowicz (438) suggested that an oxide layer on titanium decreased friction at temperatures above 700°C. This oxide was effective as a thin layer but became brittle and ineffective if allowed to become too thick. The effectiveness of an oxidized layer on copper depends on the relative amounts of cupric and cuprous oxide. Friction probably increases with an increase in the proportion of cupric oxide (653). Because of the influence of oxide films, friction and wear measurements are sensitive to the relative humidity. Daniels and West (237) reported substantially lower coefficients of friction for the eight metals examined at relative humidities of 90 to 100 percent than in dry air. The friction of many nonmetals is also very sensitive to relative humidity, but the effect may be either positive or negative (617).

The intimate relationship between friction and adhesion has been convincingly demonstrated (15, 125, 131, 501, 680, 681). Two metals pressed together with a normal force usually require only a small fraction of that force to separate them. Low values of adhesion are experienced with hard metals even after all surface films are removed (131). Such low adhesion has been attributed to the release of elastic stresses upon the removal of the load. These stresses break many of the bonds between contacting asperities. If elastic recovery can be accommodated by a ductile extension of the contacts, then the breaking force is equal to the original load. This condition is achieved when the temperature is high enough to permit the contacts to anneal (131). However, the addition of a tangential stress to the normal stress produces very strong adhesion even in air at room temperature. The adhesive bond may then be as great as the strength of the metal. Surface shear strains produced by a tangential force remove the surface oxides and bury them below the surface, roughen the surfaces, produce a work-hardened zone just below

the surface, cause the denuded metals to come into atomic contact, and sometimes cause interpenetration of the metals (15). The strength of adhesion also depends upon the time of loading (501). Relatively low coefficients of adhesion (the ratio of the force required to separate the metals to the initial loading force) and friction are associated with metals which have high resistance to plastic flow, elastic moduli, hardness, surface energy, and recrystallization energy (680). Crystal structure has a large effect on adhesion. Metals with a close-packed hexagonal structure adhere less strongly than metals with a cubic structure (680-682). Impurities in the metal lattice impede plastic flow by presenting obstacles to the motion of dislocations. Sikorski (680) has reported that the coefficient of adhesion of 99.999+ percent copper is three times as great as that of the 99.98 percent material.

The mode of asperity deformation and the growth of the contact area is a subject of controversy. Courtney-Pratt and Eisner (219, 220) found that the area of contact and the relative displacement increased regularly as the tangential force was increased from zero to a value just below that necessary to produce sliding. Because the displacement was irreversible, it was concluded that junction growth had resulted from plastic yielding, except with the smallest applied forces. The increase in the real area of contact, though small compared to the contact region, was substantial with all metals examined; e.g., with noble metals the contact resistance decreased by a factor of two. Subsequently, Tabor (719) proposed that junction growth of contaminated surfaces proceeds in the same manner as with absolutely clean surfaces until the shear stress exceeds the critical shear stress of the interface. It was concluded that if the interface is only five percent weaker than the metal, junction growth ceases when the coefficient of friction is approximately one. This theory has been reviewed and discussed by Rowe (638).

It is generally found that friction is proportional to the applied load (Amonton's law). One exception to this rule occurs when the load is smaller than that required to fully work-harden the material in the contact zone before the surfaces begin to slip relative to each other (647). The real area of contact must then be proportional to the load if friction is proportional to the real area; in effect, this is the adhesion theory. It has been believed that Amonton's law would not be obeyed if contacting asperities deformed elastically, for then $A \propto W^{2/3}$. Archard (35) has shown that while this argument applies to a single contact, it is not necessarily applicable to multiple contact conditions. If $A \propto W^N$, then the greater the number of individual elastic contacts the more nearly N approaches unity. Under multiple contact conditions the load which asperities can accommodate elastically may be as much as a million times that which can be accommodated by each individual asperity contact (36). Archard's model has been supported by the experiments of Zwicker and Jurgal (796), who compared the friction of potassium chloride before and after x-ray irradiation. This treatment produced a large increase in the yield pressure, but only a minor change in the elastic properties. Ling and Lucek (478) also concluded that, under some conditions, the hypothesis of elastic deformation of surface asperities is not inconsistent with Amonton's law. The mode of deformation is also a function of the surface geometry of the sliding specimens. Clark (200) concluded that asperity deformation with soft metal cylinders and plane surfaces of hard steel was principally elastic at low loads. With a steel cylinder and a soft metal plane, deformation was plastic at the same loading.

O'Connor and Johnson (572) studied the deformation of solids under normal load while subjected to tangential forces less than the limiting friction. Evidence of full plastic deformation was found only on a soft, artificially rough surface during the first application of the tangential force. It was concluded that elastic theory can be used to predict the behavior of engineering materials under normal and tangential forces. Kragelsky and Demkin (464) have developed a model and a formula for calculating the real area of contact as a function of load, surface geometry, and material properties. They considered three contact areas: apparent, contour, and real. They assumed that the deformation of asperities is both plastic and elastic and that the surface waves are elastically deformed.

The contact areas were increased primarily because of an increase in the number of asperity contacts.

Frictional heating affects the deformation of solids during sliding contact. Bowden and Persson (130) found that at very high velocities (up to 700 m/sec) even such brittle materials as glass flowed plastically and that softening or melting occurred. Friction decreased with sliding speed, and metals with a sufficiently low melting point melted on a large scale developing a continuous film of molten metal. Resistance to motion was then determined primarily by the molten metal film. The heating which resulted from shearing this film caused rapid melting and wearing of the metals. Thus friction at the temperature just sufficient to cause gross melting was very low, but wear was very severe. Surface melting occurs at a lower velocity with metals which have a low melting point and poor thermal conductivity (57, 127, 130). The friction of metals will also vary if the ambient temperature is increased to high values. Friction of clean metals at cryogenic temperatures, however, does not appear to be significantly different from friction at room temperature (171).

Metallic Wear

Wear is the progressive loss of material from rubbing surfaces by mechanical action. It is usually a slow, almost undetectable, process but it is steady and continuous. Small amounts of wear are sufficient to destroy the usefulness of close-tolerance modern machinery. For example, a 4000-pound automobile is worn out by the time a few ounces of material have been worn from the sliding surfaces (611).

Four types of wear are generally recognized: (a) adhesive, (b) abrasive, (c) fatigue, and (d) corrosive. Adhesive wear, sometimes called galling or scuffing, is the most common and the most difficult to control. It results from the adhesion or welding of the surface asperities and their subsequent rupture. This type of wear is particularly severe with sliding pairs of similar metals or with metals that are mutually soluble (209, 344, 624). The correlation between adhesive wear and mutual solubility increases when oxygen is excluded (243). There is a qualitative correlation between friction and adhesive wear for each sliding couple. A large increase in wear generally accompanies a small increase in friction coefficient (216). Abrasive wear, often referred to as scoring, is caused by cutting or plowing of the surface by a harder material. The harder material may be an oxide of one of the metallic surfaces, a work-hardened particle, or a foreign abrasive. Wear by fatigue is associated with rolling or sliding in which there is a cyclic change in loading. This type of wear results in surface pitting and progresses rapidly after a long period of relatively little damage. Fatigue wear often occurs on gears, and a further discussion of this type of wear is presented in Section V. 5 (Gear Oils). Corrosive wear results from a chemical reaction of the surfaces with the environment or with the lubricant during sliding. While adhesive wear is always associated with high friction, corrosive wear may lower friction. For a comprehensive survey of wear mechanisms, see Refs. 20 and 172.

Experimentally, wear is much more difficult to measure and reproduce than friction. Efforts to establish basic wear laws had for a long time met with only limited success. More recently, wear surfaces and wear debris have been examined by x-ray diffraction (630), electron diffraction (564), interferometry (259), electron microscopy (670, 738), and exoelectron emission (358). Radioactive tracer methods have been used successfully to measure minute amounts of wear, and existing friction and wear apparatus can be adapted to use this technique (124, 182). During the past ten years systematic studies, especially those of the Associated Electrical Industries, Ltd. in England, have advanced our understanding of the wear process. The wear studies of that laboratory have been reviewed by Crook (233, 234).

If wear is of the adhesive type, and if plastic deformation of the asperities is assumed, friction theory predicts that wear should be proportional to the load (W) and sliding distance (d) and inversely proportional to the mean yield pressure (P) of the softer material.

$$w = Kd \frac{W}{P} . \quad (4)$$

The constant of proportionality (K) is related to the probability that an asperity encounter will produce a wear particle and is a measure of the intensity of wear. It is analogous to the coefficient of friction and may appropriately be designated as the coefficient of wear. Archard and Hirst (38) concluded from several hundred well-controlled experiments with unlubricated sliding that the wear rate (wear per unit sliding distance) was often roughly proportional to the load and independent of the apparent area of contact after an initial "run in" period. Kayaba (420) suggested that wear of some soft bearing materials is proportional to a power function of the load. Wear rate does not become constant until the surface layers attain an equilibrium condition (37, 384). Sata (663) attributed the transition from high initial wear to a lower constant value to the gradual accumulation of adhering wear particles on the surface rather than to variation in surface roughness or the formation of any particular surface layer. Finkin (296) reported that, after a long period of sliding, surface roughness approached an equilibrium value which was independent of the original surface finish. The final roughness was determined by the sliding materials and correlated with the mean wear particle size.

A serious objection to the wear equation stems from the calculated values of K which imply that there may be only one wear particle produced in as many as ten million asperity encounters (37). Hirst and Lancaster (385) have proposed that a wear particle is produced only after a succession of encounters in which the elastic limit is only slightly exceeded. This causes a gradual development of a subsurface strain pattern which eventually produces a wear particle. This view implies that in multiple encounters, asperities are not plastically deformed. This hypothesis was supported by the subsequent studies of Archard (36). In contrast to multiple junction encounters, when single model junctions are sheared under conditions of severe wear, the calculated probability factor K suggests that all junctions produce a wear particle (149).

A factor which greatly influences wear is the protective oxide films present on the surface. Lancaster (468) and Hirst (383) have categorized wear into two regimes: mild and severe. In the mild wear regime surface films were generated during sliding, and the wear rate was several orders of magnitude less than that of the severe-wear region. Equation 4 was validated for severe wear but was not applicable to mild wear. The transition between these regimes is discontinuous and dependent upon the rates of formation and destruction of the films, which in turn are influenced by load, temperature, environment, and sliding velocity (467).

De Gee and Zaat (245) have described two adhesive-wear mechanisms with several brasses on steel. An initial "run-in" period was required before the rate of brass transfer to steel equaled the rate of removal, so that the rate of wear and the amount of brass on the steel became constant. One type of wear was initiated by the formation of highly localized, adhering, brass fragments, which during the steady-state period were active sites of metal transfer. The amount of brass on the steel surface was relatively low, and the wear particles had a relatively small volume. Both wear rate and particle size increased with increasing roughness of the steel. This mechanism governed the wear of low-zinc-content alloys in oxygen and all alloys in argon. The second type of wear was initiated by the formation of a semicontinuous layer of transferred brass which covered a large part of the steel surface. The amount of brass on the steel was relatively high, and the wear particles had a relatively large volume. This wear process was not influenced by surface roughness. This mechanism governed the wear of the higher zinc

content alloys in oxygen. The presence and continuous formation of a very thin zinc oxide layer appeared to be essential for the formation of a semicontinuous layer.

Wear is further complicated by the transfer of material back and forth between the mating surfaces (152, 302). If the apparatus used to measure wear permits a new area of the surface continually to come in contact, as with the crossed-cylinder wear machine (34), wear rates are more reproducible and there is less variation with time or sliding distance (368).

Yoshimoto and Tsukizoe (785) considered three types of wear for steel: shearing of the metal and shearing of the Fe_2O_3 and Fe_3O_4 films. They deduced a theoretical wear rate for each type as a function of load and velocity. Kerridge (424) suggested a multiple-step process for steel surfaces: (a) transfer of material from one test piece to the other, (b) the buildup of this material in a harder form, (c) oxidation of transferred material, and (d) removal of this oxide as wear debris. In the sliding of brass on steel, however, metallic debris was found which indicated that the rate of transferred material determined wear rate (425).

The process by which wear fragments are transferred implies their strong adhesion to the mating surface. Adhering particles may be removed by abrasion or by weakening the adhesion through the oxidation of the particle. An additional mechanism has been postulated by Rabinowicz (606, 608). A loose wear particle can be formed if its elastic energy exceeds the surface energy at the area of attachment. Large fragments, because of their larger volume-to-surface ratio, are more likely to detach than smaller particles. The critical diameter is proportional to the ratio of the work of adhesion of the system to the hardness of the fragment. Surface roughness, size of junctions formed during sliding, size of particles produced in a ball mill, and critical abrasive particle size have also been shown to be proportional to this ratio (607). This concept has many practical applications in selecting materials for minimum friction and wear (605), and it can be used to predict friction temperatures developed in the contact area (604).

Wear rate can also be affected by the geometry of the apparent area of contact (701), but only if the geometry can affect the mode of removal of the transferred material (706). Under this condition K may change drastically.

Recent studies have demonstrated some limitations to the common assumption that the adhesive junctions, which form at the contacting asperities, can exist for only a brief time before being broken. Cocks (202, 204, 205, 207) found that both similar and dissimilar metal couples produced several wedges of the order of 0.1 mm in the contact zone. Apparently, the junctions which formed on contact welded and continued to grow. Relative motion was believed to be accommodated by plastic deformation of the metal, and plastic shearing was believed to occur at a direction slightly inclined to the sliding surfaces. Antler (31) studied metal transfer between numerous sliding metal pairs and identified four wear processes. The most important process, prow-formation, is similar to the wedge mechanism of Cocks. With many common metals, including copper, aluminum, gold, and titanium, transfer was by prow-formation; one exception was indium (27). Prow-formation with gold or palladium results in very large, work-hardened transfer particles which tend to adhere to the mating surface (30). The plowing action of these particles contributes greatly to friction and wear. With poorly lubricated gold, prow-formation is rapid and rate of transfer high, similar to the unlubricated condition. With better lubricants prow-formation is slower and residence times longer (29). Rowe (639) has concluded that the adhesion of individual asperities can describe friction at light loads, but not the mechanism of metal transfer when one of the metals is deformed plastically. If the bulk deformation is of the order of ten percent or greater, the asperities do not retain their identity under load and complete contact can occur between dry surfaces. Metal transfer could be either adherent or nonadherent. Adherent transfer becomes progressively worse during sliding and builds up on the surface, forming prows or wedges. Finkin (297)

reported a significant difference in the distribution of wear-particle shape factors for several metals. The growth of large wear particles of aluminum and copper by the joining of smaller ones implies a wear mechanism similar to Cocks' wedge mechanism.

Abrasive wear results from the plowing or gouging of the softer material by the surface irregularities of the harder and by the action of small, hard particles trapped between the surfaces. The terms two-body and three-body are used to distinguish between the two types of abrasive wear. In the two-body process abrasive wear can be controlled by finely polishing the surfaces. "Running in" also tends to reduce surface roughness and wear. In the three-body process the abrasive particle may be (a) an oxide, which is usually harder than the parent metal, (b) a work-hardened metal wear fragment, or (c) a foreign material. The fact that oxide particles and metal fragments, which are produced by adhesive and/or corrosive wear, can act as abrasives (724) illustrates the interactions and complications of the wear process.

Abrasive wear has been studied by sliding metals on emery or silicon carbide papers, on files, or on harder roughened metals. To a first approximation abrasive wear, like adhesive wear, is proportional to the load and sliding distance and inversely proportional to the hardness of the abraded material. Spurr and Newcomb (699), however, concluded that it is determined by the elastic properties rather than hardness. Avient, Goodard, and Wilman (50) investigated the dry sliding of metals on emery paper. Initially, wear decreased and friction increased with sliding distance as the metal progressively picked up emery. After this initial period both friction and wear rates became constant. Wear at equilibrium increased with increasing mean particle diameter of the emery for small particles. When the diameter exceeded 70 microns, wear was independent of particle size. The reciprocal of the wear volume was found to be approximately proportional to the Vickers hardness. Factors other than sliding distance and size of abrasive particles which contribute significantly to this wear process are: shape, position, distribution, and deterioration of the abrasive (337, 554). Work-hardened hexagonal metals have much greater resistance to the abrasive action of steel files than work-hardened cubic metals of the same hardness (5). Buckley and Johnson (163) also found friction and wear during sliding in high vacuum to be much lower for close-packed hexagonal crystal forms than for cubic structures.

Rabinowicz et al. (612) using a three-body system also found that: (a) abrasive wear was not initially constant with sliding distance, (b) wear rate was independent of abrasive-particle size only above a minimum value, and (c) wear resistance was usually proportional to hardness. Calculations of an abrasive wear constant from their own work and from other published data were in the range of 2×10^{-1} to 2×10^{-2} for two-body systems and an order of magnitude lower for three-body systems. It was concluded that in the latter system abrasive particles were rolling 90 percent of the time and abrading only 10 percent of the time. The minimum abrasive particle size which allowed maximum abrasive action was subsequently suggested to correspond to the size of the adhesive wear fragment characteristic of the material being abraded (613).

Bayer et al. (80) have correlated metallic wear with yield point in shear of the weaker material. Wear can be virtually eliminated for a period of time if the shear stress does not exceed a certain fraction of the yield point in shear. The value of this fraction for a large number of metals was either 0.5 or 0.2. The same values were later found for metals sliding on nonmetals (201). In some sliding mechanisms a small amount of controlled wear may be advantageous, e.g., sliding electrical contacts. It is possible to predict the amount of wear in such systems with this wear model from the load, geometry, and material constants (81). Tables of design parameters and procedures based on this model have recently been published (491).

Wear resistance of metals can be improved by alloying or with surface modifications. Electric sparking of steel (761), nickel, and titanium (762) produces a large increase in

surface hardness and wear resistance. Friction and wear of nickel alloys can be reduced by the addition of approximately 5 percent silicon (463). This reduction may be attributed to the ability of the silicon to form films by surface reaction or by the smearing of the softer phase from the alloy rather than to an increase in hardness (166). Wear resistance of steel can be greatly improved by diffusing boron into the surface (778). Abrasion and corrosion resistance are increased by diffusion or impregnation treatments with silicon, chromium, or aluminum (11). Friction and wear of titanium can be alleviated by oxide, nitride, and carbide case hardening and coatings (542), with fluoride phosphate coatings (765), and by diffusing gold, nickel, copper, platinum (676) or beryllium (453) into the surface. Without some surface modifications it is impossible to obtain effective sliding of titanium with conventional lubricants.

High Polymers

The adhesion theory, originally developed to explain metallic friction, can also be applied to solid polymers. During sliding, strong adhesion generally occurs at the areas of real contact, and in many cases fragments sheared from one polymer have been observed firmly attached to the other (718). Since junction growth is not appreciable (585), the adhesion theory, in this respect, is more suited to high polymers. The friction of plastics differs from metallic friction in that the deformation may be partly elastic over a wide range of loads (585). In addition, elastic hysteresis losses and the viscoelastic nature of polymers may influence friction. Relative to metals, the plowing term and surface roughness are of greater importance.

With most plastics reasonable agreement is found between S/P and the measured coefficient of friction. Polytetrafluoroethylene (PTFE) is a striking exception; μ is much lower than that predicted by theory. Because of its uniquely low coefficient of friction, PTFE has been the subject of numerous investigations and deserves special mention. In general, μ increases rapidly with increasing velocity ($V < 100$ ft/min), decreases rapidly with increasing load ($L = 5$ to 50 lb), and is relatively constant over the temperature range 80° to 620°F (9). The low friction has been attributed to its low surface energy (139). This results in very weak adhesion, so that shearing occurs primarily at the interface rather than in the bulk material. This conclusion is reinforced by the work of Allan (8), who formed a relatively polar surface on PTFE by treating it with a solution of sodium in liquid ammonia. This treatment produced an increase in the critical surface tension of wetting and a corresponding increase in μ . The coefficient of friction of the treated surface was in close agreement with that predicted from bulk properties. Flom and Porile (305) reported a marked increase in PTFE friction with sliding velocity and an apparent irreversible change in surface properties as a result of high-speed sliding. They attributed this change to either surface degradation resulting from frictional heat or to orientation produced by sliding. The latter view contradicts a more recent study (722) in which the friction and shear strength of PTFE was found to be less in the direction of orientation. Bowers and Zisman (145) reported a value of μ_s (coefficient of static friction) for a clean steel slider on PTFE in reasonable agreement with adhesive theory. They concluded that the low values of μ_k (coefficient of kinetic friction), or of μ_s , subsequently measured with a used slider, resulted from a transferred polymer film which was highly oriented in the sliding direction. An alternate explanation for the low friction of PTFE has been presented by Makinson and Tabor (493), who found two friction regimes. At high speeds or low temperature, friction was high and was accompanied by massive transfer of polymer. At low speeds and moderate temperatures, friction was low and the polymer transferred as a strongly adherent thin film of highly oriented crystal structure. Some type of relaxation process was suggested by the manner in which friction varied with speed and temperature. They explained the low friction by the ease of shearing of the crystalline regions of the polymer (an intracrystalline process) rather than by poor adhesion. The process in the high-friction regime was believed to be inter- or polycrystalline. Increasing the intra-crystalline forces by irradiation-produced cross-linking increased friction at low sliding speeds (509). Although PTFE is

chemically very unreactive, Vinogradov et al. (751) reported the formation of a lubricating film of copper fluoride as a result of a reaction between a copper slider and the PTFE degradation products. At room temperature and with a sliding speed of 14.6 cm/sec, copper fluoride appeared on the friction surface at loads as low as 22.5 kg.

Since the deformation of polymers is not completely plastic, the area of contact and friction are not proportional to the load. The coefficient of friction is greater at small loads. At greater loads, either because there is an increase in the number of asperity contacts or because the mode of deformation is more nearly plastic, μ becomes nearly independent of the load. Accurate predictions of frictional force have been obtained with recently derived equations which contain an exponent, the deformation index (393, 394, 579, 585, 645). These equations include, in addition to the load, the geometry of the slider and number of asperities.

Elastic hysteresis losses, which arise from the difference between the energy required to produce elastic deformation and the energy stored in the deformation, are another source of friction. This source is usually small compared to adhesive friction with unlubricated surfaces. It may be significant in the sliding of steel on wood (48) and appreciable for steel on PTFE at high loads (722). If the adhesion term is reduced by an effective lubricant, hysteresis losses become relatively more important. The friction of well-lubricated rubber arises primarily from hysteresis losses (350). Bueche and Flom (168) found that curves of dielectric loss versus frequency for polymethylmethacrylate (PMM) were very similar to μ versus velocity curves obtained with steel sliding on lubricated PMM at each temperature studied. Elastic hysteresis losses have been found to correlate well with the rolling friction of many polymers (303); the rolling friction of rubber arises primarily from these losses (720, 721). Because of their higher elastic hysteresis losses, rolling friction is greater for polymers than for metals.

A related frictional mechanism has been proposed by Tanaka (729), who observed a wave-like deformation to extend a considerable distance beyond the area of contact produced by a hard hemispherical slider. He concluded that friction was caused by the tangential resistance produced by the surface deformation beyond the contact region rather than by the shearing of adhesive junctions.

Below the glass transition temperature, polymers behave more nearly like metals, and the coefficient of friction is nearly independent of the load. Above this temperature the visco-elastic nature of the polymer causes μ to be more dependent upon load and speed (679). The area of contact and, therefore, static friction will depend to some extent upon the time the surfaces remain in contact before sliding commences. Contact area and the static friction of nylon on glass have been found to increase by a factor of ten percent for each factor-of-ten increase in loading time in the range 5 to 1000 sec (4). The static coefficient of friction of lubricated PTFE on cast iron has been reported to increase at the rate of 2.5×10^{-2} per min between 0.1 and 1.0 min and 2.8×10^{-4} per min between 5 and 75 min (667). A similar effect has been observed with soft metals due to creep (696) with a hard bitumen (697, 700), a hard waxy grease (544), and several other metal-plastic or metal-metal couples (462).

McLaren and Tabor (510) have observed a maximum in the friction versus velocity curves of plastics. The effect is more pronounced with crystalline polymers than with amorphous polymers; crossed-linked polymers show practically no change with speed. These curves resemble the dynamic-loss characteristics of a polymer as a function of frequency of deformation. The authors concluded that the deformation component could account for only a small fraction of the observed friction but that the adhesion component involved speed- and temperature-dependent properties which in some manner reflected the visco-elastic properties of the solids. This conclusion is supported by a study of rubber friction (353) in which both an adhesion and a deformation mechanism were found to be visco-elastic in nature.

The dependence of μ on the experimental conditions precludes a quantitative comparison of the friction of plastics. The coefficient of friction for some familiar polymers when measured under one set of conditions is given in Table 1. The data represent the "steady-state" values usually reached after several unilateral traverses over the same area.

Table 1
Frictional Properties of High Polymers*

Polymer	μ_s	μ_k
Polytetrafluoroethylene	0.10	0.05
Tetrafluoroethylene- hexafluoropropylene copolymer	0.25	0.18
Polytrifluorochloroethylene	0.45	0.33†
Polyvinyl chloride	0.45	0.40†
Polyvinylidene chloride	0.68	0.45†
Polyvinylidene fluoride	0.33	0.25
Polyethylene (high density)	0.18	0.10
Polyethylene (low density)	0.27	0.26
Polymethylmethacrylate	0.54	0.48
Polyethylene terephthalate	0.29	0.28
Polyhexamethylene adipamide	0.37	0.34
Polycarbonate	0.60	0.53
Acetal resin	0.14	0.13

*Coefficient of friction is given for unlubricated sliding of a 1/2-in.-diameter steel sphere over an abraded surface of the polymer. Measurements were made at NRL with a load of 1 kg, a velocity of 0.01 cm/sec and at a temperature of 25°C.

†Intermittent motion ("stick-slip").

Polymers are subject to the same types of wear discussed earlier for metals. Adhesive wear is a major source of material removal. Despite their softness, the wear resistance of polymers compares favorably with that of some metals when the surfaces are unlubricated. Archard and Hirst (38) reported wear rates for several materials sliding against hardened tool steel. Relative wear was 240, 200, 100, and 0.3 for 60/40 brass, PTFE, PMM, and polyethylene, respectively. Linear (high density) polyethylene is very wear resistant (498). Polymers are more susceptible than metals to abrasive wear. Relative abrasive wear by "Carborundum" paper as measured by Selwood (674) was: PTFE, 38; polyvinylchloride, 27; PMM, 24; polyethylene, 12; nylon, 9; and brass, 4.5. Polymers are rarely affected by corrosive atmospheres, and hence corrosive wear is not often a problem.

Plastics have been used successfully as bearing materials. In many applications they are superior to metals and can perform under conditions where other materials are not suitable. The advantages of polymer bearings are: the ability to function unlubricated or with unconventional lubricants, high corrosion resistance, light weight, and low cost. The disadvantages are: low melting or softening temperature, poor mechanical strength, low abrasion resistance, low thermal conductivity, and high coefficient of thermal expansion. Listed in Table 2 are various types of plastic bearing materials and their relative advantages and disadvantages (284). Some of the liabilities can be surmounted by the use of fillers. Compositions of PTFE containing glass, asbestos, MoS₂, graphite, bronze, and iron oxide, and compositions of nylon containing graphite, MoS₂, and other fillers are commercially available. A large number of filler combinations for PTFE have been studied (24).

Table 2
Types and Properties of Plastic Bearing Materials*

Material	Advantages	Disadvantages
Nylon	High abrasion resistance, roughness and reliability; good conformability; reduces noise and vibration	Absorbs water and has low thermal conductivity and high thermal expansion; however, problems can be minimized by preconditioning and proper design
Acetal	Very low friction coefficients which are same for both static and dynamic conditions; inexpensive; resists water and most solvents	Low heat resistance; generous clearances required
Fluorocarbon	Excellent resistance to heat, water and chemicals; very low friction coefficients; easily filled to provide special properties	Relatively expensive; low thermal conductivity and high expansion; some types cannot be molded
Phenolic	High resiliency and resistance to severe shock and impact; low wear rates	Absorbs water; low thermal conductivity in large sizes
Chlorinated Polyether	Excellent dimensional stability; high water and chemical resistance	Bearing properties not as good as most other plastics
Polycarbonate	Close tolerances and good dimensional stability; good resistance to heat and impact	High coefficient of friction
High-Molecular-Weight Polyethylene	Excellent impact resistance and good wear properties	Relatively difficult to fabricate

*From Ref. 284.

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The wear of PTFE bearings is greatly diminished by the addition of 25 percent graphite (485). Bearings have been made from porous copper, silver, iron, bronze; or stainless steel impregnated with PTFE. The best performance is obtained with the impregnated bronze on a steel backing. This material has a bulk yield strength from 10,000 to 20,000 psi (545). A 60:20:20 composition of PTFE-graphite-bronze improves the thermal conductivity of PTFE by a factor of three (600). A high degree of wear resistance is obtained with a porous bronze impregnated with a mixture of PTFE and lead on a steel backing (600). A cloth made from PTFE fibers has a much greater tensile strength than the resin. Bearings made from this cloth perform satisfactorily in air at high loads and with slow oscillatory motion (225) and in sea water (224); wear life is decreased by a factor of three in the latter environment. PTFE bearings are particularly effective at cryogenic temperatures. In liquid nitrogen, PTFE containing various fillers gives low friction and wear compared to conventional materials (777). Liquid nitrogen acts as a heat sink, causing friction and wear to remain low even at very high sliding velocities.

Bearing materials consisting of a phenolic-type resinous matrix, PTFE, and a reinforcing filler also show promise (739).

The applications of both PTFE and nylon bearings have been reviewed by Allan (6) and by Cheney et al. (194). Design data for PTFE and PFEP (a copolymer of tetrafluoroethylene and hexafluoropropylene) are also available (334). Unlike PTFE, PFEP can be processed in conventional plastic injection-molding and extruding equipment, although its coefficient of friction is higher (145). Stienbuch (713) has reviewed the problems encountered in the use of nylon bearings and has investigated the effects of adding solid lubricants to this polymer. Pinchbeck (597) has published a comprehensive review of the various types of available plastic bearing materials. This paper discusses the frictional behavior in terms of bulk properties and presents special and general applications of the polymers as bearing materials.

Other Nonmetals

Single crystals provide one method of obtaining a surface of known and reproducible structure. A number of fundamental studies of nonmetallic solids have been conducted with single crystals. Friction and wear are often greatly influenced by the crystallographic plane and sliding direction. Two different types of sapphire wear are produced on the prismatic planes during sliding on tungsten carbide (703, 704). When the sliding direction is parallel to the C-axis, wear is characterized by conchoidal fracture (chipping-type wear); smooth wear occurs when the sliding direction is perpendicular. On the basal plane wear is smooth and nearly independent of sliding direction. Plastic deformation is believed to occur in the smooth-wear direction. The breaking of friction junctions may be an entirely ductile process and plastic flow part of the wear process. The direction parallel to the C-axis is perpendicular to the slip directions of the two slip systems, and brittle fracture occurs because plastic flow is not possible. Duwell and Butzke (271) observed the importance of crystal orientation and slide direction in both the friction and wear of sapphire. The wear rate could differ by a factor of 10^3 if the sliding direction was changed by 180 degrees (270). Plastic deformation was believed to occur in the high-wear direction and chemical degradation in the low-wear direction. Evidence of a chemical reaction between iron oxide and aluminum oxide has been found when single crystal sapphire slides on steel (156).

Riesz and Weber (621) found that the orientation dependence of sapphire was much less for high-temperature sliding than for low-temperature sliding and that friction at atmospheric pressure was much lower than it was in near vacuum. The lower friction was attributed to the presence of adsorbed films. The effect of adsorbed films on single crystals of diamond was demonstrated by Bowden and Hanwell (129). The surface film was believed to consist of a chemisorbed film of oxygen with a physically adsorbed gas film on top. The coefficient of friction was greatly increased if the film was removed in very high vacuum. Since there was a strong orientation dependence of friction when the surface film was present, this film must have been extremely thin. Monomolecular films of adsorbed gases covering only a fraction of the surface markedly reduced friction; one or two monolayers reduced friction by a factor of ten. The severe diamond wear that occurred in the absence of these films was attributed to cracking under a combination of the normal stress and large tangential surface stresses which were induced by strong adhesion.

There is a correlation between the anisotropy of friction and that of abrasion resistance of diamond. The abrasion rate of diamond by diamond dust between the greatest and least resistive directions may vary by a factor of 500. A thermal rather than a mechanical mechanism is believed to be the major factor in the abrasive wear of diamond (671). Magnesium oxide exhibits a marked anisotropy in hardness and friction (126). At low sliding velocities friction is much greater when sliding in the soft direction, and the

anisotropy is caused by an increase in the plowing component. A similar effect occurs with diamond. Under low-speed conditions abrasion of diamond results primarily from crystallographic cleavage and deformation. This is greatest in the direction corresponding to the greatest penetration and friction. At high sliding velocities other mechanisms may prevail. Diamond can be abraded by much softer materials. At very high sliding speeds it can be abraded by metals (128) and by glass (132). The wear of diamond sliding on glass is very dependent upon relative humidity, and it can be 100 times greater in a dry atmosphere than a humid one. The wear of diamond by metals or glass at high speeds appears to be primarily the result of degradation of diamond to amorphous carbon by frictional heat (128, 132). More recent evidence suggests that this may be only a part of a more complicated abrasion process (541). Fragments of diamond may be removed from the surface under the influence of mechanical or thermal stresses and be embedded in the mating surface. These embedded chips can act both as an abrasive and as a source of localized hot spots which cause thermal degradation. The temperature of these hot spots would be greater than those of a metal-diamond junction, since the latter could not exceed the melting point of the metal.

Steijn (705) conducted sliding tests on single crystals of CaF_2 , MgO , LiF , and NaCl . Both cleavage cracks and plastic deformation were found in CaF_2 , but only dislocation cracks initiated by plastic deformation were observed in crystals of the rock salt-type. Subsequently, the friction and track width on the cube face of NaCl -type crystals and B.C.C. and F.C.C. metals were found to have the same orientation dependence despite their different slip systems (702). In these experiments very small radii sliders were used and friction anisotropy was attributed to plowing. Dobson and Wilman (257) studied the friction and wear of single-crystal rock salt when rubbed on emery paper. The results indicated that the friction coefficient was determined primarily by plastic flow properties and not by the occurrence of fractures. Wear, however, was greatly increased by brittle fracture. Friction and deformation of copper have also been found to be strongly orientation dependent for an oxide-free sphere and plane (725) and for styli sliding on a plane with various controlled atmospheres and temperatures (59). These studies with single crystals demonstrate that there is an anisotropy in friction and wear, that hard brittle solids can deform plastically, and that friction results from adhesion and plowing.

Serious consideration is being given to ceramics and cermets for use as the primary rubbing elements in high-temperature dry bearings and seals. These materials retain their hardness and corrosive resistance at very high temperatures. Room-temperature hardness and maximum service conditions of these materials are given in Table 3 (336). Ceramics have the disadvantage of being brittle and having low thermal conductivity. Cermets are nonmetallic materials cemented together with a metal. They represent a compromise between ceramic high-temperature hardness and metallic toughness and ductility. At high temperature (1000° to 1800°F) and high velocity (100 to 200 ft/sec), the predominant wear mechanism of ceramics and cermets appears to be induced by their inability to resist thermal stresses. Al_2O_3 -Cr-Mo cermets, SiC ceramics, and TiC-Ni-Mo cermets are promising materials for the above conditions (677). Low wear and moderate friction have been reported for Cr- Al_2O_3 -W and Cr- Al_2O_3 -Mo- TiO_2 in high vacuum, at high temperature, high load and at sliding speeds of 14 to 20 ft/min (153). Zeman and Coffin (791) conducted sliding experiments between 75° and 2000°F with a variety of borides, carbides, nitrides, oxides, and silicides. None of these materials were considered readily applicable for bearings or seals over the whole temperature range. Because of their low fracture-strength-to-hardness ratio, bulk shearing and fracturing (caused by abrasive action) produced high wear. Mordike (550) concluded that the frictional behavior of refractory carbides and borides could be explained by the adhesion theory. The decrease in friction observed with increasing temperature up to about 1000°C was greatly influenced by the strength of the grain boundary. Above this temperature friction increased rapidly, and there was evidence of plastic flow and sintering.

Table 3
Properties of Wear-Resistant Ceramics and Cermets*

Material	Maximum Service Temp. (°F) (Oxidizing Conditions)	Room-Temperature Hardness (Knoop)	Melting Point (°F)
Diamond	1500	7000	1800 (carbonizes)
TiB ₂	1800	2700	5250
ZrO ₂	4200	—	4850
WC	1200	1880	4770
BeO	4300	1220	4660
TiC	1800	2460	5660 (sublimates)
BC	1800	2800	4430
SiC	1750	2500	4160
Al ₂ O ₃ (dense)	3500	2000	3720
Cr ₃ C ₂	—	—	3600
Cr-Mo-Al ₂ O ₃ cermet	2300	50 RC	3360 (approx.)

*From Ref. 336.

Dashes indicate no data.

RC indicates Rockwell C.

Data reproduced by courtesy of Wear.

The frictional behavior of a metal-ceramic couple is determined by the nature of the transferred film, provided there is no reaction or interaction. Frictional properties often are essentially those of the metal. Friction is high if the transferred film is a hard oxide; effective sliding results if the film is soft (592). If the metal does not oxidize, good sliding characteristics between metal and sapphire correlate with high contact angles for the molten metal on sapphire (208). For a comprehensive review of the thermal, physical, mechanical, environmental, and sliding properties of cermets, ceramics, and refractory metals; see Amateau and Glaeser (12).

Niven has investigated the effects of load (569) and velocity (568) on the friction of ice at several temperatures. The coefficient of friction decreased markedly at high loads or high sliding velocities. At temperatures just below the melting point, adhesion to the sliding material is believed to be relatively unimportant; thus, stainless steel and PTFE slide easily on ice. At lower temperatures adhesion becomes of great importance and PTFE, because it is not easily wet, has much lower friction than steel. The low friction of ice is usually attributed to a thin film of water on the ice surface which is produced by pressure melting or by frictional heat. Niven (567) does not believe it is necessary to postulate the presence of a water film to explain the low friction. He visualizes a

swivelling of the tetraheda to form a structure more like water. He suggested that this partial swivelling reduces friction without the production of a water film.

3. BOUNDARY LUBRICATION

General

The use of lubricants to mitigate friction and wear has its origin in antiquity. The lubricating quality of oil was known in Babylonia as early as the third millenium B.C. A mural painting in Egypt (ca. 1880 B.C.) depicts one of the earliest records of the use of lubricants. A chariot of about 1400 B.C. was found with some of the original lubricant on its axle (241). A book written by Vitruvis in 25 B.C. mentions the use of oil to lubricate two pistons of a bronze water pump (240). Almost all lubricants were obtained from animals and vegetables until the middle of the 19th century; at present, only about ten percent are derived from this source (595).

It has only been during the last 20 or 25 years that the mechanisms of boundary lubrication have been established. Under boundary conditions, friction consists of: (a) the force required to shear the metal junctions where the film has been penetrated, and (b) the force required to shear the lubricant.

It is generally believed that the surfaces are separated at their points of contact by films no greater than one or two molecules thick. The predominant opinion of Russian scientists, however, is that the influence of the boundary film of a liquid containing polar molecules extends through many molecular layers (250). Conversely, Lunn (490) suggests that the minimum film thickness of an undoped mineral oil is at least 1000 Å, but that monomolecular films are possible if the oil contains fatty acids or similar materials. The equation for boundary friction F may be written:

$$F = A [\alpha s + (1 - \alpha) s_L] \quad (5)$$

where A is the real area of contact, α is the fraction of A where the contact is metallic, s is the shear strength of the softer metal, and s_L is the shear strength of the lubricant film. The second term becomes more predominant as the effectiveness of the film increases. The force required to shear monomolecular lubricant films adsorbed on molecularly smooth mica surfaces has been determined experimentally (56, 58). Although this force was much lower than that required to slide clean mica, it was appreciable. This explains the observation that the best boundary lubricants can reduce the coefficient of friction by only a factor of 10 or 20, but can reduce wear by a factor of 10^5 . Cameron (178) believes the frictional component, due to welding and tearing of the surface, to be secondary to the molecular forces between hydrocarbon molecules adsorbed on the surface. The frictional force between two oriented layers sliding relative to each other was calculated and found to be of the correct order of magnitude. Differences between kinetic and static friction were explained by forces caused by the tails of the chain for the former and the sides of the chain for the latter.

The function of a boundary lubricant is to minimize metal-to-metal contact by adsorbing onto the surface. Adsorbed monomolecular films are capable of providing boundary lubrication. The most effective films are composed of long, straight-chain molecules which can adsorb strongly to the metal with the long chain perpendicular to the surface to form close-packed structures. Wilson (774), however, concluded from electrical-contact resistance measurements that, except at a very light load, adsorbed molecules are bent over nearly parallel to the surface so that sliding occurs along the length of the molecule.

The theory that close-packed, strongly adsorbed, monomolecular films are the most effective is supported by the studies of Levine and Zisman (475). Friction and contact angle (methylene iodide) were measured on a series of fatty acid monolayers deposited on glass. The coefficient of friction decreased and the contact angle increased with increasing chain length of the acid up to 14 carbon atoms. For all acids containing 14 or more carbon atoms, μ was 0.05 and the contact angle was 70 degrees. Therefore, maximum packing is reached with films of myristic acid. Similar studies were made with amines and alcohols. The limiting value of friction and contact angle was the same as those obtained with the fatty acids. With the short-chain members, however, amine monolayers had lower friction than the corresponding acid which had lower friction than the corresponding alcohol. Fowkes (314) also found that the strength of adsorption of long-chain polar compounds from oil onto steel decreased in the order: amine, acid, and alcohol. Since all three types have the same chain structure and terminal group, the difference can be attributed to the difference in adsorbability of the polar end groups. By making repeated traverses over the same area, Levine and Zisman (476) obtained the mechanical durability of the monolayers. Monolayers of fatty acids containing N carbon atoms behave as two-dimensional liquids, plastic solids, and crystalline solids when N is from 8 to 12, 13 to 15, and 16 or more, respectively. The durability of a monolayer is greatly influenced by the materials of the sliding combination. Close-packed fatty acid monolayers on stainless steel are quickly destroyed by a steel slider. The same monolayer on glass is exceptionally durable when traversed by a steel slider. With the former combination, the strong metal adhesive junctions formed result in larger wear particles being torn from the surface and, consequently, in the rapid depletion of the monolayer (214). The durability of mono- and multi-molecular layers of barium stearate on steel increase with increasing velocity (0.3 to 20 mm/sec) or with decreasing load (546).

Adsorbed monolayers lose most of their effectiveness at temperatures above their bulk melting point or the melting point of the reaction product if they are chemisorbed (133), although this was not supported by the results of Tamai (728). He found a sharp decrease in the average coefficient of friction during reciprocating sliding. The lower friction was attributed to the greater mobility of the molecules and their ability to repair the damaged film. However, the film may have been multimolecular.

In practice, the lubricant film must be replenished. Lubricants are usually a blend of surface-active materials dissolved in a carrier oil. As the monolayer is depleted by wear, additional molecules adsorb onto the surface. The strength of the bond between the adsorbed molecule and the surface, the heat of adsorption, and wear reduction are all related (437). The film strength measured under static conditions by electrical methods has been found by Sakurai et al. (657) to agree well with film strength calculated from adsorption energy. Groszek (356) measured both the heats of adsorption and wear-reducing properties of solutions containing various wear-reducing agents. Of the adsorbates examined, the heats of adsorption from benzene on iron correlated well with wear-reducing ability. The correlation was much less pronounced when the solvent was n-hexane. The heats of adsorption were greatly influenced by the chemical nature of the solvent.

As the temperature is increased, a critical temperature or temperature range is reached where rapid desorption occurs. This causes a marked increase in friction and wear. This critical temperature will be influenced by the sliding velocity (436), the solvent, and the concentration of the surface-active material, but will be higher for surfactants having a greater heat of adsorption at room temperature.

A transition toward higher friction and greater wear also occurs at a temperature lower than the desorption temperature, corresponding to the melting point of the adsorbed species, or its reaction product if it is chemisorbed. A solid film of lower adsorption energy is more effective than a liquid film of higher adsorption energy. The temperature at which there is a sudden transition from effective to ineffective sliding has been the

subject of several investigations. Transition temperatures determined by Fein et al. (291) were found to increase with sliding velocity, to decrease with load, and to be independent of other operating variables. The reciprocal of the absolute transition temperature varied linearly with the logarithm of the ratio of load to speed (289, 291). In agreement with these studies, a decrease in transition temperature with increasing load has been reported by others (221, 390), although Coffin (211) found it to be independent of the load. Matveesky (503) has suggested that, if the load is sufficiently low so that plastic deformation occurs only at the asperities, failure of the lubricant film is mainly the result of temperature effects. At loads great enough to cause marked plastic deformation, lubricant failure may be caused by the joint influence of temperature and plastic flow of the material at the contact surface. The effect of sliding velocity is the subject of some controversy. Hopkins and Wilson (390) and Cowley et al. (221) found a decrease in transition temperature with increasing velocity, while Fein et al. (289, 291), Coffin (211), and Rabinowicz (610) reported an increase. At low sliding velocities, where frictional heating can be neglected, the transition temperature appears to increase with velocity. At higher velocities the transition temperature appears to decrease with velocity because of frictional heating. Fein (288) explained transition data by a mechanism involving trapping and squeezing out of thick (compared to a monolayer) lubricant films between asperities, under sliding conditions previously believed to be boundary. This film provides partial hydrodynamic lubrication and its effectiveness, therefore, would increase with velocity.

Boundary lubricants remain effective at extreme loads. Golden et al. (341) studied the effectiveness of radioactive sodium stearate on steel bars drawn slowly under plane strain conditions. Pickup and surface damage did not occur until the load was great enough (5 tons) to cause a 30-percent reduction in the area of the bar. At this load the calculated film thickness was 600 Å. This film thickness was comparable to the maximum height of the surface asperities. Subsequently, Lancaster and Rowe (469) found the relative behavior of lubricants was the same at loads of a few kilograms or a few tons, provided the surface was not stretched more than a few percent. At greater loads the interfacial pressure was not greatly altered, but the surface was extended. The lubricant film was then broken and metallic pickup was observed on the die. Film failure could be avoided by grit blasting the surface. This provided pockets for a reserve supply of lubricant. Boundary lubricating characteristics again became an important factor, and the cross-sectional area of the bar could be reduced by nearly 60 percent without the occurrence of pickup when a soap was used as the lubricant.

Robertson (627) concluded, from studies with a pin on disk machine, that with good lubricants the equilibrium state of wear under boundary conditions is not one of steady wear but of zero wear. The stress at which wear ceased varied with the lubricant but was independent of the load.

Synthetic Lubricants

Liquid lubricants have been synthesized which have viscosity indexes and high-temperature stabilities superior to petroleum oils. Silicones, one of the earlier types, have remarkable viscosity-temperature properties. They are, however, inherently poor boundary lubricants, particularly for steel. Under severe conditions the effectiveness of polyorganosiloxanes as lubricants for steel decrease in the order: polymethylsiloxane, polyethylsiloxane and polymethylphenylsiloxane (753). Klaus et al. (446) concluded that the poor antiseize and antiweld properties resulted from a reaction between iron and silicon to form a low-melting ductile film that is more inert to further chemical reaction than the original steel surface, while Vinogradov et al. (752) attributed the poor lubrication to the formation of a hard layer with no soft coating. Conventional lubricant additives are not soluble in these fluids. EP additives, which are highly active in hydrocarbons, are much less active in polyethylsiloxanes and completely inactive in polymethylphenylsiloxanes (753).

When used as the additive in either mineral oils or esters, silicones can act as an antiwear additive. The solution has better antiwear properties than either component, although there is no improvement in the weld load of the base fluid (446). Vinogradov et al. (752) attributed this strong synergism of polyorganosiloxanes and mineral oils to the presence in the mineral oil of low-molecular-weight aromatic hydrocarbons. The mutual improvement resulted from a modification of the steel surface by the silicone and to the transportation of oxygen to the surface by the decomposed hydrocarbon.

Boundary lubrication has been improved by the substitution of halogen atoms in the silicone structure. The substitution of chlorine on the phenyl group of polymethylphenyl silicone causes a substantial reduction in friction and wear with hard steel and with copper and to a lesser extent with mild steel. The chlorine is believed to function as an EP additive by reaction with the metal surface to form a metal chloride film (142). Chlorination, however, reduces oxidation resistance at high temperatures (443). A further improvement in boundary lubrication is obtained with polytrifluoropropylmethyl siloxanes. Compared to polydimethyl siloxanes, these materials have a greater resistance to acids (but less to alkalis) and greater liquid oxygen impact resistance. Polyfluorosiloxanes are insoluble in and resist the action of most fuels, oils, and solvents (666). However, the gain in lubricating properties made with either halogen is partially offset by a loss in the viscosity-temperature characteristics. Boundary lubrication of halophenyl-containing fluids can be improved by the addition of a small percentage of a copolymer fluid consisting of an organometallic compound copolymerized with a methylsiloxane to achieve compatibility (665).

Esters prepared from aliphatic dibasic acids and fluorinated alcohols represent an improvement over conventional diesters. Many of these fluoroesters possess good hydrolytic and thermal stability, exceptional resistance to atmospheric oxidation at high temperatures, and resistance to oil-mist-explosion hazards. Their ability to reduce friction and wear is equal to or better than bis(2-ethylhexyl)sebacate (141). One of the most promising types of high-temperature lubricants are the polyphenyl ethers. They have excellent oxidation, thermal, and radiation stabilities and adequate lubrication properties (492, 692). The principal disadvantage of these fluids is their high pour point or melting point. The properties of many types of synthetic liquids are given in Section IV (Synthetic Lubricants).

Lubrication of High-Polymer Solids

Several systematic investigations have been conducted to determine the mechanism of high-polymer lubrication. Bowers, Clinton, and Zisman (140) studied the friction of nylon (polyhexamethylene adipamide) and steel sliding on nylon when lubricated by 16 liquids selected to permit an evaluation of the effects of varying the polar end groups and chain lengths. The most effective lubricants were those that could minimize contact between the solids by forming the most strongly adherent film with the highest intermolecular cohesion in the film molecules. The adsorption sites on nylon (the amide groups) were not sufficiently concentrated to permit the formation of a highly condensed lubricant film. Friction reduction for nylon sliding on nylon was, therefore, limited. The steel-nylon combination was more effectively lubricated because a more closely packed film could be formed on the steel surface. Vinogradov and Bezborodko (750) also have attributed the effective lubrication of a steel-polymer system to the activity of the lubricant media toward the metal. Matveeskii (502) found that the presence of a polar liquid caused a large reduction in friction and a transition from intermittent to smooth sliding for steel on polyamides. In contrast to the results described above (140), he reported no difference in friction between a polar and a nonpolar liquid used to lubricate polyamides sliding on polyamides (504). A systematic investigation of the boundary lubrication of polyethylene terephthalate (PET) has been reported by Fort (311). The effectiveness of liquids of the same chain length decreased in the order: acids, alcohols, and alkanes, i.e., in the same

order as their ability to adsorb onto the PET surface. In each homologous series of liquids, friction decreased with increasing chain length, i.e., with an increase in intermolecular cohesion in the adsorbed film. After the number of adsorption sites on the PET surface was increased by a treatment which produced carboxyl groups, a further reduction in friction was obtained. These results support the conclusion of Bowers et al. that the mechanism of boundary lubrication for plastics is generally similar to that of metals.

Pascoe (584) has suggested an alternate explanation for the relative ineffectiveness of lubricants for polymers. He reasoned that even if a close-packed adsorbed film were possible on a polymer, little reduction in friction would result since, in contrast to metals, the shear strength of the lubricant is not greatly different from the shear strength of the polymer. Another factor, proposed by Rubenstein (646), is that the lubricant can penetrate the amorphous region of a polymer, weaken the interchain forces, and reduce both the shear strength and yield pressure of the polymer. How this would increase the coefficient of friction can be understood by reference to Eq. (6) which was obtained by dividing Eq. (5) by the relationship $W = PA$.

$$F/W = \mu = \frac{\alpha s}{P} + \frac{(1 - \alpha) s_L}{P}. \quad (6)$$

If the lubricant plasticizes the polymers and reduces s and P proportionally, the first term remains unchanged but the second term will increase. It is possible that any decrease in α obtained by the lubricant can be offset by a softening of the polymer. This can explain the observations that the static coefficient of friction for nylon on nylon was greater for several lubricants than it was with dry surfaces (140) and that wear of nylon yarn was greater when lubricated with one percent octyl alcohol solution than when unlubricated (646).

It is generally agreed that the adhesion and shearing mechanism applies to the lubrication of plastics and that lubricants are more effective on metals than plastics. Three views have been presented to explain the relative ineffectiveness of lubricants on polymers. These may be summarized in terms of Eq. (6): (a) it is difficult to decrease α with an adsorbed film because of a shortage of adsorption sites; (b) with polymers s does not differ greatly from s_L ; and (c) penetration of the polymer by the lubricant decreases s and P , resulting in an increase in the second term. These views are not mutually exclusive, and each factor may contribute to the frictional force (144).

A new approach to the lubrication of polymers is by the incorporation of surface-active additives. Zisman and coworkers (279, 280, 402-404) have reported a series of fundamental surface activity studies of soluble and insoluble compounds at the interface of organic liquid and air. Various fluorocarbon derivatives having the proper organophobic-organophilic balance were found to be the most surface active. Jarvis, Fox, and Zisman (405) extended this work to include adsorption in polymeric solids by treating them as if these were supercooled organic liquids. They were able to modify significantly the wetting properties of polymers by surface-active agents added either to the monomer prior to polymerization or to a solution of the polymer in a volatile solvent. Provided sufficient time is allowed for diffusion of the solute to the interface, the surface properties of a polymeric solid can in this way be considerably modified. Bowers, Jarvis, and Zisman (143) examined both friction and contact angles on several polymers containing partially fluorinated additives. Small proportions of a suitably designed surface-active compound significantly reduced friction in both polymer films prepared by solvent evaporation and thick disks prepared from the melt. This decrease in friction was accompanied by an increase in the equilibrium contact angle of several selected liquids. Some of the low-energy surfaces formed by the fluorinated additives could be regenerated, after abrasion, by reheating the polymer at 50°C. It was suggested that under proper conditions frictional heat would be sufficient to maintain a film of low surface energy. The films

would be self-healing, and surface-active molecules lost from the film would be replaced by the movement of additional material to the interface. The specific properties of the additives and polymers that control the rate of movement through the solid polymer were not determined. The additive may have migrated to the surface through structural flaws in the bulk polymer.

Allan (7) concluded that oleylamide exuded to the surface of polyethylene film and at equilibrium formed a weakly held oriented monolayer. This equilibrium required from 1 to 500 hours, depending upon the concentration of the additive, the temperature, and the surface-to-volume ratio of the polyethylene film. Owens (578) prepared films of vinylidene-acrylonitrile copolymer containing a long-chain fatty additive by evaporation from a mutual solvent. Friction of the films, containing various additives, was found to correlate with the critical surface tension of wetting. For a homologous series of amides the quantity of additive that appeared on the surface, and hence the extent of surface coverage, increased as the molecular weight of the additive increased. The evidence indicated that the lubricants were present on the plastic surface in the form of a layer of crystals of additive rather than as an oriented adsorbed monolayer.

4. ANTIFRICTION AND ANTIWEAR ADDITIVES

Amphipathic materials (i.e., straight-chain molecules with a polar group at one end and a nonpolar group at the other) are frequently used as additives in the carrier oil to decrease friction and wear. These additives are effective only at low or moderate surface temperatures (up to ca. 120°C) in contrast to EP additives which function only at high surface temperatures. Since these surface-active molecules adsorb on the sliding surfaces in a concentration much greater than their solution concentration to form a protective film only a small proportion is necessary. This mechanism has been discussed above, Section II. 3 (Boundary Lubrication). A secondary effect is the ability of polar materials to disperse wear debris and therefore to prevent abrasive action by the hard oxides (656, 727). Recent studies have indicated that the lubricant film may include some solvent molecules. It has generally been assumed that the effectiveness of the surface-active agents was little influenced by the hydrocarbon carrier, but Cameron and Crouch (180) have shown that the load at which scuffing commenced reached a sharp maximum when the number of carbon atoms in the straight chain acids, alcohols, or amines equalled those in the paraffin base oil. Zisman and coworkers have demonstrated that monomolecular films, prepared by retraction from solution, can contain a mixture of both polar solute and nonpolar solvent. They deduced from measurements of film durabilities (476) and contact potentials (94) that mixed films are more easily formed when both species are straight-chain molecules of nearly equal length so that they can adlineate or cohere in a parallel molecular array. The proportion of solvent in the film decreased with an increase in immersion time, demonstrating the metastable nature of mixed films. When the solvent used was composed of molecules that could not adlineate (e.g., nitromethane, which is nearly spherical) mixed films never formed. The lubricant film may sometimes be polymolecular (632). It has been postulated that iron soaps produced by a fatty acid on steel in the presence of oxygen and water form a relatively thick colloidal structure with the hydrocarbon base (21).

The effectiveness of antifriction and antiwear agents will depend not only on the base oil, but may also be influenced by oxidation inhibitors, rust inhibitors, EP additives, viscosity index improvers, detergents, and other additives which are compounded into modern lubricants. These additives compete with one another to adsorb on the solid surface (693). For example, Rounds (633) has demonstrated that the frictional characteristics of some lubricants containing only a friction modifier and an oxidation inhibitor in the carrier oil were dependent upon all three components. In this study free-radical inhibitor types could either enhance or reduce the effect of the friction-modifying additives, but peroxide decomposer oxidation inhibitors had no interaction effect. One technique of

reducing the number of additives is the use of a single agent to perform several functions. The amine salts of phosphorodithioic acids have been reported to combine EP, antiwear, and friction-modifying characteristics into one molecule (255).

Another factor which can affect friction and wear is the presence of dissolved oxygen in the lubricant. Friction of steel lubricated with mineral oil containing a very low concentration of stearic acid increases with decreasing atmospheric oxygen (727). Feng and Chalk (293) reported that the removal of the dissolved oxygen from purified mineral oil decreased the wear of steel but greatly increased the wear of cast iron. Pure copper specimens lubricated with ethanol vapor experienced a continuous increase in the rate of weight loss with increasing oxygen partial pressure (292). A minimum in the wear versus dissolved-oxygen concentration curve has been reported for a super-refined mineral oil on steel surfaces (441). This minimum, which was a function of load, occurred at a concentration far below those obtained from an air atmosphere. The presence of oxygen in the lubricant molecule (e.g., an ester) reduced the effect of dissolved oxygen. Vinogradov et al. (749) found an increase in wear of steel with an increase in oxygen content in the lubricant. However, the seizure load also increased. It was concluded that molecular oxygen and hydrocarbon oxidation products enhance chemical wear and delay seizure. Fein and Kreuz (290) studied oxygen concentration in the vapor and liquid phase in benzene and cyclohexane when used to lubricate hard steel. Inorganic wear products and high wear were associated with both high and low oxygen-to-hydrocarbon ratios. Certain intermediate ratios caused the formation of an oxygenated "friction polymer" which prevented metallic contact and greatly reduced wear. The restricted range of oxygen concentration required for polymer formation may partially explain the failure of Campbell and Lee (183) to find any evidence of polymer formation on steel lubricated with benzene vapor.

5. EXTREME PRESSURE ADDITIVES

Extreme pressure additives are compounds which are incorporated into lubricating oils to prevent seizure or alleviate friction and wear when the sliding metals are subjected to high unit loads. Under conditions of high pressure, EP additives react chemically with the mechanically activated metal surface to form low-shear-strength films of metallic compounds. The term EP additive is to some extent a misnomer, since it is the high temperatures, associated with the high pressures, that control the rate of reaction. These additives greatly reduce adhesive wear by promoting a controlled and limited amount of corrosive wear. Since the sliding surfaces take part in the chemical reaction, the effectiveness of an EP agent is to a large extent determined by the metal to be lubricated. Although many of the elements have been proposed as EP materials, compounds containing reactive sulfur, phosphorus, or chlorine and other halogens are by far the most used (594). Numerous testing devices have been designed to evaluate EP properties of lubricants. Their usefulness, limitations, and differences have been discussed (19).

The effectiveness of the EP additive will be influenced by the other additives and dissolved gases in the compounded lubricant. Oxygen and lubricant oxidation products can either enhance or reduce the effectiveness of thio-, chloro- and phospho-organic compounds, depending upon the amount of oxygen present and the sliding conditions (754).

Three recent papers have successfully refuted the belief, generally accepted for the past 25 years, that phosphorus-containing EP additives function on steel surfaces by forming an iron-iron phosphide eutectic. Studies with radioactive triphenyl phosphate demonstrated that this additive formed EP films of metal phosphates and metal organophosphates (63). The authors suggested that a neutral phosphate ester adsorbs on the metal surface, then decomposes in the contact area to give acid phosphates which react with the metal surface to form metal organic phosphates. These decompose to form metal phosphates. Godfrey (340) identified iron phosphates (FePO_4 and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) by

electron diffraction on a sliding surface which had been lubricated with commercial tricresyl phosphate (TCP). No evidence of iron phosphide was found in either study. In general agreement with these two papers, Klause and Bieber (442) using P^{32} -tagged TCP found phosphorous compounds chemically adsorbed on the wear area. They attributed the EP effect to polar impurities present in the TCP.

Sanin et al. (662) have determined the EP properties of chlorine, sulfur, and phosphorus atoms in numerous compounds when used to lubricate steel. The organochlorophosphorus and organothiophosphorus compounds were the most effective. Subsequently, synthetic additives of the organophosphorus class (esters of phosphoric, thiophosphoric, and phosphonic acids) containing chlorine as a trichloromethyl group were studied (661). The chemical modification of the metal surface by the additive decomposition products were discussed, and the possibility of naturally occurring surface oxide films acting as catalysts on the decomposition of organophosphorus compounds was suggested.

Barcroft (62) has developed a technique for quickly determining the reaction rate between EP additives and metal surfaces at temperatures up to 600°C . A thin metal wire is immersed in the EP oil and heated electrically. By monitoring the change in resistance of the wire, the rate and extent of the reaction can be determined. Reaction products can be studied by x-ray diffraction. This method can be used as a rapid screening test at high temperatures to eliminate unreactive compounds. Smith et al. (688) evaluated over 100 compounds as EP agents in polyphenyl ethers. A number of compounds were effective. In general, they contained phosphorus, a halogen, or sulfur incorporated into an organic structure. Compounds containing the trichloroacetoxy functional group in an organometallic structure were superior.

A series of new long-chain phosphates and phosphonates has been evaluated as EP additives in mineral oil and in bis(2-ethylhexyl)sebacate by Peal et al. (587). The most promising extreme pressure agents for steel were di(2-ethylhexyl)lauroxyethyl phosphonate, diethyl oleoxyethyl, diethyl oleoxybutyl, and dibutyl lauroxypropyl phosphates. Loeser et al. (483) studied EP films formed on cast iron from zinc dialkyl dithiophosphate tagged with P^{32} . Tightly bound films containing phosphorus and zinc rapidly formed in both static and dynamic tests. The amount of bound phosphorus was greater by a factor of 100 in the dynamic test. With the same additive tagged with S^{35} there was only a seven-fold increase in the amount of bound sulfur in the dynamic film (484). Results of subsequent studies indicated that it was possible to relate contact pressure fairly precisely with the amount of EP films formed (775).

Manteufel and Wolfram (496) have developed a method for studying EP additives with a modified Four-Ball Machine which simultaneously records friction and the temperature of the lubricant immediately after it leaves the contact area. As the load is progressively increased friction and temperature initially increase linearly until there is a rapid increase in temperature and friction. At this load the EP additive becomes much more active and the rate of increase subsides. Radioactive EP additives containing P^{32} or S^{35} were evaluated on steel surfaces at the transition temperature. Phosphorus content in the wear scar was five to 50 times greater than the sulfur content (497).

Davey and Edwards (238) evaluated many sulfides and disulfides in mineral oil with a Four-Ball apparatus. Disulfides were superior to the corresponding monosulfides on steel surfaces. The groups attached to the sulfur atoms also had a marked effect on EP performance; dibenzyl disulfide and ditert-octyl disulfide were exceptionally effective. Dorinson and Broman (260) found that ditert-octyl disulfide in white mineral oil was 1500 times as reactive with iron powder than was di-n-octyl disulfide. The former was also a more effective EP agent for steel in the Four-Ball Machine, Falex Machine, and a pin-disk apparatus. Sakurai et al. (658, 659) studied the reaction of radioactive sulfur and sulfur compounds with steel during boundary lubrication. Dibenzyl disulfide and diphenyl disulfide were more effective lubricant additives than elementary sulfur even though the

latter was more reactive. The rate of wear of the iron sulfide film formed by the compounds was less than that formed by the element because the compounds probably adsorbed on the worn surface. The iron sulfide film formed by the elementary sulfur wears rapidly; this promotes corrosive wear. The effective surface concentration of sulfur additives decreases markedly as the sliding velocity increases. Increasing the load does not affect the chemical activity of the sulfur compounds but does increase the reacting area of the friction surface.

It has been commonly accepted that iron sulfide is the reaction product which provides EP lubrication for sulfur compounds. Godfrey (338) has analyzed, by six methods, EP films formed on steel surfaces from mineral oil saturated with elemental sulfur. The major component was Fe_3O_4 ; minor constituents were FeS , FeO , and an "iron carbide." The sulfur is believed to promote the oxidation of iron. The combination of both oxide and sulfide in the films were necessary for high load-carrying capacity.

Titanium is susceptible to galling and seizure and is a particularly difficult metal to lubricate. One successful approach is the use of charge-transfer complexes of iodine and aromatic compounds (625). A mixture of these complexes in a straight-chain hydrocarbon greatly reduces friction and wear by forming titanium diiodide at the rubbing interface. Titanium diiodide is a low-shear-strength laminar solid. Although titanium disulfide has a similar structure, sulfur-containing EP additives are not effective on titanium. Iodine-containing lubricants were also effective in reducing friction and wear of high chromium steels, presumably through the formation of FeI_2 (580).

The characteristics of the metals contained in some additives may influence the anti-suff performance of a lubricant. Cadmium, zinc, and nickel dialkyldithiophosphate additives have shown some correlation between their anti-suff performance and the relative score resistance of these metals to steel (85).

EP films are formed by a chemical reaction between lubricant and metal surface. A closely related approach is to generate a protective film at the areas of high pressure from the decomposition products of the lubricant. Organometallics are an example of additives that can produce protective metallic films through degradation by frictional heat. Antler (28) has identified Pb and PbO films formed from tetraethyllead and tetraphenyllead. Feng et al. (294) used electron diffraction patterns to establish the presence of MoS_2 in films formed in situ from a reaction between a molybdenum complex and a mixture of zinc dialkylphosphorodithioates. The effectiveness of the organometallics increases with concentration and with hardness of the rubbing surfaces (28). The advantages of this approach are that there is no sacrificial corrosive wear to the surface and that these compounds can be used to lubricate nonreactive solids.

Reactive gases have been used as high-temperature lubricants. The mechanism involved is fundamentally the same as employed in extreme pressure lubrication. Halogen-substituted methane and ethane compounds can react with metal surfaces at the friction-produced "hot spots" to form metal halides which function as solid lubricants. Corrosive wear can be controlled by promoting competitive reactions at the sliding surface, i.e., by adding gases that react with the metal in competition with the halogen-containing gas. A mixture of 70 percent air and 30 percent CF_2Cl_2 is effective in providing lubrication with low corrosive wear (164).

6. SOLID FILM LUBRICANTS

A thin film of a low-shear-strength material deposited on a harder substrate can function as an effective lubricant. If the film is very thin, the contact area is determined primarily by the yield pressure of the substrate, while the force required to shear the junctions is determined primarily by the film. In the limiting case, as the film thickness

approaches zero, s in Eq. (3) becomes the bulk shear strength of the film material and P the yield pressure of the substrate. This assumes that s is independent of pressure. It follows that μ for a solid-film lubricant is equal to the product of μ for the film material in bulk form and the ratio of the hardness of film material to substrate (139).

$$\mu = \frac{s_f}{P_s} = \frac{\mu_f P_f}{P_s} . \quad (7)$$

Friction is lower and film durability is greater when the films are used on harder surfaces (236, 370). As discussed below, such an idealized relationship is not attained in practice. The film thickness must be at least comparable to surface roughness to prevent contact through the film. For any finite film thickness, the proportion of the load carried by the substrate will be a function of the load, and μ will increase with decreasing load. Conversely, for any load, μ will increase if the thickness of the film is increased (591). Because the bulk deformation will be partially determined by the elastic properties of the substrate, the contact area will not be proportional to the load. This will also cause μ to increase with decreasing load (170, 417, 641). The shear strength of the film material is not independent of pressure, as Eq. (7) assumes; high pressure can greatly increase the shear strength (452). This is probably the major source of error. Values calculated from Eq. (7) are, therefore, invariably low. The lowest coefficient of friction obtained by Tsuya and Takagi (737) for thin films of lead on copper was an order of magnitude greater than the value predicted by thin-film theory. This result was attributed to an increase in the area actually sheared. The greater area resulted from the growth of adhesive masses that occur on the application of frictional force. The discrepancy between theory and experimental results appears to increase as the ratio of hardnesses increases. The coefficient of friction for a thin film of paraffin on sapphire is 0.04. The hardness ratio is 1/1600, and the theoretical value of μ is approximately 10^{-4} (138).

Although the quantitative agreement between Eq. (5) and experimental results is frequently poor, thin films of solids can be effective lubricants. Solid-film lubricants are used primarily where conventional oils would be lost by evaporation in high vacuum (space vehicles) or would be an explosion hazard (rockets) or a contaminant (food processing). They are frequently used where the lubricant must function over extremes of temperature or where the lubricant cannot be renewed because of the inaccessibility of parts. Although it is not necessary that the thin-film material have a low coefficient of friction in bulk form, the most widely used materials, graphite, molybdenum disulfide, and polytetrafluoroethylene, all have low bulk friction. Of these materials graphite has the highest decomposition temperature, maximum service temperature in air for both continual or intermittent use, highest electrical conductance, and is by far the least expensive (714). Its liabilities are high friction at very low temperatures and in near vacuum. Graphite is ineffective in high vacuum because of the high energy necessary for lamellar cleavage. The cleavage energy is significantly lowered by small amounts of adsorbed gases (161), and at atmospheric pressure its friction is very low. Low friction with graphite may be obtained in the presence of some vapors at pressures less than that required for a monomolecular film. It has been proposed that effective lubrication is related to the formation of patches of a liquid-like phase. Patch formations involve migration of adsorbing molecules to sites where substrate failure has started. The formation of the liquid-like film at these sites reduces the critical shear stress (184). The increase in shear and tensile strength of graphite between 20°C and 1600°C is probably caused by the desorption of gases rather than to temperature per se (643). The removal of adsorbed gases increases the cohesion between graphite crystallites (242). The friction of carbon is influenced by the graphite content. Buckley and Johnson (165) reported lower friction at 10^{-7} torr for carbon containing 20 to 60 percent graphite than for either amorphous carbon or 100 percent electrographitized carbon. An additional mechanism to account for the low friction of graphite at normal temperatures and pressures has

been suggested by Spreadborough (695). This involves a surface orientation of crystallites and subsequent formation of rolls which act as small roller bearings.

Molybdenum disulfide, in contrast to graphite, retains its low friction in high vacuum. Lubrication does not depend upon adsorbed vapors and, in fact, the presence of water vapor increases friction. Although it has been postulated that the low friction in vacuum of MoS_2 and WS_2 results from an amorphous layer of sulfur formed on the sliding surface (413, 472), it now appears that it is the weak binding forces between lattice layers which permits easy shear and low friction (161, 304, 369). Mordike, however, believes the low friction of lamellar solids arises from the weak forces between crystallites rather than interplanar slip within crystals (549). Molybdenum disulfide will lubricate at temperatures up to 750°F ; at this temperature it begins to oxidize in air (747). The rate of oxidation increases steadily with increasing temperature, becoming rapid at 1050°F . However, low friction and good protection from surface damage is provided by bonded MoS_2 even after most of the film has been oxidized (99). Unlike many metallic oxides, molydic oxide does not act as an abrasive (748).

Unlike graphite or molybdenum disulfide, PTFE is not a lamellar solid. The principal advantages of this material as a dry-film lubricant are a low coefficient of friction in high vacuum and at temperatures from cryogenic (514) up to its melting point (327°C). The disadvantages are: its tendency to cold flow under pressure, poor heat conductivity, and high coefficient of thermal expansion.

Other lattice-layer solids have also been evaluated as potential lubricants for use in high vacuum. The friction of cadmium iodide, bismuth iodide, tungsten sulfide, and phthalocyanine in vacuum is equal to or less than that in air (304). The friction of molybdenum disilicide at room temperature is not greatly influenced by a prior outgassing treatment at 1100°C in a vacuum of 10^{-3} microns (640). It has a higher friction than MoS_2 , but prevents seizure between molybdenum surfaces in air up to 1300°F (637). Thin films of titanous oxide, chromic chloride, and molybdenum disulfide on their respective metals do not depend upon the presence of oxygen or water vapor for effective lubrication (644). Until recently it had been assumed that, since graphite was ineffective in high vacuum, all lamellar solids required a film or an adsorbed gas to provide effective lubrication. It can now be concluded that this is not a requirement for most lamellar solids; graphite and boron nitride are exceptions (642).

Thus far the discussion has applied to the frictional characteristics of solid lubricating materials in bulk form. Their effectiveness as thin films depends upon retaining the material on the surface. The bonding of the film to the substrate is of particular concern. Adherent films can be formed in situ by exposing clean metal surfaces to the action of special atmospheres (61). For some applications graphite or MoS_2 can simply be rubbed onto the metal. Films are frequently deposited from colloidal suspensions. For strong bonding, it is necessary to combine the solid lubricant with other materials which have greater adherence to the substrate. Surface pretreatments also influence the bonding strength. The load-carrying capacity and durability of soft materials, such as PTFE, can be greatly improved by the addition of a variety of solids. Dry-film lubricant combinations are often used to obtain the beneficial effects of the individual constituents at different operating conditions. Bearings, ball-bearing retainers, and even idler gears have been fabricated from composite materials containing a solid lubricant which transfers to the mating surface during sliding. Several hundred compounds, mixtures, and composites have been reported as potential solid lubricants. A review covering solid-lubricant classification and application, and techniques used for evaluating different properties of solid lubricating materials, has recently been prepared by Devine et al. (253).

The initial rate of film deposition produced by rubbing a MoS_2 compact depends primarily on the surface finish of the metal. After the surface irregularities have been filled in, transfer increases linearly with sliding distance. The rate of film formation

and degree of orientation of MoS_2 particles is much greater at higher humidities (414). Films transferred to a low-carbon steel from compacts of MoS_2 or graphite are reported to be comparable to bonded coatings in both frictional characteristics and load carrying capacity (466). Small blisters which form between a "rubbed on" MoS_2 film and the substrate are responsible for film failure. These voids represent regions of stress concentration and act as points of enhanced chemical reactivity (660). Sintering of the MoS_2 particles takes place during sliding. Oxidation promotes sintering which leads to embrittlement, blistering, and scaling. Oxygen and water vapor are believed to react instantaneously with the mechanically activated surface (244).

Film life can be greatly extended by bonding the lubricant to the surface by means of a thermosetting resin. The metal part is coated with the mixture and carrier and then heated and cured. For optimum performance careful consideration of the metal pretreatment is essential. Strong adhesion between film and substrate requires that the surface be thoroughly degreased. A controlled amount of surface roughness improves film durability by mechanically "keying in" the film. Phosphating the surface promotes adhesion and corrosion resistance. Milne (543) has suggested that the observed increase in MoS_2 film life obtained by phosphating or sulphiding the metal surface may result from the ability of these coatings to promote the incorporation of the MoS_2 particles within the surface layers in the preferred orientation. Palmer (581) reported that greatest wear life for resin-bonded MoS_2 on ferrous metals was obtained with surfaces degreased in perchloroethylene, sandblasted to a 20-microinch finish, and covered with a 0.09 to 0.16 mil iron manganese phosphate layer. The MoS_2 film should be 0.2 to 0.5 mil. Resin-bonded solid lubricant films have been studied over a twelve-year period at Rock Island Arsenal (175). The following conditions are recommended for maximum life with steel surfaces at ambient temperature and pressure:

1. Lubricant: MoS_2 and/or graphite
2. Resin: epoxy-phenolic
3. Resin-lubricant ratio: 3 to 7
4. Cure: 400°F for 30 min to 1 hr
5. Surface pretreatment: grit blasted and zinc phosphated.

Conventional petroleum oils and greases decrease the durability and corrosion protection of some resin-bonded MoS_2 films (175, 787). Contaminating oils or greases can be removed with solvents with no detrimental effect to the film.

Methods of preparing thin polytetrafluoroethylene resin films and many practical applications of these films have been described by FitzSimmons and Zisman (301). They recommended a maximum total film thickness of 0.7 mil, not to exceed 0.3 mil for each layer. The use of two coats greatly enhanced the corrosion protection. The best adhesion to steel, brass, and aluminum was obtained when the surfaces were degreased without removing the natural oxide. Adhesion was also increased by roughening the surface; the roughness should not exceed 32 microinch. The hardness of brass decreases nearly 50 percent after a brief heating at the PTFE sintering temperature, 725°F. This difficulty could be circumvented by high-frequency induction heating, followed by a water quench. The wear resistance of PTFE films on hard steel can be considerably increased by using a surface phosphating treatment prior to film application (419). The mechanical strength, durability, and wear resistance of PTFE films can be improved by the addition of three to five percent of a synthetic colloidal boehmite, hydrated aluminum oxide (300). This was accomplished without any change in the coefficient of friction. The mechanical reinforcement of the film results from electrostatic attractive forces between the boehmite and PTFE particles and from the specific adhesion forces between boehmite particles.

One of the major uses of solid-film lubricants is at temperature extremes where conventional oils and greases are inoperative. PTFE is particularly valuable at low temperatures. An experimental composition containing PTFE, a modified epoxy resin, and a lithium silicate ceramic filler has been compounded which has a thermal expansion approximating that of structural metals (776). This mixture has the advantage not only of permitting closer dimensional tolerances but also of limiting spalling of the film due to shrinkage. This composition performed well in liquid nitrogen at high-speed sliding, both as a film and as a solid slider material.

One limitation to the use of solid lubricant films at high temperature is the thermal decomposition of the binder; the decomposition products may be effective lubricants but they only temporarily delay film failure (435). Organic binders are generally restricted to temperatures well below 350°C, while many solid-film lubricants including bismuth sulfide, lead oxide, molybdenum disulfide, and tungsten disulfide have been shown to retain some lubricating properties at 1000°C (217). Metal-free phthalocyanine has been used successfully as a dry-film lubricant between 800° and 1300°F. Best results were obtained by forming a film of the metal phthalocyanine on the bearing surface. Presumably the coating formed and adhered by a reaction of the metal-free phthalocyanine with the metal surface to give the metal phthalocyanine (465). Johnson and Sliney (411) reported that lead monoxide coatings bonded to stainless steel with lead silicate are effective to 1250°F and calcium fluoride with a fused cobalt oxide-base ceramic binder lubricated nickel alloys to 1900°F. Klemgard (451) has evaluated 230 multi-component solid materials as lubricants for a nickel alloy at temperatures between 100° and 1700°F. These lubricants contained graphite, boron oxide, silver chloride, silver fluoride, metal phthalocyanine, molybdenum disulfide, lead oxide and sodium silicate. Results are discussed in terms of physical and chemical changes in the surface layer, changes in the metal substrate, and changes in the lubricant film. Sodium phosphate, potassium phosphate, and some metals, particularly silver, appear to be effective binders at high temperatures for MoS₂-graphite mixtures (716). The metal binders were formed by decomposing an organic metal complex after the lubricant film mixture was applied to the surface. Inorganic lubricant films which use sodium silicate binders with MoS₂, graphite, or silver iodide are thermally stable from -300°F to 750°F, compatible with liquid oxygen, and resistant to nuclear radiation (252). Ball bearings have been operated in liquid oxygen and at 750°F with one of these films. MoS₂-graphite-sodium silicate films do not show any visible degradation or change in friction after five months storage at 10⁻⁷ to 10⁻⁸ torr (223). The addition of bismuth or gold to these films has been reported to improve their friction in vacuum (389). A film of MoS₂ burnished into a flame-sprayed zirconium silicate coating and a film deposited from a sprayable suspension of MoS₂-gold-graphite-sodium silicate effectively lubricated steel on aluminum in high vacuum, at high loads, and at temperatures between -150° and 500°F (508).

One method of replenishing a solid lubricant is to make one of the sliding solids of a composite material containing a metal matrix, a film former, and a load-carrying component. Ball bearing retainers made from Ag-PTFE-WSe₂ or Cu-PTFE-WSe₂ composites have been operated at 10⁻⁷ torr with no additional lubrication (108, 136, 137). MoS₂-Fe-Pt and MoS₂-Fe-Pd separators have adequately lubricated ball and roller bearings operating in vacuum at 15,000 rpm (181). Brown, Burton, and Ku (154) report that a bearing with a PTFE-glass-MoS₂ retainer ran for five million revolutions, and another with an epoxy-MoS₂ retainer ran for more than 900 million revolutions in high vacuum at light loads. Ball bearings using retainers fabricated from an aromatic polyimide plastic containing graphite, MoS₂, or WSe₂ have been operated in air to 700°F at 10,000 rpm (251). Polyimide plastics have excellent mechanical, electrical, and wear properties from 480° to 750°F and excellent chemical and radiation resistance (734). Gears are more difficult to lubricate than ball bearings by composite materials, but satisfactory lubrication of gears from -180° to 300°F in high vacuum has been obtained by using idlers of Ag-PTFE-WSe₂ or Ag bronze-PTFE-WeS₂ (136).

The first book devoted exclusively to solid lubricants has recently been published (146). The subject is treated from both an engineering and technical outlook, which includes the necessary background material for an understanding of solid lubrication. The use of solids in colloidal form is emphasized. Particular attention is given to MoS_2 and graphite.

7. INTERMITTENT MOTION

Friction is not always constant with sliding distance. It may vary irregularly or in many cases in an oscillatory manner. This intermittent variation produces an intermittent motion sometimes referred to as stick-slip or frictional vibration. Familiar examples are the vibration of a violin string and the squeal of an automobile brake. From the results of nearly 600 tests, Niemann and Ehrlenspiel (565) have determined the types of materials, lubricants, surface treatment, and surface roughness which tend to minimize or eliminate stick-slip.

The cause of the frictional vibrations may be entirely mechanical if the apparatus or machine permits the tangential force to increase the load. Stick-slip motion can also occur if the static friction is greater than the kinetic friction, or if the kinetic friction varies inversely with sliding velocity. The frequency and amplitude of the vibration at small rates of sliding are essentially determined by the static friction of the couple (462). This type of vibration and its occurrence, although greatly influenced by the mechanical system involved, can be eliminated or reduced by a surface treatment that produces a kinetic coefficient of friction that increases with increasing sliding velocity (683). Polar-type antifriction agents reduce the static coefficient of friction several fold and lower the rate of change of friction with velocity (693). Rounds (636) observed that with polyhydroxyl alcohols, kinetic friction increased and static friction decreased as either the number of atoms between primary hydroxyl groups increases or primary hydroxyl groups are replaced with secondary hydroxyl groups. Electrical transients have been observed to accompany the stick-slip motion. The characteristics of the electrical discharge indicate a charge-discharge mechanism rather than a thermoelectric potential or a dielectric breakdown (690). Schnurmann (669), however, concluded that there is an electrostatic component of friction which accounts for an appreciable proportion when there is a very thin dielectric film at the contact area. With very violent stick-slip the electrostatic component could be 30 percent of the total friction. A boundary film of a definite dielectric strength provided a trigger device for cycles of slow charging and rapid discharging.

The stick-slip process and variables which affect it have been carefully analyzed (609, 683, 758). In addition to kinetic friction-velocity and static friction-time-of-stick characteristics, a critical sliding distance was introduced into the analysis by Rabinowicz (609). This distance, approximately 10^{-3} cm for steel, is the minimum resolving power of the friction process. The concept of a critical distance was suggested by several previous studies. First, it was shown that when sliding is suddenly produced by impact, μ_s remains constant for the first 2×10^{-4} cm and drops to the lower μ_k only after sliding a distance of approximately 10^{-3} cm. Subsequently, it was observed that with the sudden application of a different velocity, μ_k changed gradually and became constant only after sliding 10^{-3} cm (379). Finally, at a constant velocity, intrinsic fluctuations of the frictional force were observed, and statistical tests showed a persistence of the order of 10^{-3} cm (603). The first observation differs from the results of Wiid and Beezhold (767), who concluded that if there was a distance over which μ_s persisted it was smaller than 5×10^{-6} cm in the case of steel on steel. This conclusion does not necessarily invalidate Rabinowicz's conclusion that the instantaneous value of μ_k is determined by the average sliding velocity over the previous 10^{-3} cm. The critical-distance concept can be used to deduce a simple relationship between the static and kinetic coefficient of friction.

8. SPECIAL APPLICATIONS

Reactors

Liquid sodium is used as a heat-transfer medium in some engineering systems, e.g., nuclear reactors. The sliding of metals in this environment presents special problems in boundary lubrication. The metals must have high-temperature strength and corrosion resistance. Some boundary lubrication of molybdenum (439, 440), tungsten (439), and Mo-W-Cr alloys (626) is provided by molten sodium. This effect has been attributed to the formation of chemisorbed double oxide films formed by reaction with the metals. The availability of oxygen as metal oxide films on the substrate or as sodium oxide is essential. Only trace amounts are required to promote these reactions. Balchin (60) also reports evidence for the formation of double oxides on a series of metals from oxygen present as an oxide in sodium. His results indicate that friction will be high if the sodium only dissolves the surface oxide and low if it can react with the metal and the oxide to form a protective layer of double oxide.

Lubricants must sometimes function in a new environment, nuclear radiation. Effective operation of equipment in such an environment requires a knowledge of the effect of irradiation on the lubricants. King and Rice (433) conducted specification-type tests on petroleum- and synthetic-based lubricants after exposure to gamma radiation. Radiation dosages were approximately 10^8 roentgens. After exposure the chlorophenyl silicone solidified, and a polymer-thickened, petroleum-based hydraulic fluid suffered a severe viscosity increase. Only a slight viscosity decrease occurred with a silicate-based fluid. A small increase in viscosity was observed with petroleum oils and a somewhat greater increase with a diester. However, irradiation improved the performance of the diester in the Ryder Gear Test. The improvement resulted from the production of small amounts of acid rather than from an increase in the hydrodynamic component which could result from the viscosity increase. Three lubricants previously shown to have unusual radiation stability have been studied in bearings and gears in the presence of pile radiation (185). The compounded poly(propene oxide) outperformed the diester-based and the octadecylbenzene-based fluids. The presence of pile radiation (slow neutron component 5×10^{17} neutrons/cm²) markedly shortened the life of each lubricant. Lubricant degradation produced by test conditions other than irradiation was minor compared to changes caused by pile radiation. Carroll and Calish (187) have reported the effects of gamma radiation on 28 commercial lubricants. Several oils and greases were found to be satisfactory for use in the presence of 10^8 r. In some cases the degradation of the additive was more significant than damage to the base stock, e.g., chlorinated EP additives and polymeric viscosity index improvers. Irradiation improved the lubricating properties of some oils and the viscosity index of petroleum oils.

A pile exposure expressed as 5×10^{18} slow neutrons/cm² reduces conventional greases to brittle porous solids. Gamma radiation (6×10^8 r) causes an initial softening of these greases, followed by eventual hardening. This exposure was found to reduce bearing life from 2 to 20 fold (186). The initial softening results from the disintegration of soap crystallites. The hardening is probably caused by oil polymerization and cross-linking. Both the initial softening and final hardening can be reduced if conventional gelling agents are replaced with synthetic aromatic compounds (391).

Lubrication in Space

Many unusual conditions are encountered in the lubrication of space vehicles: meteoroids, zero gravity, high temperatures, radiation, and near vacuum. Of greatest concern in lubrication are the problems associated with the low pressure of space, 10^{-14} to 10^{-12} torr. Some of the effects — lubricant volatilization, condensation of volatiles, lack of essential reactants and adsorbates, and poor thermal conductivity — have been reviewed

and discussed by Jackson (401). The loss of lubricant by evaporation is a serious problem. Because of their high vapor pressures, conventional petroleum fluids cannot be considered for space applications. Silicones, diesters, polyphenylethers, and special mineral oils have relatively low vapor pressures and may have some use at moderate temperatures (167). The properties and some applications of these fluids have been described by Adamczak et al. (3). Buckley and Johnson (162) have suggested the use of gallium films. Gallium, a liquid between 86° and 3600°F , has a very low vapor pressure. The lubricating effectiveness of molten metals probably depends upon their ability to adsorb onto the solid and thereby reduce its energy of adhesion (397). Surface adsorption requires the ability of the molten metal to wet the solid surface. Gallium will wet nearly all surfaces. The use of a relatively inert material as one of the sliding surfaces was recommended to reduce the corrosion problem (162).

Evaporation losses can be greatly reduced by partially shielding the lubricant. Type R-2 bearings with two shields mounted on the outer rings have performed satisfactorily at 75°C and 10^{-5} torr when lubricated with a mineral oil, a silicone oil, or a silicone oil and grease. After 1000 hours the bearings retained a large amount of lubricant and showed no wear on the balls, races, or retainer rings (321). Young et al. (789) have operated lightly loaded, double-shielded bearings in excess of one year at pressures as low as 10^{-8} torr with oil and grease lubricants. A new approach to retaining fluid lubricants has been developed by FitzSimmons et al. (299). They eliminated creeping of the lubricants from ball bearings by the use of low-energy fluorochemical barrier films. Although vacuum lubrication was not the objective of this technique, such films could also curtail evaporation by confining the fluid.

A second, and perhaps more serious, problem resulting from lubricant evaporation is the contamination of mirrors, lenses, and electrical contacts by the condensate.

The importance of oxide films in preventing seizure has been discussed. In vacuum these films are soon depleted by sliding surfaces. A decrease in atmospheric pressure can occasionally be beneficial. Friction of ferrous metals decreases at 10^{-2} torr as a result of the formation of Fe_3O_4 instead of the more abrasive Fe_2O_3 (167, 618). However, at 10^{-7} torr the formation of sufficient oxide is prevented. Oxygen and/or water vapor are believed to be necessary for the chemical reaction by which friction-reducing and EP additives function. Reichenbach et al. (618) found the effectiveness of 2 percent elemental sulfur in a mineral oil and of SAE 90 EP gear oil was greatly reduced at 10^{-5} torr. Such additives could possibly be more effective in a base oil whose molecules contained oxygen.

Many of the problems incurred with fluid lubricants can be eliminated or alleviated by the use of solid-film lubricants, or for some applications by employing certain ceramic materials as the sliding couple without lubrication. One disadvantage of solid films is the difficulty of repairing film damage. Graphite relies on adsorbed vapor to affect lubrication and is unsuitable for space applications. MoS_2 and PTFE have intrinsically low friction and perform as well in high vacuum as in air. These have been discussed previously in detail.

One set of friction experiments has been conducted in an orbiting spacecraft (623). Because of the low orbit, the measurements were exposed to a vacuum only in the range 3×10^{-6} to 8×10^{-9} torr. Although the tests were completed in only 22 hours, and although there probably was some contamination of adjacent experiments by volatile constituents of the lubricants, this work represents a significant achievement in friction research. Very low coefficients of friction were obtained with PTFE and MoS_2 films. Intermediate values were found with unlubricated ceramic-metal couples and with metals lubricated with grease or metals which had been gold plated. Friction measurements in space were not, in general, systematically different from those in the laboratory at 5×10^{-6} to 10^{-5} torr.

Space exploration requires lubricants which must function at the extreme temperatures of burning rocket fuel or atmospheric friction during high-velocity reentry. The continuous exposure of some components to ambient temperature in excess of 1000°F in nuclear-power generation, die erosion that occurs as molten metal at ca. 1200°F is ejected at high pressure, and temperatures encountered in metal cutting are further examples of the need for high temperature lubricants (410). The upper limit for liquids is about 700°F, although polyphenyl ethers and a few others may be used for brief periods at slightly higher temperatures. Some promising materials for special applications include liquid metals, reactive liquids or gases which can form low-shear-strength films, organo-metallics, soft metals, metal oxides and sulphides, and ceramic glass formers. The lubricating properties of these materials have been mentioned above. The temperature ranges and limitations of several classes of high-temperature lubricants summarized in Table 4 are taken from Peterson et al. (593).

Table 4
Summary of the Potential High-Temperature Lubricants*

Lubricant	Potential Temperature Range	Limitation
Graphite	27° to 980°C 80° to 1800°F	Must be resupplied in sufficient quantities to compensate for oxidation loss
Silver	316° to 982°C 600° to 1800°F	Oxidation of underlying surface removes silver film
PbO	204° to 649°C 400° to 1200°F	Oxidation to Pb ₃ O ₄ at 800°F
Salts and oxides with graphite	27° to 649°C 80° to 1200°F	Must resupply to compensate for oxidation of graphite
Lead and other liquid metals	27°C and higher 80°F and higher	Oxidation at higher temperature, reduction in fatigue life
Glasses	427°C and higher 800°F and higher	Not effective at low temperatures
Molybdates	538°C and higher 1000°F and higher	Not effective at low temperatures
CuO	538°C and higher 1000°F and higher	Not effective at low temperatures

*From Ref. 593.

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III. PROPERTIES OF LIQUID LUBRICANTS: ADDITIVES FOR PROPERTY ENHANCEMENT

1. FREEZING POINT AND POUR POINT DEPRESSANTS

Physical properties determine to a great extent the suitability of a liquid lubricant for a specific application. It is obvious that a liquid lubricant is not usable at temperatures below its pour point or freezing point. Petroleum oils are a complex mixture of hydrocarbons. Among the hydrocarbons present in many lubricating fractions are long-chain paraffins and isoparaffins which have high freezing points. These high-melting paraffins are removed to various extents by dewaxing procedures (Section V, Petroleum Base Lubricating Oils). When the oil temperature is lowered, a network of wax crystals forms that traps the oil and prevents it from flowing. The temperature 5 °F above that at which the waxy network is strong or extensive enough to prevent the oil from flowing under specified conditions is the ASTM Pour Point (46). When the concentration of precipitated wax reaches approximately 2 percent by weight, the oil will not pour (386, 387, 388).

It has been found economically expedient to depress the pour points of wax-bearing oils by the use of additives rather than dewaxing to lower temperatures. Depressions of 40 °F or more in the pour points of waxy oils can be obtained with small concentrations of additives. The most common depressants in current use are: wax-phenol and wax-naphthalene condensation products; and polymeric materials that include alkyl methacrylates, polyolefins, vinyl esters, alkyl styrenes, and various copolymers (16, 487, 711, 795). Some of the polymeric ashless detergents and V.I. improvers also have pour-depressant properties. Gavlin et al. (328) attribute the pour-depressant action to the adsorption of the additive on the wax crystals which prevents them from growing into a crystal network. Cocrystallization is the mechanism responsible for the pour-depressant action of methacrylates. The length of the alkyl ester group in polymethacrylate esters is critical; for optimum effect the alkyl groups should be chosen so that the melting point of the polymer is close to the pour point of the oil. This promotes cocrystallization of the polymer and wax and results in maximum pour depression (459, 648). Lorensen et al. (486, 487) concluded that depressant molecules either adsorbed or cocrystallized on the wax crystal, depending upon whether the additive was aromatic or comb-like. Although low-molecular weight materials may be effective pour-point depressants in specific instances, their usefulness is limited to blends containing highly crystalline waxes. Polymeric materials have no specific solubility and also contain a multiplicity of cocrystallizable segments that direct crystal growth more efficiently than small molecules.

Holder and Winkler (386, 387, 388) studied the precipitation and growth of wax crystals from petroleum fractions as well as the action of depressants in modifying and inhibiting the growth pattern. They concluded that n-paraffins crystallized from solution independently as solid solutions, and that n-paraffins were potent crystal modifiers. As the differences in molecular weights between two n-paraffins increased, independent crystallization predominated. The response of n-paraffin wax to pour depressants was a function of its crystal structure rather than its chain length. They proposed that the polymeric additives, by virtue of their great chain length and structure, were able to incorporate themselves at the crystal growth step and stop the growth of crystals. However, crystal growth in the Z axis direction was continuously promoted by wax molecules as they precipitated from solution, and crystal growth in the Z direction occurred more readily with mixtures of paraffins than with a single paraffin. Consequently, pour depressants were more effective with mixtures of paraffins. Increasing the concentration of the additive above that required for maximum depression may have produced smaller crystals, thus resulting in better low-temperature flow properties. They could detect no differences in the mechanism by which hydrocarbon and methacrylate ester polymers depressed the pour points of waxy oils.

It is not possible to predict the effectiveness of a pour-point depressant in different petroleum oil base stocks, since the composition of the n-paraffin components may be different. Furthermore, in the presence of a pour depressant, wax-crystal size and shape are greatly affected by the cooling rate. Cycling procedures, which simulate the time-temperature history of oils during storage, have been developed to predict more accurately the stable pour points of additive-containing oils (46). Pour depressants, although remarkably effective in waxy oils, do not appreciably lower the freezing points of synthetic oils.

Freezing-Point Depression

It is well known that the freezing point of a liquid can be depressed by the addition of a solute and that the freezing point depression is directly proportional to the solute concentration. This principle is often used in depressing the freezing points of synthetic oils. A blend of two diesters, RA_2 and RB_2 , will have a lower freezing point than either component. A still greater freezing-point depression will be obtained if the dibasic acid is esterified with a mixture of the two alcohols, since the resulting ester mixture contains a third component, RAB. Very complex ester mixtures can be obtained when a tetrafunctional polyol is esterified with a mixture of different monobasic acids. When two different acids are used, five esters result; with three acids 15 esters and with four acids 31 esters are obtained. Some lubricants derived from mixed acid esters of pentaerythritol (547, 577) have freezing points below -60°F . The average acid chain length used to prepare the ester mixture is approximately six carbon atoms. By contrast, pentaerythritol tetrahexanoate has a freezing point of $+25^\circ\text{F}$. Thus, a freezing-point depression of 85°F has been obtained by esterification with mixed acids.

Compounds which have the requisite dissymmetry (795), and complex mixtures (esters of mixed acids, liquid polymers, e.g., silicones and polyalkyl ethers, and super-refined petroleum fractions) may have viscous pour points that are considerably above their freezing or glass points. Pour points of such oils are essentially crude viscosity determinations, the viscous pour point being in the range of 1/4 to 1/2 million centistokes. Because of the inordinate amount of power required to overcome the viscous drag of the lubricants at temperatures approaching their pour points, lubricants are in general not useful down to such temperatures. The temperature at which the pour point is reached is primarily dependent upon the viscosity level and temperature coefficient of viscosity, to be discussed in the next section.

2. VISCOSITY AND VISCOSITY-TEMPERATURE COEFFICIENT

The rules and generalizations governing the structural requirements for liquids with small temperature coefficients of viscosity and low freezing or pour points have been reported (558, 795). They will be repeated here in condensed form because of their importance in this review.

1. The molecule should have a linear or reticulated structure, with the greatest possible flexibility through free rotation about chemical bonds.
2. The molecule should not contain chemical groups with strong associating tendencies.
3. The addition of side chains or the introduction of bulky groups in the principal chain (i.e., increased breadth-to-length ratio) have an adverse effect on the temperature coefficient of viscosity.

4. Other things being equal, the greater the coefficient of thermal expansion, the greater the temperature coefficient of viscosity.
5. Low freezing points are obtained by introducing side chains, but they raise the temperature coefficient of viscosity. Therefore, the number and length of the side chains should not exceed the minimum required to prevent close alignment or interlocking of neighboring molecules.
6. The freezing point may also be depressed by increasing the number of components in the lubricant fraction, e.g., polyol esters of mixed acids and dewaxed petroleum oil fractions.

The most common method of rating oils by their temperature coefficients of viscosity is the ASTM Viscosity Index or V.I., Method D457 (46). However, this system gives anomalous results at V.I.'s above 100 and rates low-viscosity oil inordinately high. Some other methods of rating oils by their temperature coefficients of viscosity have been reviewed by Geniesse (329). These include the systems of Blott and Verver (107), Malschaert (494), Larson and Schwaderer (470), Hardiman and Nissan (374), Wright (781), Klaus and Fenske (444), Ramser (614), and Cornelissen and Waterman (215). Although several of these systems eliminated the anomalies of the V.I. system (ASTM Method D567), some introduced new anomalies, others were too cumbersome for convenient use or failed to give similar ratings to members of an homologous series, or were not accurate over a wide range of viscosities and temperatures.

Another common method of predicting the viscosity-temperature behavior of oils is by the ASTM Viscosity-Temperature Charts, Method D341 (46). These charts are based on the Walther equation, $\log \log (\mu + c) = A \log T + B$, where μ is the viscosity in centistokes, c is a constant (0.6 in lubricating oil viscosity range), A and B are constants characteristic of each liquid, and T is the absolute temperature. The use of the equation in chart form obviates the necessity of determining the constants A and B . Although straight-line graphs on this chart adequately represent the changes in viscosity with temperature of petroleum oils and a variety of synthetic oils over a restricted temperature range, deviations from linearity are observed at both extremes of temperature, especially at high temperatures and low viscosities (557).

Cameron (179) reported that most of the viscosity-temperature equations have been based on the requirement that $(-1/\eta \cdot d\eta/dt)$ should be a single function of temperature. He found that better correlation was obtained if $\log (d\eta/dt)$ was plotted against $\log \eta$. His graph was so condensed that variations in the viscosity-temperature properties of oils were not apparent. He (177) therefore introduced a new system based on a modified Vogel equation, $n = k \exp [b/(t+95)]$. The exponent b depended only on the viscosity at a given temperature. For 0 V.I. oils with a reference temperature of 100°F, $b_0 = 184 + 450 \log \mu$, where μ is kinematic viscosity in centistokes at 100°F. Then any other oil with the same viscosity at 100°F but a different value of b would have an R-rating defined as $R = [(b_0 - 1)/b] 1000$. This system gives higher relative ratings to viscous oils than does the ASTM V.I. Further attempts (235) using Vogel's three-constant equation, $n = k \exp [b/(t + \theta)]$ showed that it gave more accurate results over extended ranges than do two constant equations, e.g., the ASTM Viscosity-Temperature Chart. However, three-constant equations are difficult to use in ordinary work.

The most recent viscosity-temperature equation is that of Roelands et al. (628), a two-constant equation. In logarithmic form, it is $\log (1.200 + \log \eta) = \log G - S \log (1 + t_c/135)$ where η is viscosity in centipoises; t_c is temperature in °C; and G and S are parameters characteristic of the oil. Parameter G is indicative of viscosity level, since at 0°C, $G = 1.200 + \log \eta_{0^\circ\text{C}}$, and S is a measure of the variation of viscosity with temperature. When prepared in chart form, a great variety of liquids, both associated and nonassociated, including petroleum oils, synthetic oils, water, and liquid metals,

give essentially linear plots over a rather extended temperature range. The viscosity-temperature graphs on this chart show some curvatures; however, it is more generally applicable to liquids than the ASTM D341 Charts. The parameter S , or the slope on the Roelands' Chart (628) of liquids showing no change in viscosity with temperature, is 0. The n -paraffins have an S value of 1.00. Other homologous series of liquids exhibit relatively constant S values at viscosities above about 7.5 cP at 210°F (Fig. 1). A formula was derived to convert S values to Dynamic Viscosity Index, D.V.I., i.e., $D.V.I. = 220 - 7 \times 10^S$. The D.V.I. values agree very well with ASTM V.I. values in the 0 to 100 range for petroleum oils and other liquids having comparable densities. Viscosity-temperature properties of some homologous families and other liquids as given by Roelands et al. are shown in Fig. 1. It is seen that only the n -paraffins and liquids showing no change in viscosity with temperature exhibit constant S values. The H and L Series petroleum oils (L Series, O ASTM V.I. and H Series, 100 ASTM V.I.) have constant S and D.V.I. values above 7.5 cP at 100°C but deviate to smaller S values at low viscosities. Other homologous series of liquids also show a rapid change in S values as viscosities decrease below 7.5 cP at 100°C.

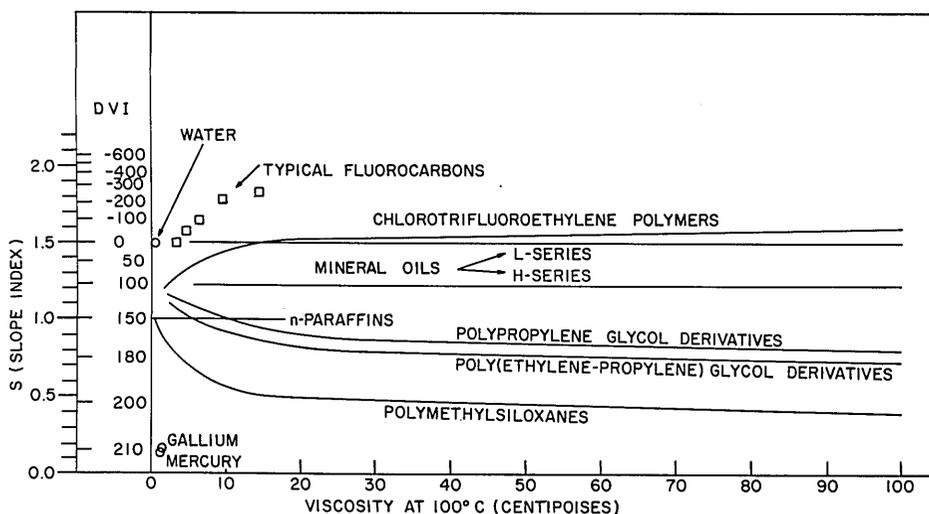


Fig. 1 - Viscosity-temperature criterion of Roelands, Blok and Vlugter (628). Figure reproduced by courtesy of The American Society of Mechanical Engineers.

Since the ASTM V.I. system was so well established (both in the production and marketing of lubricating oils), and since the new systems were (a) not free of anomalies or (b) too complex for general use, Research Division VII on Flow Properties of ASTM Committee D-2 was instructed to correct the anomalies at V.I.'s above 100 without shifting the values between 0 and 100. This procedure was adopted as ASTM Method 2270 in 1964 (46). Values above 100 are designated Viscosity Index Extended, $V.I.E$, to distinguish them from the values obtained by the previous method. Research Division VII was also instructed to adopt or develop a new viscosity-temperature rating system that would minimize the objections to existing proposed systems and that would be generally adaptable over extended viscosity and temperature ranges. Another assigned task was to correct or devise a new Viscosity-Temperature Chart in place of D341 which will give linear graphs over greater temperature ranges.

Graphs of liquids with different temperature coefficients of viscosity are plotted on the ASTM D341 chart in Fig. 2 to demonstrate the importance of small temperature coefficients of viscosity in oils required to operate down to low temperatures. The viscous

pour points of the oils having a viscosity of 5 centistokes at 210°F range from -40°F for the 0 V.I. oil to -80°F for the oil with V.I._E of 150. A similar spread in viscous pour points is observed for the oils having a reference viscosity of 50 cS at 210°F. The higher V.I. oils (smaller temperature coefficient of viscosity) not only have lower pour points but also are more viscous at temperatures above 210°F than are the oils with smaller V.I.'s. The graph of a superrefined mineral oil shows deviations from linearity at both high and low temperatures on this chart, which reveals the desirability of improving the chart.

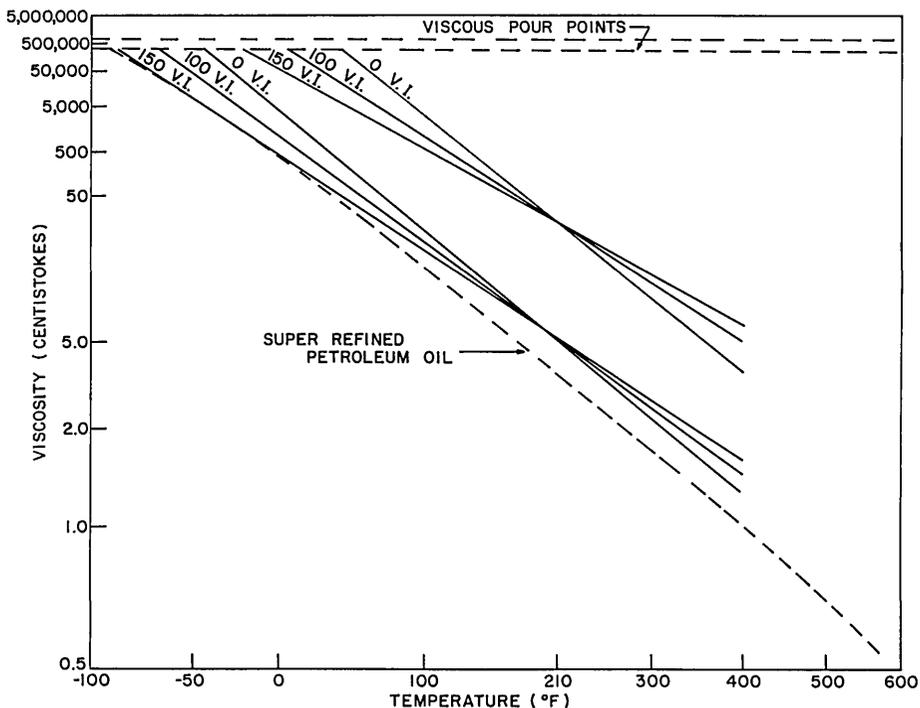
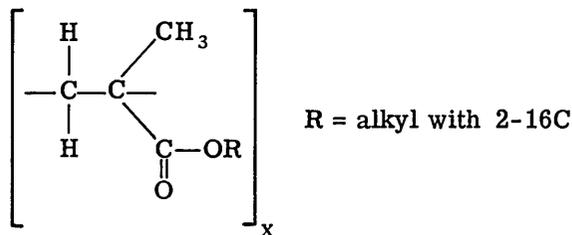


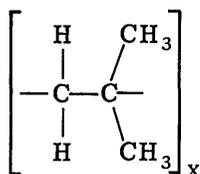
Fig. 2 - Oils on ASTM viscosity-temperature chart

Polymeric additives are now commonly used to improve the viscosity-temperature characteristics of oils. Two products have dominated the market, polymethacrylate esters and isobutylene polymers. Their general formulas are:

Polymethacrylate ester



Polyisobutylene



In addition to the polymethacrylates and polyisobutylenes, polyalkyl styrenes, and styrene-olefin copolymers have been marketed as V.I. improvers. A large number of other polymeric materials, e.g., alkyl maleates and fumarates, alkyl and vinyl esters and ethers, and 1-olefins (16, 416, 711) have been patented as V.I. improvers but have not yet gained commercial acceptance.

The mechanism of the action of polymers as V.I. improvers has been reviewed in an earlier publication (795) and by Stewart and Stuart (711). Some of the important considerations will be reviewed briefly. The viscosity of a polymer solution is governed by the concentration and molecular weight of the polymer according to the following expression:

$$\eta_{sp/c} = [\eta] = KM^a$$

$[\eta]$ = intrinsic viscosity

$$\eta_{sp} = \frac{\eta_{\text{soln}} - \eta_{\text{solvent}}}{\eta_{\text{solvent}}}$$

c = polymer concentration

M = polymer molecular weight

a = constant for a given polymer-solvent system.

The value of a varies from 0 to 2, depending upon the shape and size of the polymer molecule in solution. Most polymer-thickened oils have values of a varying from 0.5 to 0.8. The polymer molecule in poor solvents is a tightly rolled up mass of small size, and its solution has a low intrinsic viscosity (lesser thickening effect).

The effect of temperature upon intrinsic viscosity is dependent upon the nature of the solvent. In a poor solvent, increasing the temperature generally increases polymer solubility and intrinsic viscosity. In a good solvent the polymer is already in its fully extended and solvated state, so the intrinsic viscosity is relatively unchanged. To obtain the greatest V.I. improvement from polymers, its thickening action should be greater at high than at low temperatures. For minimum thickening at low temperatures the polymer should approach its precipitation point at its lowest operating temperature.

Stewart and Stuart (711) reported that regardless of the temperature, the thickening action of a polyisobutylene in a petroleum fraction was relatively constant by a factor of 3, and the cause was the high solubility of the hydrocarbon polymer in the hydrocarbon solvent. A polyalkylmethacrylate produced a three-fold viscosity increase at 210°F and only a 2.3-fold increase at 100°F. The methacrylate polymer contained oil desolubilizing groups, which decreased its solubility with decreasing temperature.

Polymers have also been used to improve the viscosity-temperature properties of synthetic oils. Because of differences in solubilities and temperature coefficients of solubility, the polymer must be tailored for a specific fluid type if maximum V.I. improvement is to be attained. This is true to a lesser extent for petroleum oils because

of smaller differences in polymer solubility in various types of hydrocarbons. However, these differences have been sufficiently great so that it has not been possible to predict the thickening action of a given polymer in various petroleum fractions. Wright and Crouse (783) have developed a generalized relationship for polymer blends. They found that when the $\log \eta_{rel} = \eta_{sol'n} / \eta_{solvent}$ was plotted against \log polymer concentration, a straight line was obtained at both 210° and 100°F with a slope of 45 degrees. This relation held not only for polymer-oil blends but also for a variety of polymer-solvent systems. Thus it is possible with only one graphical point and a 45-degree straight line through it, to calculate the thickening effect for different polymer concentrations. As η_{rel} is related to $[\eta]$, it is possible to calculate the polymer molecular weight if the value of a for that polymer family is known.

Polymer solutions are non-Newtonian liquids whose apparent viscosities decrease with increasing shearing stresses as the result of the orientation of the polymer molecule in the direction of flow. Solutions containing polymers of the highest molecular weights show the greatest viscosity decreases at equivalent shear rates. When the shearing stresses are removed, the polymer-thickened solutions revert to their original viscosities. The principal flow parameter in many non-Newtonian steady-state flow curves is the rate of energy input (shear rate Γ times shear stress t) (782). A straight line is obtained when Γt is plotted versus viscosity parameter

$$\phi = \frac{\log \mu_a - \log \mu_2}{\log \mu_1 - \log \mu_2}$$

on probability paper. Here μ_a , μ_1 , and μ_2 are the apparent, first, and second Newtonian viscosities in poises, respectively. Such plots are insensitive to polymer concentration. The graphs are displaced in a parallel manner for different temperatures.

When polymer-thickened fluids are repeatedly subjected to turbulence at high shear rates, cavitation results, and that leads to irreversible viscosity decreases. Decreasing viscosity losses are accompanied by decreasing V.I.'s. The higher the molecular weight of the polymer, the greater the viscosity loss. Viscosity losses in polymer-thickened lubricants and hydraulic fluids are of concern, since they have an adverse effect on wear and pump efficiencies. Decreases in viscosity follow rupture of the polymer chain, because the resulting lower-molecular-weight polymers have less thickening power. The critical factor that controls shear stability of polymer solutions is the average molecular weight of the polymer. Polymers of wide molecular-weight distribution have shear characteristics that are inferior to that of the same type polymer with a narrow molecular-weight distribution but the same average molecular weight.

The shear-stability characteristics of polymer-thickened lubricants and hydraulic fluids are commonly evaluated by hydraulic pump tests and sonic shear apparatus. Rupture of covalent bonds in the principal chain of the polymer is influenced by factors other than molecular weight (313). These include: viscosity of polymer blend, the shearing stress and cavitation, solvent type, bond concentration, length of principal molecular chain, molecular diameter, and bond strength. Selby (673) showed that in a good solvent, where the polymer molecule was in its extended state, bond rupture occurred more readily than in a poor solvent where the polymer molecule was in a tightly rolled configuration. Molecular diameter was also a factor, as shown by the decreasing shear stability of polyacrylate esters with increasing side-chain length (406). However, this effect was minor when compared with the effect of molecular weight.

Polymer-thickened oils may also be degraded by other sources of energy. Klaus et al. (450) showed that thermal and nuclear radiation caused extensive polymer degradation. In combination with oxidization, degradation was very rapid. Jellinek (406) showed that although random polymer-chain scission was a minor reaction from the chemical point of

view, it had a profound effect on the rheological properties of polymer solutions. He also showed that polymer degradation due to other energy sources could be very rapid as compared to random chain scission.

Laboratory methods of predicting the service performance of polymer-thickened lubricants and hydraulic oils are desired to eliminate the extensive field testing and for setting specification requirements. The shear stability of hydraulic oils conforming to Military Specifications MIL-H-13866A, MIL-H-13919A and MIL-H-5606 have been investigated by both the mechanical shear-stability method and sonic shear apparatus, and discordant results were obtained (473). Discrepancies were attributed to differences in polymer type and molecular weights. Vick and Goodson (745) tried to correlate the shear stability of polymer-thickened crankcase oils with breakdown in a sonic shear apparatus. Correlations were obtained for different oils thickened with the same polymer but failed when different polymeric V.I. improvers were compared. They believed that the amount of sonic breakdown relative to mechanical breakdown varied with polymer composition or with other mechanisms operating in the engine that were not operable in the sonic test.

3. VISCOSITY-VOLATILITY RELATIONSHIPS

Lubricants and hydraulic fluids having low vapor pressures are desired for use at high temperatures and in outer space. The most effective method of raising the boiling point is to increase the molecular weight. If the molecular weight is increased by increasing the chain length, e.g., n-alkanes, there is a concomitant increase in viscosity and freezing point. Although the higher members of the homologous series may be useful to higher temperatures, their utility at low temperatures is decreased. Molecular structural requirements for low viscosity and low volatility are mutually contradictory; therefore it is difficult to obtain an organic liquid lubricant having both a low viscosity and a low vapor pressure at a given temperature. The most satisfactory compromise has been to introduce nonhydrocarbon nonassociating groups into the molecule. Esters are an example of use of this expedient. Critchley and Miles (231) studied the volatilities of trimethylol propane, pentaerythritol and dipentaerythritol esters and showed that evaporation weight losses were generally a direct function of molecular weight. Branched chain esters, however, were more volatile than the unbranched isomers. Relative volatilities of these esters, as with petroleum oils, was reflected by their flash points.

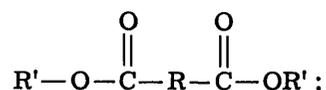
The introduction of inorganic substituents into the molecular structure of the liquid also increases molecular weight and decreases volatility. The substitution of halogens for hydrogen effectively raises the boiling point. The substitution of fluorine for hydrogen is an exception, there being little change in boiling point but a considerable increase in viscosity. In general, halogen substituents do not improve the viscosity-volatility characteristics, because decreases in vapor pressures are more than compensated for by the concomitant increases in viscosity. The outstanding example of improvement in viscosity-volatility properties is by the introduction of dimethyl siloxy groups, e.g., the methyl silicones or polydimethylsiloxanes. Unfortunately, since silicones are deficient in lubricity, their use is restricted in many lubricant applications. Additional requirements of good thermal and oxidation stabilities further restrict the choice among candidate liquid lubricants for extreme temperature and vacuum environments. Therefore, research has been directed increasingly toward solid lubricants for such applications.

4. HYDROLYTIC STABILITY

Since it is rarely possible to exclude moisture and the condensation of water completely from lubricant and hydraulic systems, hydrolytic stability is an important requirement of liquids for such systems. Until the advent of synthetic oils, little consideration was given to this requirement because of the outstanding hydrolytic stability of

hydrocarbons and petroleum oils. However, the stability of additives in finished lubricant formulations must be considered. Synthetic lubricants of concern are usually those containing ester linkages. The principal types are: carboxylates, silicates, phosphates, and halogen esters.

Certain generalizations relating the hydrolytic stability to chemical bonding and other structural considerations were given in a previous review (795). The more important generalizations are repeated here. Esters of strong acids, e.g., phosphoric, perfluorocarboxylic, etc., are inherently less stable to hydrolysis than esters of weak acids. Their acid hydrolysis products are more corrosive than are those from esters of weak acids. Temperature influences the hydrolysis reaction by shifting the equilibrium and changing the reaction rate. Hydrolysis is catalyzed by Bronsted bases, hydrogen, and hydroxyl ions. The introduction of branched chains which shield the ester groups from contact with water molecules is an effective method of improving the hydrolytic stability of a given ester type. Further confirmation of the effect of chain branching on stabilizing carboxylate esters to hydrolysis was obtained by Critchley and Miles (231), who showed that the 2-ethylhexanoate and iso-octyl esters of trimethylolpropane and pentaerythritol were much more resistant to hydrolysis than their straight-chain isomers. However, these polyol esters of straight-chain carboxylic acids were, in general, adequately stable to hydrolysis for use as gas turbine lubricating oils. Murphy et al. (556) showed that the development of lead corrosive constituents in stored MIL-L-7808 type jet engine oils was caused by the catalytic hydrolysis of the dibasic acid ester



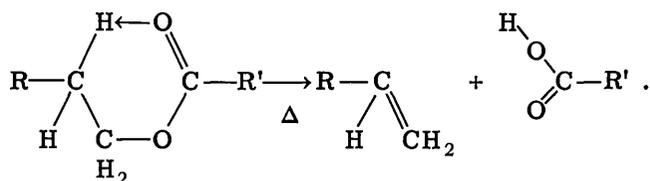
the catalysts were acid phosphates present as impurities in, or resulting from, the hydrolysis of the phosphate antiwear agent.

5. THERMAL STABILITY

As operating-equipment temperatures continue to rise, the thermal stabilities of lubricants and hydraulic fluids become increasingly important. Blake et al. (104) made a comprehensive study of the effect of chemical structure on molecular thermal stability using the isothermal pressure rise from thermal decomposition in order to determine the decomposition temperature, T_D . Classes of compounds studied include hydrocarbons, carboxylic esters, ethers, amides, amines, inorganic esters, phenyl derivatives of Groups IIIA, IVA, VA, VIA, and VIIA, heterocyclics, sulfones, ketones, silanes, and siloxanes. In diatomic molecules, rupture occurs when the vibrational energy due to increasing temperature equals the bond strength. In complex molecules, the strength of the weakest bond determines the upper limit of thermal stability if there are no low-energy decomposition paths. Resonance interaction, e.g., in benzene, is responsible for its stability. Here the six equivalent bonds equal about 1-1/2 C-C bonds. Bond strength and resonance interaction are, however, seldom limiting factors in the thermal stability of organic compounds, because most molecules decompose with activation energies lower than those of their weakest bonds. Such compounds decompose via a transition state in which bonds are broken and reformed simultaneously. Blocking the low-energy decomposition path should raise the decomposition temperature of compounds of a particular type. Except for the first members of the series, paraffinic hydrocarbons have T_D around 660°F. Branch chain hydrocarbons, because of steric crowding, have lower T_D , the lowering depending upon the extent of crowding. Highly refined paraffin-base petroleum oils which are mainly cycloparaffins with alkyl substituents, have somewhat lower T_D , around 630° to 640°F. The most stable hydrocarbons are the aromatics, having T_D around 850°F (104, 760).

Condensed ring aromatics have higher T_D than perphenyls, up to 1000°F for the former as compared to 850°F (409) for the latter. Johns et al. (408, 409) showed that certain heterocyclics, substituted aromatics, aromatic silanes, and perfluorinated ring compounds had T_D equal to or slightly better than aromatic hydrocarbons.

Dibasic acid esters derived from alcohols having hydrogen on the β carbon atom have T_D in the range of 500° to 540°F , which is much lower than the T_D of n-paraffins. Although the ester bonds are at least as strong as C—C bonds, these esters decompose by a low-energy path to give a carboxylic acid and olefin.



Esters without hydrogens on the β carbons of the alcohol moiety (blocking the low-energy decomposition path) show improved stabilities but do not equal that of n-paraffins. Decomposition products resulting from the pyrolysis of esters of different structures have been studied (10, 269, 342, 622). Amides have thermal stabilities slightly higher than dibasic acid esters, 560° to 590°F . Primary and secondary aliphatic ethers decompose to a paraffin and an aldehyde or ketone. Decomposition to an aldehyde is by an energy route intermediate between that for the production of the acid from an ester and for the free radical decomposition of a paraffin; thus the T_D of aliphatic ethers should be intermediate between those of esters and paraffin hydrocarbons. This was observed to be true, but the T_D of the aliphatic ethers more closely approached those of the esters. Unsubstituted aromatic ethers have T_D approximating those of the corresponding polyphenyls (104, 408, 409), i.e., in the 850°F range. Their stabilities are equaled only by the polyphenyls, aromatic amines, and heterocyclics, all of which have strong resonating structures. Alkyl-substituted aromatic ethers have T_D lower than their unsubstituted analogs (104, 409). Increasing the number and/or size of alkyl substituents causes a steady decline in stability. The effect of alkyl substituents on the decomposition temperatures of some aromatic ethers (104) is indicated in Table 5.

Table 5
Effect of Alkyl Substituents on Thermal Stability*

Compound	Decomposition Point ($^\circ\text{F}$)
m Bis(m-phenoxyphenoxy)benzene	848
p Bis(p-toloxo)benzene	721
p Bis(p-propylphenoxy)benzene	670
p Bis(p-octylphenoxy)benzene	639
p-Cyclohexylphenyl-p-phenoxy-phenyl ether	706

*Reference 104.

Data reproduced by courtesy of Journal of Chemical Engineering Data.

Thermal stabilities of a variety of heterocyclic compounds have been investigated (104, 408, 409). Johns et al. (409) reported that the molecular configuration, the position of the heteroatom or atoms, and the nature of substituents all affected stability. Dibenzothiophene (T_D 1010°F) and dibenzofuran (T_D 967°F) were approximately 180°F more stable than fluorene, and the fluorene ring was more stable than the anthracene ring. Quinoline (T_D 968°F) was more stable than isoquinoline (T_D 842°F), showing that position

of heteroatom affected stability. The effect of substituents was illustrated by triphenyl-s-triazine (T_D 872°F) and tri-2-pyridyl-s-triazine (T_D 658°F).

Alkyl silanes have T_D of the same order as the corresponding alkyl, in the 600°F range. Replacing the alkyl substituents by aryl groups has little effect on stability, unless the alkyl groups are completely replaced (104, 477). Tetraarylsilanes have T_D of ca. 800°F, approaching those of aromatics and heterocyclics. Levy et al. (477) reported T_D above 1000°F for aryl silanes, but their procedures and apparatus differed from that of Blake (104). They showed that there was a progressive decrease in T_D as aryl groups were replaced by alkyls. Siloxanes or silicones have decomposition temperatures of ca. 700° to 740°F.

The thermal stabilities of inorganic esters vary with acid strength and nature of the organic group. Triphenylphosphate has a T_D of 800°F as compared to ca. 400°F for trioctyl phosphate. Aryl borates have T_D of 800°F higher as compared to 660°F for alkyl borates. As with the phosphates and borates, aryl silicates are more thermally stable than alkyl derivatives, with T_D of 630° to 640°F.

As functional fluids and lubricants do not operate in glass systems, the effect of steel on thermal stability was investigated. As seen from Table 6, the thermal stability of esters is adversely affected by contact with 52100 steel. Hydrocarbons, silicones, silanes, amines, and polyphenyl ethers show no significant change in T_D in the presence of steel. It is possible that other metals of construction and certain environmental conditions may also influence stability and service life. Resonance stabilization appears to be an essential requirement for molecules of high thermal stability. If good oxidation stability is also required, only resonance-stabilized compounds can be used. Ring-type molecules have high breadth-to-length ratios; therefore, such fluids will have large temperature coefficients of viscosity. Low volatility is also a requirement for a high-temperature fluid. Thus fluids with low volatilities and good thermal oxidative stabilities are expected to have low V.I. and high pour points (or freezing points), and to be viscous at room temperature. Fluid types rated according to decreasing thermal stability are: aromatics, aromatic ethers and amines, certain heterocyclics > aryl silanes, aryl esters of inorganic acids > silicones > petroleum oils, alkyl silicates, borates, and silanes > polyol esters > dibasic acid esters.

Table 6
Effect of Steel on Thermal Decomposition Points of Some Organic Compounds*

Compound	Decomposition Point (°F)		Difference
	No Metal	52100 Steel	
Bis(2-ethylhexyl)sebacate	543	441	-102
Bis(1-methylcyclohexylmethyl)sebacate	623	563	-60
Propane-1,1,1-trimethylol triheptanoate	603	493	-110
Octacosane	662	658	-4
Dow Corning Silicone 710	732	727	-5
Tris(3,4-dimethylphenyl)phosphate	718	652	-66
Triphenyl-p-biphenylsilane	799	803	+4
N,N,N',N'-Tetraphenyl-p-phenylenediamine	856	860	+4
m-Phenoxyphenyl-p-phenoxyphenyl ether	802	795	-7

*Reference 104.

Data reproduced by courtesy of Journal of Chemical Engineering Data.

6. OXIDATION

Oxidation stability is generally the requirement that governs not only the upper temperature of usefulness of lubricants, but also its service life. Oxidative deterioration is manifested by changes in certain physical and chemical properties of the lubricant, e.g., viscosity, precipitation of insolubles, lacquer and varnish formation, increase in acidity, and corrosiveness. When the concentration of deterioration products reaches some limiting value, depending upon the application, the lubricant should be changed. Since the rate of formation of oxidative degradation products increases with increasing temperature, more frequent oil changes are required as the operating temperature rises. Economic considerations determine the advisability of changing to a more oxidation-stable, but more expensive, lubricant.

As both the efficiency and economy of engine and mechanism operation and maintenance is related to lubricant performance, the oxidation stability of the lubricant is of prime importance. Therefore, an enormous amount of research effort has been expended in determining the mechanism of oil oxidation and methods of inhibiting oxidation. Ever since the classic works of Bateman, Bolland, Gee, and coworkers, it has generally been agreed that the liquid-phase oxidation of hydrocarbons is autocatalytic and involves the formation of peroxides and free-radical intermediates (69-76, 110-116).

A number of excellent reviews on oxidation of oils have appeared since 1950 (70, 110, 320, 333, 488, 489, 570, 650, 711). The important steps in the oxidation reaction are shown below. As in other chain reactions, the sequence is initiation, propagation, and termination. In the reaction scheme RH = organic substrate, $R\cdot$ = organic radical, $ROOH$ = hydroperoxide, $ROO\cdot$ = peroxy radical, and $RO\cdot$ = oxy radical.

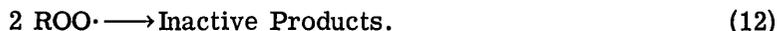
Initiation



Propagation



Termination



The above reaction scheme applies to petroleum and to synthetic oils containing more oxidation labile hydrocarbon groups than nonhydrocarbon groups. The usual initiation route is by Eq. (8); however, it has been postulated that oxygen may add directly to certain olefins and possibly to petroleum oils during thermal oxidation, Eq. (9). When formed, the radical $R\cdot$ reacts rapidly with oxygen, Eq. (10), giving the peroxy radical $ROO\cdot$, which in turn reacts with the substrate to form the hydroperoxide $ROOH$ and the free radical, $R\cdot$, Eq. (11). The propagating reactions (Eqs. 10 and 11) are repeated many times. In each cycle, one molecule of oxygen is consumed, producing a molecule of hydroperoxide, and the radical $R\cdot$ is regenerated. Retarding the autocatalytic reaction is the termination reaction (Eq. 12) whereby free radicals react to form nonradical products, e.g., alcohols, aldehydes, ketones, olefins, etc. These compounds are, however, subject to further oxidation.

Most of the oxygen consumed in low-temperature oxidations can be accounted for as the hydroperoxide. Continued oxidation, particularly at elevated temperatures, results in the decomposition of the hydroperoxide. Hydroperoxide decomposition may be either unimolecular or bimolecular.



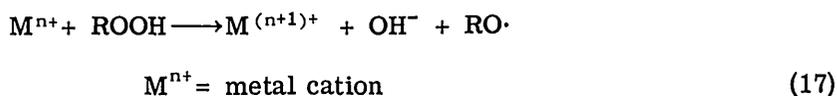
The bimolecular mechanism (Eq. 14) predominates except at low hydroperoxide concentrations. Peroxy radical $\text{ROO}\cdot$, produced by the reaction shown in Eq. (14), then reacts with the substrate to form another molecule of hydroperoxide and the organic radical $\text{R}\cdot$, Eq. (11). The radical $\text{R}\cdot$ may also be produced by the abstraction of hydrogen from the substrate, Eqs. (15) and (16).



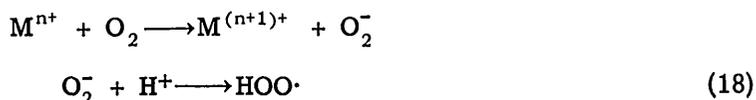
Early in the course of oxidation, the reactions shown in Eqs. (13), (14), (15), and (16) supersede those in Eqs. (8) and (9) as sources of initiating radicals. Thus, the decomposition of hydroperoxides is the rate-controlling step in most autocatalytic oxidations of lubricating oils. As the rate of the thermal decomposition of hydroperoxides increases with increasing temperature, the oxidation rate is increased by raising the temperature. The steady-state hydroperoxide concentration is thus inversely proportional to the temperature.

Initiating reactions in Eqs. (8) and (9) can also be activated by light, heat, heavy metals, ionizing radiation, and compounds that decompose or react to yield free radicals. Since metals are commonly used as structural materials, the lubricant is in continuing contact with them. The initiating activity of metals can be pronounced. Uri (742) is of the opinion that the very large differences in induction periods reported for the same compound can only be explained by the assumption of initiation due to trace metals. Different metals and metal compounds may react by different mechanisms. The mechanism for the same metal may also vary with the substrate. Metal initiating mechanisms (79, 517, 742) include:

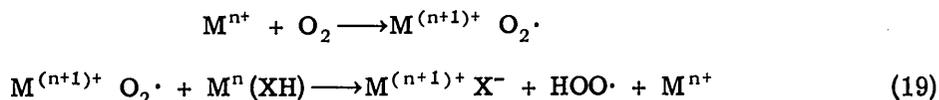
A. Reduction activation of hydroperoxides



B. Reaction of metal ion with oxygen

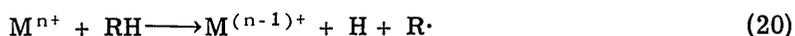


C. Complex formation

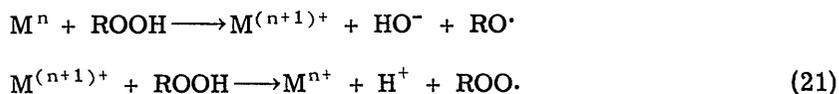


X = organic group

D. Directly with hydrocarbons



E. Metal ion acts both as reductant and oxidant



It should be noted that the sum of the steps in mechanism E is identical to the bimolecular decomposition of hydroperoxide, Eq. (14), whereas that of mechanism A is identical to the unimolecular decomposition, Eq. (13).

As light is generally excluded from lubricant packages and systems, it is of minor importance as an initiator in most applications. However, it may be an important initiator for edible fats packaged in clear glass bottles or jars. Thermal energy may be responsible for the initiation of autoxidation in olefins with labile C—H bonds, but it has not been established whether this mechanism is significant for saturated hydrocarbons. Free radicals resulting from the degradation of a lubricant or additive exposed to ionizing or nuclear radiation (118) are also initiators of autoxidation. The most common source of free-radical initiators is from the used oil remaining in a lubricant system after an oil change. Although the steady-state hydroperoxide concentration varies inversely with the initiator concentration, the oxidation rate is independent of the initiator concentration. The induction period, however, varies inversely with the initiator concentration.

It should not be assumed from the above discussion that the susceptibilities of all hydrocarbons to oxidation are the same. On the contrary, hydrocarbons differ markedly in their oxidation resistance. Hydrocarbons, or organic compounds containing unsaturated bonds, are more oxidation labile than those with saturated bonds. The relative order of increasing oxidation lability in saturated compounds is primary, secondary, and tertiary C—H bonds. Aromatic C—H bonds are more resistant to oxidation than primary aliphatic C—H bonds. Structural modifications can also have a profound influence on oxidative activity (331, 570, 652). Benzene derivatives with long alkyl side chains, or a number of alkyl substituents, are less resistant to oxidation than naphthenes, paraffins, and benzene derivatives having short side chains. The highly condensed ring derivatives of naphthalene, anthracene, and phenanthrene are the most resistant to oxidation (570). Since petroleum oils are complex mixtures of hydrocarbons having a variety of different structures (42, 359, 744), it is difficult to predict the oxidation characteristics of a given oil fraction. A further complication is the complexity of the competitive oxidative reactions of hydrocarbons. The oxidation of a mixture of two hydrocarbons proceeds by a six-step propagation process, whereas a single compound oxidizes by a two-step propagation process. It has been shown that the addition of a very oxidation-labile hydrocarbon will frequently retard the oxidation of one of lower reactivity (651), due primarily to faster termination reactions.

7. ANTIOXIDATION

Metal Deactivators

Oxidation inhibitors are generally classified (423) as: (a) metal deactivators, (b) free-radical acceptors (i.e., agents that break the reaction chain in the propagation steps), and (c) hydroperoxide destroyers (i.e., agents that inhibit the formation of free radicals from the hydroperoxide decomposition). Oxidation can also be inhibited by reducing the sources and concentration of initiators. Initiators such as light and ionizing and nuclear

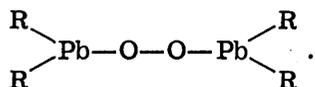
radiation are not of primary concern in most lubricant applications; exceptions are in space vehicles and nuclear power plant lubrication. As lubricant operating temperatures continue to rise, thermal energy is of increasing concern. Thermal energy not only initiates the oxidation reaction but also accelerates it by the production of free radicals from hydroperoxide decomposition. Other sources of initiators are impurities in lubricants that react or decompose to form free radicals. Appropriate purification and refining procedures can reduce such compounds to a minimum.

Although metal ions can initiate the oxidation reaction (Eq. 20), it is the acceleration of oxidation resulting from free radicals produced by reactions of metal ions (Eqs. 17, 18, 19, and 21) that is primarily responsible for rapid oxidative deterioration. Soluble metal ions are formed by the reaction of organic acids with metals. The most common ions in lubricant systems are: copper, cadmium, iron, lead, tin, and silver. The catalytic activity of these metal ions may vary with the conditions of oxidation (570), e.g., temperature, degree of oil agitation, type of substrate, and presence of inhibitors. Thus it is not possible to rate these ions in the order of their relative prooxidant action except under exactly specified conditions. Laboratory oxidation tests show that these metals are prooxidants; in general, copper is the most active (190).

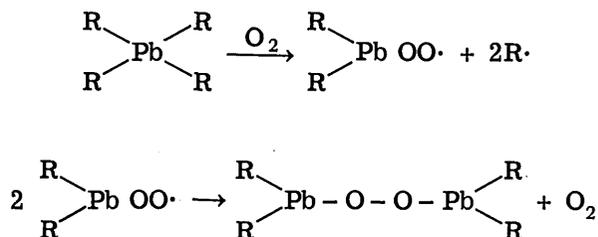
An effective method of reducing the prooxidant action of metal ions is by the use of additives that react with them to form insoluble compounds. Such additives are also known as metal deactivators, or sequestering agents. Generally, these additives are chelating agents. Although many organic groups form chelates with metals (272), only those groups are effective that are sufficiently soluble in the oil substrate but yield insoluble and stable metal chelates. Useful chelating agents include derivatives of N,N'-disalicylidene diamine, mercaptothiadiazole, quinizarin, and alizarin. Chalk and Smith (192, 193) showed that chelating agents may suppress, activate, or not affect the metal-catalyzed oxidation of olefins. In general, agents less than sexidentate had relatively little effect on a catalyst. Lodwick (481) concluded that the effectiveness of a deactivator depended on structural factors: chelation, ring size, inner-complex salt formation, electron-donating tendency of heteroatoms, trying together of chelate groups, and coplanar configuration. Agents that chelate with or sequester metal ions are not antioxidants in the absence of metal initiators; such additives are most commonly used in fuels, but lubricant applications are increasing.

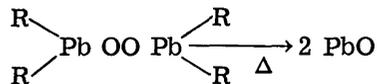
Ions of copper, lead, tin, cadmium, and silver in lubricants are generally manifestations of bearing corrosion. It has been shown that bearing corrosion results from the reaction of organic acids with the metal under oxidizing conditions (246, 247, 248, 556, 601, 602, 732, 770). Both peroxides and oxygen can participate in the corrosion process.

Chakravarty (189, 190, 191) showed that the yellow deposit formed on lead specimens in oxidizing oil is



He proposed the following scheme for lead corrosion:



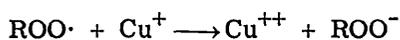
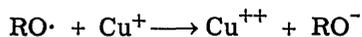
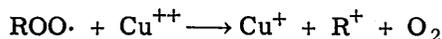


The factor controlling the corrosion rate is the reactivity and mobility of the free radical R·, which reacts with lead to form the tetraalkyl or aryl. The smaller lead corrosion rate observed in mineral oils than is observed in white oils or decane is attributed to the greater size and lesser reactivity of naphthyl radicals as compared to alkyl radicals.

The addition to lubricants of compounds that form stable, insoluble films on the bearing metals can prevent attack by acids and radicals. Such additives include zinc dithiophosphates, carbamates, and alkyl polysulfides (664, 711, 790). It has been shown that the films formed by zinc dithiophosphate include the undecomposed additive, zinc sulfate, as well as an unidentified zinc decomposition product (72, 319). In addition to the film-forming properties of the dithiophosphate derivatives and alkyl sulfides, these compounds are also active hydroperoxide decomposers; this property will be discussed in a later section. Derivatives of mercaptothiazoles and mercaptothiazines are also used to form protective films on bearings. Field (295) is of the opinion that mercaptothiadiazoles form films by chelating with metal and also provide a steady source of sulfur which forms a protective film of the sulfide. Stewart and Stuart (711) have listed a number of sulfur-free bearing corrosion inhibitors including antimonates, arsenates, borates, molybdates, titanates, vanadates, and iso- and terephthalic acids.

Antioxidant Action of Metals

There are occasional reports in the literature that metals or metal ions inhibit oxidation reactions. The presence of an induction period has been observed during oxidations catalyzed by Mn^{++} and CO^{++} (192, 193), and this has been attributed to the formation of an intermediate catalyst-hydroperoxide complex. It has also been suggested that ROOM formed a complex with alkyl benzenes that rearranged to nonionic oxidation products (345). Decomposition of the complex yields the metal ion in its catalytic higher-valence state; then the autocatalytic oxidation proceeds normally. Copper stearate inhibits the ferric-stearate-catalyzed oxidation of tetralin and the cobalt-stearate-catalyzed oxidation of paraffins (330). Chain termination reactions:



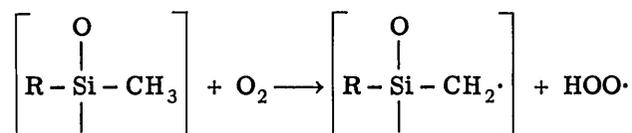
could be responsible (430, 431), but recent work indicates that a radical-copper ion complex of reduced activity may be formed. Hammond et al. (373) reported that ferric chloride inhibits the oxidation of cumene and tetralin in chlorobenzene solution but not that of cyclohexane. Phenols produced by rearrangements of cumyl and tetralyl hydroperoxides were the inhibiting species. Copper naphthenate has been shown to reduce the oxidation rate of toluene (575) and p-xylene (574); also, some copper salts inhibit the oxidation of gasoline (588). Cobalt stearate inhibited the oxidation of n-heptaldehyde (330). Cupric stearate acted on n-decane as a catalyst at low concentrations and as an inhibitor at high concentrations (455). Copper naphthenate acted on p-xylene in a similar manner (574). The change from a catalyst to an inhibitor suggests that at high concentrations the destruction of free radicals by the above-mentioned termination reactions were important enough to reduce the reaction rate (398). The patent literature also cites examples of heavy-metal compounds that act as inhibitors. Downing and Fitch (261) claimed a variety of copper salts as stabilizers of lubricating oil.

Heavy metal compounds have also been cited as oxidation inhibitors for nonhydrocarbon synthetic oils. Elliott (275) claimed the iron, cobalt, nickel, and copper salts of carboxylic acids as stabilizers for silicones. Further research on the stabilization of silicones (51, 151) showed that other types of iron compounds were effective stabilizers. Work at NRL demonstrated that a wide range of redox metal ions inhibited silicones against oxidation, provided the ions were dispersed or solubilized in the liquid (55). Cerium compounds were the most effective inhibitors. Recent work (54) showed that when cerium was complexed with certain organic groups and then reacted with polymethylhydrogen silicones, the product could be solubilized in silicones without the subsequent precipitation of insoluble products. No mechanism has been proposed to account for the antioxidant activity of the various metal compounds in silicones. In general, the active inhibiting metal ions are prooxidants in hydrocarbon, petroleum oils, and a number of other synthetic oils.

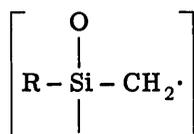
Other examples of the inhibiting action of metals and metal compounds are iron, copper, barium, nickel, chromium, cobalt, manganese, titanium, strontium, praseodymium, and ytterbium in fluoroesters and polyphenyl ethers (615). Stelmiski, et al. (707) showed that such common antioxidants as amines and phenols were ineffective or detrimental as additives for improving the oxidation stability of the polyphenyl ethers; however, they found that a variety of metal chelates, organometallic compounds, and metal oxides were effective. The antioxidant action of chelates was found to depend not only on the cation but also on the ligand (707).

Certain generalities and similarities can be deduced from the oxidative behavior of the following lubricants: silicones, fluoroesters, and polyphenyl ethers. These fluids are inherently stable to oxidation, requiring temperatures of 350°F or more for appreciable reaction. The most effective antioxidants are compounds of metals of variable valence. Such metals are prooxidants for hydrocarbons and a number of synthetic fluids (Eq. 21). No experimental evidence has been reported that hydroperoxides or peroxy radicals are present during oxidation. However, the high temperatures required for reaction would probably cause rapid decomposition and fleeting lifetimes.

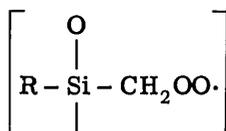
It has been postulated that the initial oxidative attack on methyl substituted silicones is on the methyl group with the formation of free radical intermediates (2).



The peroxy radical initiates other reactions leading to additional

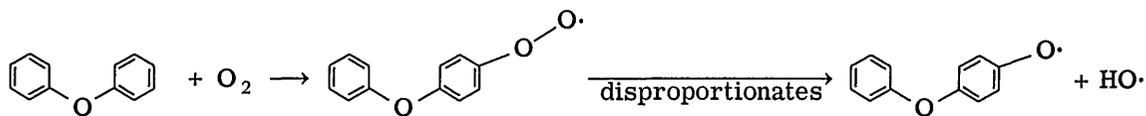


which then reacts with oxygen to form



This radical rearranges or reacts to give formaldehyde and siloxy radicals.

Polyphenyl ether oxidation is believed to be initiated by the addition of oxygen to one of the polyphenyl ether rings (771).



The phenoxy free radical reacts with a second polyphenyl ether molecule, with subsequent ring closure and dehydrogenation to form higher-molecular-weight, fused-ring ethers.

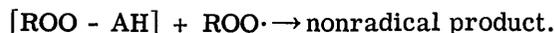
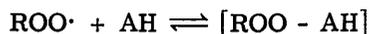
Fluoroesters are believed to be oxidized in the hydrocarbon portion of the molecule, quite like hydrocarbons, by a free-radical mechanism involving decomposition of hydroperoxides and the formation of free radicals. The greater oxidation resistance of the fluoroesters probably results from the shielding action of the stable fluorocarbon groups.

If silicone, polyphenyl ether, and fluoroester fluids are oxidized by a free-radical mechanism involving hydroperoxides and their free-radical decomposition products, the lives of the peroxy radicals are so fleeting that they have not been positively detected. Since the concentration of hydroperoxides would be small and dimer formations unlikely at elevated temperatures, unimolecular decomposition would be expected. The dominant radical products would be $\text{RO}\cdot$ and $\text{HO}\cdot$, and reactions in Eqs. (15) and (16) would be the major source of the initiating radical $\text{R}\cdot$. It is possible that metal compounds inhibit oxidation by changing the course of hydroperoxide decomposition to nonradical products, or by reacting with free radicals to terminate the reaction chain. Kharasch and associates (427, 429, 430, 431) showed that metal ion complexes were formed with free radicals. Ingold (398) suggested that the reported inhibiting action of metals resulted from the stability of metal free-radical complexes. Recent work (86, 620a, 620b) has shown that cobalt and copper ions could catalyze the decomposition of hydroperoxides without being oxidized or reduced.

Free-Radical Acceptors

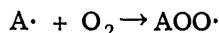
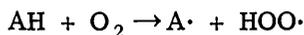
Antioxidants are generally classified as: (a) free-radical acceptors (i.e., agents that break the reaction chain in the propagation steps), and (b) peroxide decomposers (i.e., agents that decompose hydroperoxides into nonfree-radical products) (423). Bolland and ten Have (115, 116) concluded that free-radical acceptors react with $\text{ROO}\cdot$ and not $\text{RO}\cdot$ radicals. The reaction is $\text{ROO}\cdot + \text{AH} \rightarrow \text{ROOH} + \text{A}\cdot$. The free radical, $\text{A}\cdot$, derived from the antioxidant is resonance stabilized and should be insufficiently active to start a new oxidation chain. Bulky substituents around the active group stabilize the inhibitor free radical. This radical can react with $\text{ROO}\cdot + \text{A}\cdot \rightarrow \text{ROOA}$, thus breaking another chain. The inhibitor free radical may be destroyed by several mechanisms (488, 489, 735, 741): (a) by reactions with another free radical, (b) by reactions with itself — dimerize, (c) by rearrangement to an ion or another structure. The reaction route may vary with both the substrate and temperature. For an antioxidant to be practical and effective, it must not be so active as to be consumed by reactions with oxygen.

Boozer, Hammond, and coworkers (122, 372) proposed another mechanism for anti-oxidation involving complex formation between the inhibitor and peroxy radicals.



Uri (741) was of the opinion that complex formation was of importance only when hydrogen abstraction by $\text{ROO}\cdot$ was not fast enough to be competitive. It has been shown both stoichiometrically and kinetically that a large variety of substituted amine and phenolic inhibitors terminate two reaction chains, as shown in the above equations. Stoichiometric factors can exceed two if the reaction product of the inhibitor reaction is itself an inhibitor.

As the inhibitor is consumed by reactions with peroxy radicals, its life is limited. Thus the period of inhibitor effectiveness is proportional to its concentration; when the inhibitor is exhausted the oxidation rate is that of the uninhibited substrate. If the inhibitor is too active, it may also be consumed by reactions with oxygen.

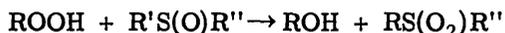
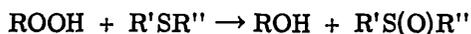


For practical reasons the inhibitor should not be consumed by direct oxidation.

Inhibitors of the free-radical acceptor type are of particular importance for materials that must show as little oxidative deterioration as possible for long periods of time. Specific applications are for: (a) edible foods and shortenings that must not develop rancidity during shelf life, (b) gasolines and distillate fuels that must remain free of gums and insolubles during storage, and (c) dielectric and transformer oils that must remain free of polar and ionic impurities during storage and use. Lubricant applications include inhibitors for instrument oils, hydraulic fluids, steam turbine oils, and industrial applications where operating temperatures are not high. Many methods are used to rate lubricant antioxidants according to their effectiveness, and the most common are measurements of: induction period, hydroperoxide concentration, viscosity changes, acidity increases, insoluble formation, etc. General conclusions have been drawn from such tests about the effect of structure on inhibiting efficiency (398, 741). The efficiency of a given type of inhibitor is generally increased by an increase in electron density at the reaction site, i.e., a decrease in oxidation-reduction potential. However, too low an oxidation-reduction potential results in a very reactive compound which is likely to be consumed by direct oxidation. Steric protection of the reactive site usually increases inhibiting efficiency, but there are a number of exceptions. Very little information is available about the temperature coefficient of inhibitor activity. The effectiveness of inhibitors may vary not only with the temperature but also with the substrate, as their activity varies with their ability to abstract hydrogen from the hydrocarbon substrate and initiate new oxidation chains. Free-radical acceptors type inhibitors of most commercial importance are substituted phenols and amines. Many inhibitors of oxidation are listed in Refs. 16, 17, 416, 570.

Peroxide Decomposers

Hydroperoxide decomposition is a major source of initiating radicals, Eqs. (13) and (14). Thus the decomposition of hydroperoxides to stable nonradical products would be an effective method of reducing the oxidation rate. Such inhibitors would be particularly desirable at high temperatures, since the rate of formation of radical products from the hydroperoxides increases with increasing temperature. Denison and Condit (246, 247, 248) first showed that certain sulfur and selenium compounds reacted with hydroperoxides to produce the corresponding alcohols rather than free radicals.



Monosulfides containing at least one alkyl group attached to sulfur are more effective antioxidants than mercaptans and disulfides. Diaryl sulfide and sulfones are inactive. Selenides (709, 710) are more effective peroxide decomposers than the corresponding sulfides, as the selenoxides are partially regenerated to the original selenide.

Peroxide-destroying additives include phenothiazine, phosphorus pentasulfide-olefin reaction products, zinc dialkyldithiophosphates, sulfurized olefins, alkyl polysulfides,

dialkylphosphonates, trialkyl phosphites (757), zinc dialkyl dithiocarbamate, alkyl tri-thiocarbamate, and various selenium compounds. These peroxide-destroying compounds are more effective than the free-radical acceptors as oxidation inhibitors for many applications, particularly for those where initiators remain in the system and where the lubricant is subjected to high temperatures. Certain of these additives destroy an amount of peroxides greatly in excess of that which can be accounted for by the oxidation of the antioxidant (423, 555, 571).

Kennerly and Patterson (423) suggested that intermediate decomposition products of zinc dialkyldithiophosphates were the active inhibitors. They function by a molecular process at low temperatures and perhaps by an ionic process at high temperatures to give nonradical hydroperoxide decomposition products. Oberriht et al. (571) proposed that phosphorus- and sulfur-containing additives functioned by two mechanisms: (a) at high antioxidant concentrations the hydroperoxide was reduced, (b) a catalytic decomposition of hydroperoxides by strong acids formed by oxidation of the inhibitor. The latter reaction is analogous to action of ferric chloride in benzene (strong Lewis acid) on hydroperoxides (428) where the rearrangement is by an ionic rather than a free-radical mechanism. The oxidation of sulfur- and/or phosphorus-containing antioxidants produces strong acids, probably sulfonic and phosphoric. Although strong acids can reduce the rate of oxidation, they may direct the oxidation toward the formation of resins and sludges (573, 769).

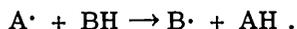
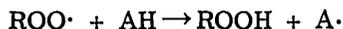
Phenols and aromatic amines are generally classified as free-radical acceptors (chain-breaking inhibitors); however, they also appear to decompose hydroperoxides without producing free radicals. Ingold (399) is of the opinion that the division of antioxidants into "free-radical acceptors" and "hydroperoxide decomposers" is arbitrary, as the former may also decompose hydroperoxides. This point will be discussed in the following section, on Synergism.

It was mentioned earlier that acid-oxidation products of certain sulfur- and phosphorus-containing antioxidants contributed to the formation of resin and sludge. As operating temperatures have risen, insolubles (or dirt) from the antioxidant systems have become increasing problems, particularly for synthetic gas turbine and instrument lubricants. Phenothiazine, the common antioxidant for gas-turbine oils, was shown to form insoluble polymeric products at high temperature (212, 276, 555). A similar phenomenon occurs when N-phenyl-1-naphthylamine is used as an antioxidant, the insoluble 1,4-naphthalenediamine polymer being formed. Elliott and Edwards (276) showed that an alkylated phenothiazine (3,7-dioctyl phenothiazine) almost completely eliminated insolubles, but it was a less effective inhibitor than the parent compound. Peeler (589) found that alkylation adjacent to the amino group of N-phenyl-1-naphthylamine also reduced insoluble formations. Alkyl substitution in the phenyl ring increased, and in the naphthyl ring decreased, oxidation inhibition. Sludging was most effectively prevented by substitution of long alkyl groups on the phenyl ring.

Synergism

Synergism occurs in antioxidant systems consisting of two or more inhibitors when the combined action of the components is greater than the sum of the actions of the individual inhibitors. When the efficiency is less than that of the sum of the action of the individual inhibitors, they exhibit antagonism. In synergism, the compound that is least active or even inactive is called a synergist for the other component.

Many examples of synergistic antioxidant combinations have been reported. Uri (741) proposed a mechanism to explain the synergistic effects obtained with certain free-radical acceptor-type inhibitors. Assume that of two antioxidants AH and BH, BH is the least effective and has the smaller bond dissociation energy. If the radical ROO· from the autoxidizing substrate reacts slowly with BH because of a low steric factor, then



Such a mechanism explains the synergistic activity of ascorbic acid (BH) with a phenolic antioxidant (AH), whereby the stronger inhibitor is regenerated from weaker by the transfer of hydrogen. Thus this combination of inhibitors is a more effective antioxidant than the sum of the individual components.

The most generally effective synergistic mixtures of antioxidants are those where one component functions as a decomposer of peroxides and the other as a free-radical inhibitor. Since hydroperoxides are a source of initiating radicals, Eqs. (13) through (16), their destruction to nonradical products decreases the rate of chain initiation. The free-radical inhibitor decreases the rate of formation of hydroperoxide, Eq. (11), thus conserving the peroxide destroyer. Since some hydroperoxide is formed, its destruction by the peroxide decomposer before it can decompose into free radicals increases the effectiveness of the free-radical inhibitor. The effectiveness of many synergistic combinations can be explained by this mechanism. Examples of such combinations include alkyl phenols or aromatic amines with peroxide destroyers of sulfur or phosphorus types (376, 454). Synergistic effects between natural sulfur compounds and aromatics in lubricating oils have been attributed to oxidation of sulfur compounds to sulfonic acids, which are peroxide destroyers, and to the rearrangement of aromatic hydroperoxides to phenolic inhibitors, which are free-radical acceptors.

Ingold (398, 399) studied combinations of inhibitors that are generally classed as free-radical acceptors, e.g., phenols and aromatic amines. He observed that the combinations exhibited additive, antagonistic, and synergistic effects, depending upon the inhibitors chosen and the substrate. His results indicate that synergism is due to one inhibitor functioning as a peroxide destroyer rather than by regeneration of the stronger free-radical acceptor by hydrogen transfer. Among the free-radical acceptor type inhibitors acting as peroxide destroyers are 2,6-ditertbutyl-4-methylphenol, 2,2'-methylene-bis(6 tertbutyl)-4-methylphenol, phenyl- α -naphthylamine, and diphenyl amine. The peroxide-destroying activity of these compounds was not equivalent. Antagonism was generally attributed to crosscombination reactions, although the formation of association complexes with low reactivities for peroxy radicals probably is a factor for mixtures of strong acid phenols and basic amines. Additivity of two active inhibitors suggests that both are probably active in only a single inhibiting reaction. The high efficiency of many antioxidants containing two or more functional groups, e.g., OH and NH, OH and S, NH and S, etc., may be explained by different inhibiting reactions at each group.

Recently (239) a new combination of synergistic antioxidants was reported. Alkali metal salts of phenols and carboxylic acids were synergists for aryl amines in synthetic ester liquids at temperatures of 347° to 500°F. Group II metal salts were inactive, and iron and vanadium salts catalyzed oxidation of the ester substrate. To obtain better solubility of the alkali metal salts, EDTA was neutralized with 3 moles of a branched primary alkylamine and 1 mole of KOH. The efficiency of this synergist in combination with aryl amines was confirmed by laboratory oxidation tests and service-simulating bearing tests. However, when the inhibited composition was tested in a jet engine, it showed such large increases in viscosity and acidity that the 100-hour test was terminated after 20 hours. Subsequent investigation indicated that the loss in efficiency of the inhibiting combination in the engine test was due to reduced air flow as compared to laboratory oxidation and bearing rig tests. No mechanism for the inhibiting action was proposed for the combination at high air flow. It is probable that the efficiency of this synergistic combination is also due to different inhibiting reactions of the two components. Presumably, the amine is the free-radical acceptor. It has been suggested that ROOK forms a complex with RH that rearranges to oxygenated products without the formation of free radicals; thus the potassium salt acts as a peroxide decomposer. The inefficiency of this combination

at low air flows could be due to the presence of a free radical or its precursor that is swept from the system at high air flows.

8. FLAMMABILITY

Fire-resistant fluids and lubricants are desired for many military and industrial applications where there is danger of fires resulting from the ignition of the working fluids. Measurement of fire resistance is complex, since there is no single test able to evaluate this property. Furthermore, the relative ratings of liquids in a particular test can be changed by varying the experimental conditions, e.g., temperature or type of ignition source. As the number, variety, and intensity of the ignition sources may vary from application to application, a great number of flammability tests have been devised to rate fire resistance. The parameters in a given type test may vary greatly, since the experimental conditions are designed to duplicate the hazards of the application under consideration. A further complication is that fluids show different degrees of fire resistance to different ignition hazards. Because of the multiplicity of test procedures and parameters, Section VI of Technical Committee N of ASTM D-2 is trying to standardize on tests used to rate fire resistance.

Hatton (378) has reviewed the tests devised to rate flammabilities to different hazards and discusses the effect of some test variables on the ratings. These tests fall into the following categories:

1. Temperature for ignition by an open flame or spark (Flash and Fire Point type tests).
2. Temperature for ignition by hot surfaces (Autogenous or Spontaneous Ignition Tests; Molten Metal; Hot Manifold; etc.).
3. Ignition of oil mists or sprays. (Covers a great variety of tests where pressure and ignition sources vary.)
4. Ignition by adiabatic heating (compression-ignition type tests).
5. Incendiary gunfire test (designed to simulate ignition hazard when incendiary bullets pierce an aircraft hydraulic line or system).

Ignition may be the result of the flammability of the undecomposed fluid vapor or pyrolytic decomposition products. As would be expected, the fire resistance of liquids varies greatly from highly flammable at room temperature to those that are fire resistant at high temperatures. The degree of fire resistance required is governed by the hazards and environments for different applications.

Three types of fire-resistant fluids have been commercially available for about ten years: glycol-water, water-in-oil emulsions, and phosphate esters (361, 378, 795). Although these fluids are used industrially, their military application is limited because of deficiencies in one or more properties, not necessarily fire resistance. Since operating temperatures of military equipment continue to rise, there is an increasing need for fire-resistant hydraulic fluids and lubricants, particularly the former. Additional requirements for high-temperature operation are low vapor pressures and good hydrolytic, thermal, and oxidation stabilities. Where operation over an extended temperature range is required, low pour (or freezing) points and high V.I.'s are also necessary. As some of the structural requirements for optimizing one property are mutually incompatible for the optimum in another property, compromises are necessary to obtain a fluid with the best combination of properties.

A basic research program was undertaken by the Monsanto Research Corporation under a contract with the Aeronautical Systems Division (371) to correlate structure with flammability, thermal stability and viscosity. Fire-resistant fluids useful over two temperature ranges were to be considered.

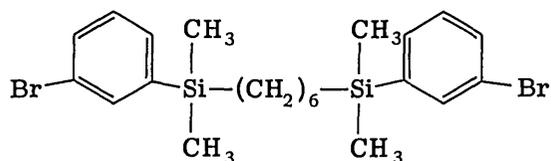
1. Operable from -65° to 450°F
2. Operable from $+40^{\circ}$ to 700°F .

Type 1 fluids were to have an autogenous ignition temperature (AIT) $> 900^{\circ}\text{F}$ and a viscosity at $-65^{\circ}\text{F} < 2500$ cS. Type 2 fluids were to have AIT $> 1000^{\circ}\text{F}$ and a viscosity at $+40 < 2500$ cS. Generalizations as to the effect of structure on properties were developed. Some of the important conclusions reached in that investigation are repeated here.

For the Type 1 fluids it was found that mono-halogen substitution in aliphatic hydrocarbons increased fire resistance, but such compounds did not possess adequate thermal stability. Compounds containing trifluoromethyl and possibly trihalomethyl or perfluoroalkyl groups may possess the desired thermal stability. However, the perfluoroalkyl groups have an adverse effect on the temperature coefficient of viscosity. Fluoroalkyl phosphates, silicates, and possibly alkylcarbonyl-dialkyl phosphenates containing some halogen may have the requisite stability. The hydrolytic stability of such compounds is suspect. Aliphatic phosphates, phosphonates, phosphenates, and phosphites are eliminated because of thermal instability. Metalloorganic compounds of elements in Groups IIIA, IVA, IVB, and VA with the exception of phosphorus and silicon (and possibly beryllium and boron) do not have the requisite properties. Phosphine oxides, although having good thermal stabilities, are not outstanding in flammability resistance and have poor viscometric properties. Aliphatic sulfides, sulfoxides and sulfones have low thermal stabilities.

Type 2 fluids will probably be derived from aromatics, heterocyclics, fluoroaromatics, or possibly halogen-containing aromatics or heterocyclics, or combinations of the two. A promising candidate for Type 2 fluid (not considered in the investigation) is the perfluorinated liquid (267, 360) reviewed here in the section on Synthetic Lubricants. Some interesting heterocyclics are also discussed in this section.

The more promising fluid types for application from -65° to 450°F and from -40° to 550°F were investigated further (102, 105). These included phosphorus esters, partially fluorinated aliphatics, halogenated α,ω -diphenyl-alkanes, halogenated α,ω -bis(aryldimethylsilyl) alkanes, and fluoroaromatic ethers. Although the phosphate esters approached the temperature stability and flammability requirement, they were not hydrolytically stable at 400°F . Fluorinated alkyl silicates appeared to require about 65 wt percent fluorine to obtain the desired flammability resistance. Although $(\text{C}_7\text{F}_{15}\text{C}_3\text{H}_6\text{O})_4\text{Si}$ had a high freezing point, it seemed probable that it could be readily depressed by using a mixture of fluoroalkyl groups. No information was given as to hydrolytic stability of these compounds. Halogenated α,ω -diphenylalkanes were promising candidate compounds. The introduction of halogens on the ring improved flammability resistance, as indicated by increases in flash, fire, and AIT points. The introduction of one bromine atom was approximately equivalent to two chlorine atoms. However, it is suspected that the bromo compounds will be more susceptible to hydrolysis. Halogenated α,ω -bis(aryldimethylsilyl) alkanes were exemplified by



and the chlorine-substituted analog. These compounds have low volatilities, good thermal stabilities, and an appreciable fire resistance. This class was considered worthy of

continued investigation. Partially fluorinated polyphenyl ethers, although having good thermal stabilities, had freezing or pour points which were too high to be of interest for low-temperature applications.

The Bureau of Ships, U.S. Navy, requires a fire-resistant hydraulic oil for submarine use. In addition to fire resistance, stability, lubricity, and viscosity, it should be compatible with paints, elastomers, insulation, gaskets, seals, and electric insulation. Research by Monsanto during the first year of the contract (101) showed that the introduction of fluorine into phosphorus-containing molecules reduced their destructive action on paints and elastomers. Fluorinated alkylaryl phosphates and phosphonates fulfilled the requirements for fluid properties, fire resistance, and paint and elastomer compatibility. Further research (103) showed that compounds containing sufficient fluorine for paint and elastomer compatibility did not have adequate hydrolytic stability. The introduction of phosphoramido linkage,



improved hydrolytic stability while retaining comparable fire resistance.

9. DETERGENTS

Detergents in Crankcase Oils

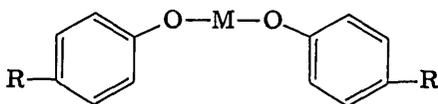
One of the desirable functions of a crankcase oil is to keep the engine clean and free from deposits and varnishes that may stick piston rings, foul oil lines, decrease heat transfer from hot parts to the oil, etc. Internal-combustion engines have increased in power, efficiency, operating temperatures, and operating life. Increased operating life requires increased fuel consumption, with the attendant increase in the amount of combustion byproducts reaching the crankcase. These increased stresses may accelerate the formation of oil-insoluble products.

The relative importance of the factors contributing to deposit formation differ with the engine type and the kind of service. Deposit formation in diesel engines results primarily from: (a) oxidation of the lubricating oil; (b) blow-by of oxidized fuel; and (c) attack of the lubricant by sulfuric acid (711). Under high-temperature operating conditions, deposit formation in gasoline engines follows the same pattern as in diesel engines. Since modern gasolines are low in sulfur, sulfuric acid makes a minor contribution to deposit formation in automotive engines. In low-temperature automotive engine operation, e.g., winter stop-and-go driving, a different mechanism of varnish and sludge formation is operable. The polymerization of blow-by fuel oxidation products that accumulate in the crankcase is a major source of deposits. Such deposits increase as the jacket temperature is lowered below ca. 160°F. The appreciable nitrogen content of engine deposits suggested that a reaction of hydrocarbon or hydrocarbon decomposition products with nitrogen oxides play an important role in deposit formation (711). Under operating conditions favoring the production of nitric oxide, increased engine fouling was observed, particularly when cracked gasolines were used as the fuel. Complex diolefins, heavy aromatics, and certain naphthenes in gasolines are especially harmful as regards deposit formation. To alleviate the difficulties caused by the buildup of deposits in internal-combustion engines, additives that disperse and/or suspend the insoluble products and their precursors in the oil are used. Such additives, commonly known as detergents, constitute the largest volume of any single type of additive used in lubricating oils (16, 17, 733).

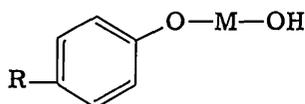
A large number of compounds have been claimed as detergents, most of the early ones being metal salts of organic compounds (16, 416). Apparent oil solubility is attained by having a sufficiently large and complex hydrocarbon group in the molecule. The previous review (795) established that the solubility of these metal salts is due to micelle formation. Critical concentration for micelle formation may be as small as 10^{-6} molar for some systems. Micelles are composed of a number of molecules in which the hydrocarbon portions of the molecules surround a central polar core. The number of individual molecules in a micelle may vary from a few to thousands. In hydrocarbon solvents most micelles contain from 10 to 40 molecules, depending upon the solvent, the cation, the anion, and the presence of polar compounds in the system. The micelle may be spherical or may have various ellipsoidal shapes. In certain cases linear micelles are formed.

Metal Salt Dispersants-Detergents

Stewart and Stuart (711) have reviewed detergent additives. They reported that the most widely used metal-salt detergents are calcium and barium phenates, the same sulfonates and salts of acids of phosphorus. In addition to salts of alkyl phenols, those of alkyl phenol sulfides are used. The introduction of sulfur into alkyl phenols lowers the corrosivity of the compounded oil toward bearing metals. Methylene bridging in the additive is reported to improve its oxidation stability and lower bearing corrosion. Methods of producing the various phenates are also reported (711). So-called basic phenates are produced by using an excess of the metal oxide or hydroxide over that required for the normal phenate. Structures of these phenates are postulated as:



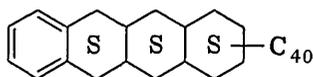
Normal Phenate



Basic Phenate

Basic alkaline earth phenates have been reported containing two or three times the stoichiometric amount of metal in a normal phenate. The existence of a basic phenate containing two equivalents of metal has been postulated. It is more probable that the excess metal oxide or hydroxide is contained within the polar core of the phenate micelle. These so-called basic phenates have an advantage over the normal phenates in that they possess greater neutralizing power per unit weight.

Calcium and barium sulfonates are the most widely used of the detergent additives. They are derived from oil-soluble mahogany sulfonic acids, a byproduct from the refining of oils, and also from the sulfonation of alkylbenzenes and naphthalenes. Sulfonic acids should have molecular weights of 400 or higher if the calcium or barium salts are to have the requisite oil solubility. Recently a petroleum sulfonic acid was described (52) with an average molecular weight of ca. 900; this is about twice the molecular weight of the conventional acids used to prepare detergents. The schematic structure of the unsulfonated oil was given as:



Sulfonates derived from this oil differed from conventional mahogany sulfonic acids in that several naphthalene rings were present. Alkaline-earth sulfonates prepared from these fractions were reported to be effective detergents for both heavy-duty diesel oils and for automotive crankcase oils in stop-and-go service. Like the phenates, sulfonates can be prepared with more than the stoichiometric amount of metal oxide or hydroxide (711). It is probable that the excess oxide or hydroxide is held by micelles of the normal

sulfonates. Stable suspensions of calcium carbonate in calcium sulfonates can also be prepared. Phenols and alkyl phenols are employed to promote incorporation of basic compounds in sulfonate additives.

Commercially important detergents based on phosphorus are the calcium alkyl phosphates and the potassium and barium salts of olefin-phosphorus pentasulfide reaction products (711). A variety of other phosphorus-base detergents, including thiophosphates, phosphinates, and phosphonates, have been patented. Oil-soluble calcium alkyl phosphates are good detergents. Metal salts of the reaction product of polybutenes and other olefins, with phosphorus pentasulfide, are used as detergents. Little information is available about the structure of olefin-phosphorus pentasulfide reaction products (711).

Ashless Detergents

Ashless detergents are an important recent development. There are two classes of ashless detergents: the low-molecular-weight type and the dual-purpose polymeric type for both V.I. improvement and detergency. Ashless detergents are more effective than metal salts in controlling sludge and varnish deposits in automotive equipment operating at low-temperature stop-and-go service. Another advantage is that they leave no ash on decomposition as do metal-salt detergents. Thus, there is no increase in the octane requirement for the engine. A variety of low-molecular-weight ashless detergents are listed by Stewart and Stuart (711). Many of these additives contain basic nitrogen groups. Additives recommended for stop-and-go automotive service include acylated polyamines, esters of sugar, polyesters containing amino groups, polyglycol carbonates and carbamates, guanidine sulfonates, hydrazine and hydrazinium phenates, and urethanes. Those for diesel and high-temperature automotive operation include acylated polyamines, alkylamines, pentaerythritol esters, polyesters containing amino groups, and guanidine sulfonates.

The introduction of polar groups into polymeric viscosity index improvers was first described by Biswell et al. (100), although some patents had been issued earlier. The polar groups described by these authors were basic nitrogen types and included diethylaminomethyl, diethylaminoethyl, octylaminoethyl, dimethylaminoethyl, dimethylaminocyclohexyl, dibutylamino, and 4-vinylpyridine. The oil-solubilizing or oleophilic groups include alkylacrylates and methacrylates, polymerizable polycarboxylic acids, vinyl esters of carboxylic acids, vinyl ethers, or vinyl-substituted aromatic compounds. A variety of other copolymers of an oil-solubilizing monomer and a polar monomer have been described in the patent literature (711). The oleophilic groups are of the types used in simple V.I. improvers, and the polar groups are amide, amine, nitrile, hydroxyl, pyrrolidone, polyglycol, free carboxylic acids, and anhydrides. Stewart et al. (712) concluded that amino, amido, hydroxy, and carboxy groups imparted the same order of detergency, whereas polyethylene glycol substituents gave markedly increased levels of detergency.

Detergents Mechanisms

It is now well established that metal salts exist as micelles in hydrocarbons (711, 795). Singleterry (68, 684) in his review on nonaqueous micelles reported that most such micelles in hydrocarbon solutions contained from 10 to 40 molecules. Fowkes et al. (316) showed that copolymers of α -olefins and vinylacetate or acrylonitrile formed aggregates containing ten or more molecules. Bowden and Dimitroff (135) concluded from electron microscopy studies that polymeric ashless detergents formed aggregates in hydrocarbon media similar to the micelles of metal organic dispersants. Metal organic micelles in hydrocarbon media have a polar inner core surrounded by the hydrocarbon outer layer. Bernelin (87) concluded from studies with a Hittorf type cell that such micelles were ionic colloids. Furthermore, he found that in the case of the basic calcium sulfonates

there was no change in the calcium concentration during transport to the electrodes; therefore, the basic portion must be incorporated within the micelle.

In the previous review (795) the ability of soap micelles in nonaqueous solutions to sequester or "solubilize" otherwise insoluble materials such as water, acids, alcohols, etc., was reported. Such polar materials are adsorbed within the polar core of the micelle. This mechanism is often used to explain the ability of metal soap detergents to keep an engine clean and free of deposits (68). More recently it has been suggested that in the latter stages of such solubilization, hydrogen bonding plays an important part (68). Infrared spectroscopic evidence of hydrogen bonding in such systems was presented by Kaufman (418). Polymeric ashless methacrylate dispersants were shown by infrared studies to form hydrogen bonds with polar solid silica (307). Stewart et al. (712) postulated that hydrogen bonding was the dominant mechanism in the action of polymeric ashless detergents.

Gallopoulos (325), using differential infrared spectrometry, showed that both a low-molecular-weight ashless dispersant (polyaminomonoalkenylsuccinimide) and one of a high molecular weight (polyalkylmethacrylate and N-vinyl-2-pyrrolidone) formed hydrogen bonds with alcohols. The bonds were formed between the hydroxylic hydrogen of the alcohol and the oxygen and nitrogen atoms of the dispersant. He concluded that hydrogen bonding was only one of the processes by which dispersants contributed to engine cleanliness. Electrodeposition studies with carbon blacks in hydrocarbon solutions of organic dispersants were used by Fowkes et al. (315) to demonstrate that the electric charges on these solids resulted from hydrogen ion transfer between the solid surfaces and dissolved dispersant. Carbon blacks rendered acidic became negatively charged in the presence of basic dispersants (polymethacrylates with basic comonomers). Carbon blacks with basic surfaces become positively charged by polymeric dispersants having carboxylic acid groups. Little charge transfer resulted with basic solids and basic dispersants or with acid solids and acid dispersants. They concluded that the better dispersants were micellar substances or oil-soluble polymers having the ability to accept or donate hydrogen ions.

Detergent-type additives used in crankcase oils function to keep the engine clean by several mechanisms (415, 711):

1. By neutralizing and/or sequestering acidic oxidation products derived from oil oxidation and partially burned fuel, thus preventing reactions that would form insoluble deposits.
2. By acting as a basic material that neutralizes sulfuric acid formed by the combustion of sulfur containing fuels. This prevents the reaction of sulfuric acid with the oil to form deposits.
3. By dispersing both insolubles and deposit-forming substances.
4. By acting as true detergents that remove previously formed deposits.

It is now generally agreed that these crankcase-oil additives function primarily as dispersants, not solubilizers.

There is some question as to the exact mechanisms by which detergents function. As mentioned earlier, basic phenates and sulfonates are capable of neutralizing greater quantities of acidic materials per unit weight of additive. Furthermore, the condensation of hydroxy acids and certain other deposit-forming precursors is inhibited when the oil has an alkaline reserve (119, 400). The sequestering of oxygenated oil or fuel residues within the polar core of the detergent micelle also prevents deposit formation. It has not been resolved whether the principal mechanism is the isolation of one reactant from the

other, thus preventing condensation or polymerization to insoluble products, or whether insoluble reaction products are formed within the micelle but are kept in suspension after formation. As the nature and type of deposits formed in a given engine can vary with the operating conditions and with the fuel used, the mechanisms by which detergent additives function may be numerous and complex. However, progress is being made on determining the types of deposits formed under specific operating conditions and on determining the source and nature of their precursors.

IV. SYNTHETIC LUBRICANTS

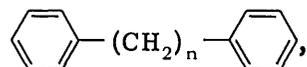
Synthetic oils now have a well-established place in lubrication technology. Each type of synthetic may offer advantages and disadvantages in properties and characteristics when compared with the others or with petroleum oils. Unless the synthetic oil has some outstanding property, or combination of properties, that will improve performance, decrease maintenance costs, or alleviate some hazard, its adoption is not probable, because synthetic oils are inherently more expensive than conventional petroleum oils. There are large variations in the unit prices of different synthetic oils, depending not only on the cost of the starting materials and processing but also on the volume produced.

Since the NRL review of 1959 (795), a comprehensive treatise on synthetic lubricants has been published (361). The latter volume contains chapters on each of the well-established synthetic oils (phosphate esters, dibasic acid esters, chlorofluorocarbon polymers, silicones, polyglycols, silicate esters, fluoroesters, neopentyl polyol esters, and polyphenyl ethers). There are also well-documented sections on preparation, physical properties, performance properties and uses of these oils. The newer or rare types, whose utility as lubricants has not been established, are covered in another chapter of Ref. 361.

Another volume, published in the same year (378), reviewed many of these synthetic oils, with emphasis on their properties and characteristics of interest for hydraulic applications. In many ways these two volumes (361, 378) supplement and complement each other. As the well-established synthetic oils are comprehensively covered by Refs. 361 and 378 up to 1961, we shall cover here the more recent advances made and the new types introduced since then.

1. DIARYLALKANES

A variety of diarylalkanes were synthesized and studied in a program to develop hydraulic oils having not only a wide liquidus range but also good stability to oxidation, pyrolysis, and radiation (768). A series of α, ω -diarylalkanes was prepared having the general structure



where n varies from 1 to 10. These fluids ranged in viscosity at 210°F from 0.97 to 2.57 cS. Viscosity indexes dropped from 116 for diphenylmethane to a minimum of 46 for diphenylbutane and then rose gradually to a maximum of 128 for diphenyldecane, the compound with the longest alkane chain examined. All of these fluids had such high freezing or pour points as to exclude their use at low temperatures. Branching of the paraffin chain between the phenyl groups resulted in pronounced improvements in low-temperature properties, but with a sacrifice in the V.I. Alkyl groups symmetrically substituted on both phenyl groups were effective in lowering the freezing points, but again there was an accompanying decrease in V.I. The best combination of properties resulted when only

one phenyl group was alkylated; thus isopropyl- and butyl-1,9-diphenylnonanes exhibited the most desirable properties. Both compounds were liquid to below -65°F and had V.I.'s above 135. The isopropyl- and butyl-substituted derivatives had viscosities of 3.46 and 3.81 centistokes at 210°F , respectively.

None of the inhibited diarylalkanes were stable to oxidation at 500°F for 48 hours; however, it appeared that they can be stabilized at 350°F . Isopropyl-1,9-diphenylnonane, a typical member of this family, exhibited a 16-percent decrease in the 100°F viscosity after six hours at 700°F , showing that it is more stable to pyrolysis than conventional dibasic acid esters and is comparable in stability to naphthenic hydrocarbons. Its stability to radiation was superior to that of polyorgano siloxanes, polyglycols, naphthenic hydrocarbons, silicate esters, dibasic acid esters, and petroleum fractions, but it was inferior to aromatic hydrocarbons and polyphenyl ethers. Lubricity tests show that these fluids are comparable to petroleum oils and that they could be improved by common additives. There has been no production of this type of oil.

2. POLYNUCLEAR ALKYL-POLYPHENYL HYDROCARBONS

Polynuclear aromatics such as biphenyl, the terphenyls, and the quaterphenyls are resistant to oxidation and thermal radiation, but their high melting points preclude their use as liquid lubricants. Biphenyl is also so volatile that it could not be used at high temperatures. Melting points of the terphenyls vary from 133°F for the orthoisomer to 415°F for the paraisomer. Quaterphenyls melt from 187°F to 604°F , the paraisomer being the higher melting. In an effort to increase the liquid range of these thermally stable and radiation resistant synthetics, the effect of alkyl substituents was investigated (668). A substantial reduction in freezing points could be obtained by alkylation, the greatest depression being obtained by substituting a straight chain undecyl group in the 3 position on orthoterphenyl. The resulting compound had a pour point of -20°F . Introduction of long alkyl chains also improved the lubricity as determined in the Shell Four-Ball Wear Tester. This improvement in liquid range and lubricity by alkylation was accompanied, however, by a decrease in thermal and radiation resistance. The best compromise in properties was obtained by alkylation with heptyl groups. Such compounds have a liquid range of -20° to 800°F , are thermally stable to 700°F , and are resistant for long periods of time to high-intensity gamma radiation. These alkylated terphenyls are somewhat inferior to the higher polyphenyl ethers in overall properties, especially as regards nonvolatility and viscosity-temperature properties. There has been no commercial production of the higher alkylated terphenyls.

3. SILICATE ESTERS

The physical properties of silicate esters, with emphasis on viscosity-temperature properties of a number of alkoxysilanes, disiloxanes, and trisiloxanes not reported in Ref. (361), were given by Abbott et al. (1). In addition to alkoxy silanes and siloxanes, physical properties of silicate derivatives of aliphatic and aromatic diols were also reported. Some miscellaneous silicate derivatives containing nitrogen, phosphorus, and halogens were included in this work.

Silicate esters, in particular the n-alkyl derivatives, have good viscosity-temperature characteristics, which, as the siloxy chain is increased, tend to approach those of silicoes of comparable viscosities. Hydrolytic stability of alkoxy silanes and siloxanes vary, depending upon the shielding of the Si-O bonds by nearby alkyl groups. Straight-chain alkyl silicates are more readily hydrolyzed than those containing highly branched structures, e.g., tert. alkoxy groups. Thus the requirements of optimum hydrolytic stability and high V.I. are mutually incompatible. No information on oxidation, thermal or radiation stability has been reported.

4. NEOPENTYL POLYOL ESTERS

Polyol esters are assuming an increasingly important role as synthetic lubricants (231, 265, 535). Esters derived from polyols having a neopentyl structure, such as trimethylolpropane, trimethylolpropane and pentaerythritol, contain no hydrogen on the beta carbon and are thus more thermally stable than conventional monohydric alcohol esters of dibasic acids (231). Bohner et al. (109) described the properties of a number of symmetrical and mixed esters of trimethylolpropane (TMP), pentaerythritol, di- and tri-pentaerythritol (PE, DPE and TPE). In general the freezing points of the symmetrical PE, DPE, and TPE esters reported in Ref. 109 had lower freezing points or pour points than are reported elsewhere in the literature (147, 231). Unpublished data from NRL further confirm the high freezing points of the symmetrical esters of straight-chain acids. Esters of branched-chain acids have lower freezing points but less desirable viscosity-temperature properties (109, 231). A number of esters prepared by esterifying the polyol with mixed acids were also characterized (109). Neglecting steric factors, such ester mixtures would contain a statistical distribution of the possible configurations. Thus the number of different esters in these mixtures would increase with the functionality of the polyol and the variety of acids used. Viscosity characteristics of a mixed ester approximate that of the average composition. For example, PE esterified with an acid mixture containing equivalent molar quantities of butyric, hexanoic, octanoic, and decanoic acids would have viscometric properties comparable to that of PE tetraheptanoate. Because of the great variety of esters in such a mixture, its freezing point would be lower than that of a mixture of the four symmetrical tetraesters. Polyol esters prepared from acids containing an odd number of carbon atoms have lower freezing points than those derived from acids with an even number of carbon atoms (231). Therefore, mixtures of odd-membered acids are preferred for preparing polyesters with low freezing points.

As these polyols increase in functionality from 3 to 4 to 6 to 8 on going from TMP to PE to DPE to TPE, there would be an increase in the molecular weight of esters from a given acid for the series. Viscosities would also increase on ascending the series (109, 231), as shown in Table 7. It is possible to obtain polyol esters, derived from commercially available acids having viscosities up to several hundred centistokes, at 100°F. Such viscous esters cannot be obtained from commercially available dibasic acids and monohydric alcohols. A much wider viscosity spectrum of oils can therefore be obtained with the polyol esters. Intermediate viscosity grades can also be attained by blending esters or by esterification with mixed acids.

Table 7
Effect of Functionality on Properties of Some Polyol Esters

Compound	Functionality	Mol. Wt.	Viscosity (cS)	
			210°F	100°F
TMP tricaproate	3	429	2.99	12.36
PE tetracaproate	4	529	4.18	19.97
DPE hexacaproate	6	843	8.76	solid
TPE octacaproate	8	1157	13.9	107.0

Boiling points are a function of molecular weight, the esters of higher molecular weight boiling at higher temperatures. Critchley and Miles (231) show that there was a dramatic decrease in weight losses through evaporation at 400°F on going from TMP trihexanoate to the triheptanoate, but the evaporation-loss increments between consecutive pairs becomes increasingly smaller as the molecular weights increased. Esters of branched-chain acids have lower boiling points and greater volatilities than do the straight-chain isomers; the more volatile esters also have the lower flash points.

In general, the hydrolytic stabilities of the polyol esters are of the same order as those of diesters derived from dibasic acids. Hydrolytic stabilities vary with structure of the acid moiety, depending primarily upon the shielding of the ester linkage. Esters of long, straight-chain acids are more hydrolytically stable than the short-chain analogs. Branching near the ester linkage is an effective method of producing hydrolytically stable polyol esters.

Like petroleum oils and many other synthetic oils, the polyol esters require anti-oxidants to raise their resistance to oxidative deterioration to a level suitable for high-temperature applications. These esters are responsive to known antioxidants and anti-oxidant combinations. When suitably inhibited they are capable of satisfactory operation at temperatures of 400°F, which is somewhat higher than the maximum operating temperatures of dibasic acid esters.

If the incipient seizure load is used as a criterion, the load-carrying ability of the TMP, PE, and DPE esters appears to be primarily a function of viscosity (231). However, in each of the parent polyol series there appears to be a reduction in load-carrying ability with increasing acid chain length which reaches a minimum at C₇; it then rises with increasing acid chain length. When wear scar diameters were used as the criterion, an analogous minimum was also noted (231). The lubricating ability of the polyol esters is equal or possibly slightly superior to that of dibasic acid esters of comparable viscosity. Any deterioration that produced the straight-chain acid from which the ester was derived, or the presence of such as an impurity, would tend to reduce the coefficient of friction and improve the wear properties.

A variety of viscosity grades of TMP, PE, and DPE esters are commercially available from several sources. The most important present lubricant application is as an aircraft jet-engine lubricant (535).

5. OLEFIN POLYMER OILS

The possibilities of preparing lubricating fractions by the polymerization of olefins has attracted many investigators over the years, and research has continued in this area. Liquid pyrolysis products of paraffin wax consist largely of homologous linear α -olefins. The ratio of the various olefins is influenced by temperature, catalyst, and contact times. Polymerization of olefins to oily products may be obtained by heat and various catalysts. Polymerization products prepared with new catalyst systems have been described recently (32, 82, 97). Beck et al. (82) studied the glass transition temperatures of polymers of α -olefins varying from C₄ to C₂₀ using a tetrachloride and aluminum triisobutyl catalyst system. Glass transition temperatures which were at a minimum for polymers produced from octene-1 were attributed to a change in mode of crystallization from main-chain to side-chain crystallization. Biritz (97) compared the properties of olefin polymers prepared via a trimethyl-tin chloride-aluminum chloride complex with those via aluminum chloride. Although the degree of polymerization decreased with increasing chain length of the olefin polymer, the average molecular weight of product was independent of olefin chain length when the complex catalyst was used. The viscosities of the olefin polymers decreased with increasing olefin chain length, but the V.I. increased. Polymeric olefins produced with the aluminum chloride catalyst did not have as low pour points as those produced via the complex catalysts. The C₄, C₆, C₈, and C₁₀ polymers had pour points of -60° to -70°F, whereas those from olefins having either shorter or longer chains were higher.

Antonsen et al. (32) studied octene-1 polymers produced with coordination complex catalysts with and without the presence of propylene oxide. They also compared the products with those obtained using aluminum chloride and concluded that the complex catalyst produced superior products. Dimer-free polymers could be obtained ranging in

viscosity from 5 to 60 centistokes at 210°F and with V.I.'s approaching 140. Viscometric properties of the trimer, tetramer and pentamer were 2.45, 4.46, and 6.62 centistokes, respectively, at 210°F, and the V.I. increased from 100 for the trimer to 128 for the pentamer.

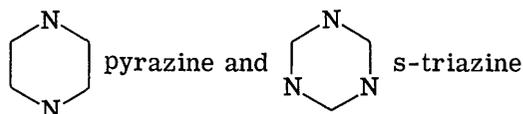
Properties of α -olefin oligimers and lubricant compositions based on these oligimers have been reported (266). Hydrogenated polyolefins derived from octene-1 and the C₆-C₁₀ α -olefin mixtures have good low-temperature properties. Pour points of fractions having viscosities below 8 centistokes at 210°F are less than -65°F. ASTM (D567) V.I.'s are around 125. Viscosity versus temperature graphs of polyolefin oligimers on ASTM Viscosity-Temperature charts hook downward at low temperatures quite like those of the super-refined petroleum oils; thus their low-temperature fluidities are better than would be predicted from their viscosities at 210° and 100°F.

Hydrogenated oligimers are quite responsive to antioxidants. Stable oxidation lives of the same magnitude as those of inhibited super-refined oils and diesters are obtained. Thermal stabilities of hydrogenated oligimers approach 600° to 650°F, which approximate those of super-refined petroleum oils.

Friction and wear properties of these oligimers are equivalent to those of petroleum oils. Viscosity-volatility characteristics are better than those of conventionally refined petroleum fractions but inferior to those of aliphatic diesters.

6. PYRAZINES AND TRIAZINES

Theoretical considerations suggest aromatic and heterocyclic nuclei as starting points for the synthesis of fluids stable to oxidation and pyrolysis at high temperatures. Two heterocyclic nuclei containing nitrogen have been considered:



or 1,3,5-triazine. Behun and Kan (83, 84) synthesized and investigated the fluidities and the thermal and oxidative stabilities of a number of substituted pyrazines. They concluded that for monosubstituted methyl pyrazines the alkyl group offered the best fluid properties, followed by alkoxy, dialkylamino, phenoxy, phenylmercapto, and anilino, in that order. Thermal stabilities approximately paralleled the order of increasing fluidity for these compounds. As expected, the aryl-substituted pyrazines exhibited the greatest resistance to oxidation. Straight-chain alkyl-substituted compounds were more readily oxidized. Branched-chain, alkyl derivatives were more stable than n-alkyl analogs.

The viscosities of the monosubstituted pyrazines were generally low; therefore, disubstituted derivatives were investigated. Such derivatives had viscosities in the range of 10 to 100 centistokes at 100°F, the majority having viscosities of about 20 centistokes at this temperature. Properties of these fluids varied with the type and position of substituents. Compounds containing aryl or aryloxy substituents were more resistant to oxidation but had high melting points and large temperature coefficients of viscosity. Alkyl derivatives had better viscometric properties but were less stable to oxidation. Compounds with both alkyl and aryl groups had intermediate properties. Perfluoroalkyl derivatives, although stable to oxidation at 500°F, had high melting points. Pyrazine derivatives were prepared in several viscosity ranges. In general, the more oxidation-stable fluids had high pour points, but compounds can be prepared that have pour points below 0°F and are stable to oxidation at temperatures approaching 500°F. There is no commercial production of pyrazine type oils.

Kober et al. (458) synthesized and studied a variety of substituted s-triazines and condensed s-triazine systems. Substituent groups included alkyl, benzyl, phenyl, and substituted phenyls. Although compounds with excellent thermal stability were prepared, their melting points were considerably above room temperature. No heat-stable liquids were obtained.

7. AROMATIC ESTERS

The Celanese Chemical Company under an Air Force contract (731) investigated carboxylic acid esters as potential high-temperature gas-turbine engine lubricants. Emphasis was placed on esters containing aromatic or highly branched alkyl groups such as neopentyl configurations. The investigators concluded that:

1. It is possible to synthesize esters of substituted phenoxyphenols and esters of neopentyl glycol with thermal stabilities up to at least 750°F, depending upon the structure of the substituent group. Alkyl substituents could be used when the group was tertiary to the aromatic nucleus.
2. Oxidative stabilities up to 500°F could be obtained from phenolic esters of neopentanoic acid, although these esters were generally very viscous liquids or solids. The oxidative stabilities of neoheptanoic acid esters were lower; and, depending on the phenol, these were stable up to 450° to 475°F. Esters of 2,2,4,4-tetramethylpentanoic acid were more stable than those of neoheptanoic acid, although the physical properties of esters of this acid were inferior.
3. It was possible to obtain a purely aliphatic ester of dibasic acids with thermal stabilities up to 750°F and, with inhibitors, oxidative stabilities up to 450°F and possibly above. This type of ester had viscosity properties superior to aromatic esters. Phenolic esters of dibasic acids were not thermally stable at 750°F and generally were solids at room temperature.
4. For the practical purposes of obtaining an operational fluid, the best choice appeared to be a phenoxyphenol esterified with a 2,2-dimethyl substituted acid, or a mono-ester of neopentyl glycol and a 2,2-dimethyl substituted acid crosslinked with a dibasic acid. [Di-(neopentylglycol mononeoheptanoate)azelate had a pour point of -40°F.]

These esters are not commercially available.

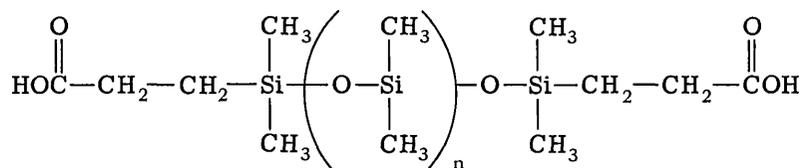
8. DICARBOXYLIC ACID ESTERS

In an investigation to develop diesters with improved thermal and hydrolytic stability, Durr et al. (269) synthesized esters from alkyl-substituted dibasic acids and branched-chain alcohols having no hydrogens on the β carbon atom. They showed that such diesters, as exemplified by bis(2,2-dimethylhexyl)2,2,8,8-tetraethylazelate, were stable to pyrolysis at 600°F and resistant to hydrolysis. The highly branched structure, however, resulted in fluids with temperature coefficients of viscosity larger than those derived from unsubstituted dibasic acids. No information was reported on the oxidation stabilities of these esters.

9. ORGANOSILICON FLUOROESTERS

Work at NRL showed that fluoroalcohol esters of dicarboxylic acids were superior to the perfluorocarbons in viscosity-temperature properties and had greater resistance to oxidation than aliphatic esters. Kerschner (426) in an effort to further improve the

properties of fluoroester derivatives as lubricants incorporated the siloxane structure into the molecule. Carbon functional siloxanes having the general structure shown below were the carboxylic acids used.



$n = 0$ to 6 .

Halogenated alcohols of two types were used: $\text{H}(\text{CF}_2\text{CF}_2)_m\text{CH}_2\text{OH}$ where m is 1 to 4, and $\text{Cl}(\text{CF}_2\text{CFCl})_p\text{CF}_2\text{CH}_2\text{OH}$ where $p = 2$ or 3 .

Diesters derived from siloxane carboxylic acids and fluoroalcohols had Hardiman and Nissan (H-N) V.I.'s of 50 to 180 (Ref. 374); there was an approximate linear relationship between H-N V.I. and the Si/F ratio of the diester. A number of these diesters had pour points of -65°F . Lubricating properties, as indicated by Shell Four-Ball Wear scars and seizure loads, indicated that these esters were equal or superior to alkyl diesters. Limited oxidation data, as determined by MIL-L-7808 test of 72 hours at 347°F , indicate adequate stability at this temperature. Additional information will be required at higher temperatures to ascertain their suitability for more severe applications.

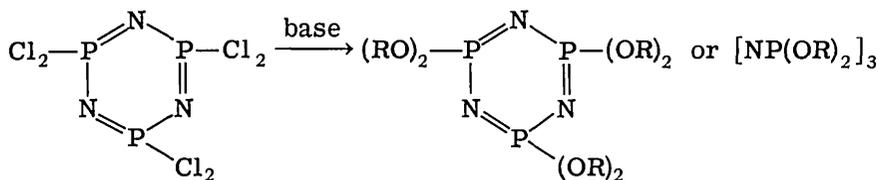
Diesters prepared from chlorofluoro alcohols and siloxane dicarboxylic acids were inferior to those of the fluoroalcohols as regards V.I., pour points, and wear scars, but they had higher load-carrying ability. Polyesters were also prepared from the siloxane dicarboxylic acids with alkyl and fluoro glycols, which were chain stoppered with monohydric alcohols with and without fluorosubstituents. Viscosities of the products ranged from 23 to 85 cS at 100°F and V.I.'s increased with increasing Si/F ratio. No oxidation data have been made available to date.

10. FLUOROCARBONATES

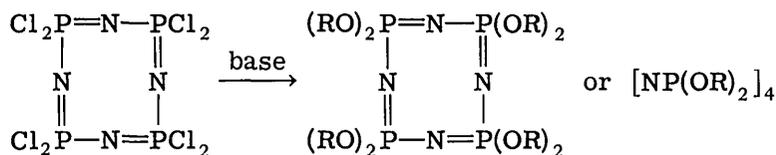
Under a Bureau of Ships contract, Hill et al. (382) investigated the properties of fluoroalkyl carbonates. Octafluoropentyl and dodecafluoroheptyl carbonates and ortho-carbonates were prepared and studied. The carbonates had the general formula $(\text{R}_f\text{O})_2\text{CO}$ and orthocarbonates $(\text{R}_f\text{O})_4\text{C}$. Densities of these compounds were 1.64 g/ml at 60°F for the octafluoropentyl carbonate and 1.81 for the dodecafluoroheptyl orthocarbonate. Flash points ranged from 350° to 450°F (tentative values) and viscosities from 7 to 66 cS at 100°F . V.I. values for all the fluorocarbonates were negative. Since these compounds are predominately fluoroalkyl in structure they should be resistant to oxidation. No data were given on their oxidation characteristics. The orthocarbonates appear to be more stable to hydrolysis than the carbonates. No information on other properties has been reported.

11. PHOSPHONITRILATES

Phosphonitrilates are of interest as lubricants because of their high thermal stabilities and the fire resistance of certain derivatives. Both the trimeric and tetrameric phosphonitrilate derivatives have been investigated (298, 456, 457). They are prepared by reacting the phosphonitrilic chloride with an alcohol or phenol.



Trimeric



Tetrameric

Completely phenoxy substituted derivatives were solids at room temperature (298). Therefore, Kober et al. (456, 457) investigated the fluoroalkoxy and mixed fluoroalkoxy-phenoxy derivatives in the hope of obtaining liquid products. The fluoroalkoxy substituent had the formula $-\text{OCH}_2(\text{CF}_2)_x$ where x varied from 2 to 8. Optimum physical properties of both the trimeric and tetrameric products were obtained with fluoroalkoxy groups where $x = 4$. Viscosities of the products varied from 100 to 250 cS at 100°F , the trimeric product having the lower viscosity. All the fluoroalkoxy derivatives had autogenous ignition temperatures around 1000°F .

Mixtures of fluoroalcohols when reacted with the phosphonitrilic chlorides yielded asymmetrical products which were lower melting than the symmetrical ones. Pour points of the liquid products ranged from -10 to -55°F and viscosities from ca. 100 to 450 cS at 100°F . Fluoroalkoxy substituents where $x = 10$ resulted in solid products. Densities were approximately 1.8 and the autogenous ignition temperatures were 1000°F or above, except for products containing a large proportion of short fluoalkoxy groups.

A series of mixed phenoxy-fluoroalkoxy derivatives were also prepared. In general, the partial substitution of phenoxy for fluoroalkoxy groups resulted in products with higher pour points, viscosities, ASTM slopes, and autogenous ignition temperatures. The viscosity range of these liquids was 120 to 250 cS at 100°F , the tetrameric phosphonitrilates being more viscous than the trimeric ones. In general, substituents on the phenoxy group increase the viscosity and pour points. Compounds were also prepared from the commercial mixture of trimeric and tetrameric phosphonitrilic chlorides (80 percent trimer), since the mixture was cheaper than the pure component. Properties of such products were as would be predicted from that of the pure components. When properly purified, the phosphonitrilates were stable to the hydrolysis test of Military Specification MIL-H-19457A.

Falex wear tests, in which the load was increased hourly by 100-pound increments to a total of 800 pounds, showed that these phosphonitrilates were superior to either tricresylphosphate or a commercial alkylene oxide oil as regards diameter decrease of the pin and takeup notches. The load was increased to failure for the tetrameric bis(1,1,7-tri 1-1-dodecafluoroheptyl)phosphonitrilate. The failure point was 3500 pounds as compared to 3100 pounds for tricresyl phosphate, and the decrease in diameter of the pin was almost three times as great when lubricated with the latter oil. Four-Ball Wear test data (258) at 10 and 40 kg loads with both M-10 and 52100 steel balls showed that the ball-wear scar diameters with phosphonitrilates were much smaller than when lubricated with m-bis(m-phenoxy-phenoxy)benzene.

Products reported to date were too viscous, and their densities were too great, for naval hydraulic application as covered by Military Specification MIL-H-19457A. Oxidation data are needed to evaluate these fluids for high-temperature applications.

12. PERFLUORINATED LIQUIDS

A synthetic liquid, identified as a polymeric perfluorinated fluid, has been produced and studied as a potential high-temperature lubricant by E. I. du Pont de Nemours and Company, Inc. (267, 360). This fluid can be produced in a variety of viscosity grades, but experimental data are confined primarily to fluids in the range of 25 to 35 cS at 100°F. In contrast to the negative V.I.'s of perfluorocarbons, these perfluorinated materials have V.I.'s above 100.

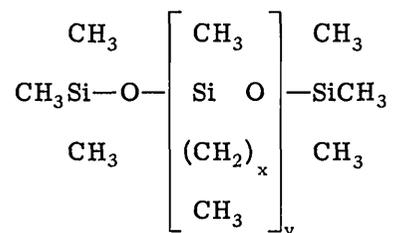
Since these liquids are perfluorinated they would be expected to have high densities. That of the fraction having a viscosity at 100°F of ca. 25 cS is 1.9, which may be so high as to be restrictive for certain applications. The surface tension of 17.8 dynes/cm at 20°C is also indicative of a high degree of fluorination. Data on these liquids indicate that they are fractions, or narrow cuts. ASTM D-972 evaporation weight losses after 6-1/2 hours at 500°F ranged from 1.4 to 4.5 weight percent for three fluids of 25 to 30 cS (at 100°F). The excellent thermal stabilities of these fluids is reflected by their low decomposition rates at 790°F, varying from 5 to 13 percent per day by the isoteniscope method.

Microoxidation tests on 20-ml samples in the presence of a variety of metals using both dry and moist air have been reported. An Inconel test tube was used instead of glass in most of the studies as the fluid reacted with glass. At 550°F, with an air flow of 20 l/hr and no condenser, viscosity change after 48 hours was +33 percent and fluid weight loss was 39 percent. Weight changes of the metal test specimens were all less than ±0.2 mg/cm²/day, except for QQ-S-636 steel, which was marginal. Increasing the test temperature to 600°F raised the viscosity change to +48 percent and fluid weight loss to 61 percent. At this temperature a number of alloy steels exhibited weight changes in the order of +1.5 mg/cm²/day. Certain stainless steels, however, showed only minimal changes in weight. When the test temperature was raised to 700°F, a number of the stainless steels showed excessive weight changes. Humid air at 650°F had a varied effect: nickel and cobalt alloys were unaffected, whereas the corrosion of steels (except certain stainless types) and copper was accelerated. The air flow was varied from 2 to 5 to 20 l/hr in tests at 650°F. In general, the corrosion rate of metals was increased when air flow was increased from 2 to 5 l/hr. At 20 l/hr the corrosion rate was less than at 5 l/hr, and in some instances less than for 2-l/hr air flow. Fluid weight losses were 5, 5, and 77 percent, respectively, for 2, 5, and 20 l/hr air flows, and viscosity changes were -12, +9, and +71 percent.

Although there are limitations on the materials of construction compatible with these fluids at oxidizing temperatures above 500°F, certain other materials are useful up to 700°F. Research is continuing on this type of synthetic oil.

13. METHYL ALKYL SILICONES

Recently polysiloxanes have been prepared containing linear alkyl radicals up to 40 carbons in length (150). These fluids have the general formula:



Fluids have been prepared as homopolymers containing one species of hydrocarbon in the repeating unit and as copolymers containing several different hydrocarbon species. Homopolymers with viscosities of 20 cS at 210°F were liquid at room temperature. In general, the pour point increased with increasing alkyl chain length. There was a progressive drop in temperature coefficients of viscosity as the length of the alkyl side chain was increased.

As expected, the specific gravity decreased with increasing alkyl chain length dropping from 0.96 for methylethyl siloxy groups to 0.89 for methyltetradecyl. The surface tension rose from 26 dynes/cm to 33.5 for the same series of compounds.

These long alkyl-substituted siloxanes differed markedly in lubricating ability from the dimethyl and methylphenyl analogs. Four Ball Wear tests showed that the wear-scar diameter, after tests at 167°F with 50-kg load, 600-rpm speed, and 52100 steel balls, dropped from 2 mm to a minimum of 0.5 mm when the alkyl group contained a chain of eight carbon atoms or more. The minimum wear-scar diameter at a 500°F test temperature also reached a minimum when the alkyl group had a chain length of eight carbon atoms, although the wear-scar diameters were greater at the higher temperature. The coefficient of friction followed a similar pattern. Wear-scar diameters at loads up to 40 to 50 kg were of the same magnitude as that of a SAE 30 lubricating oil. At such high loads as 100 kg, the methyltetradecyl siloxane was the better lubricant; the wear-scar diameter of 0.6 mm is to be compared with 1.6 mm for the petroleum oil. The good lubricating properties of the methyldecyl and the methyltetradecyl siloxanes were further confirmed in the Falex wear tester. Seizure loads were 750 psi with soft steel blocks and pins. The addition of an active E.P. agent (chlorine type) raised the seizure load to 2500 psi, equivalent to that of an E.P. type petroleum oil. These long-chain alkyl siloxanes also showed promise for the lubrication of aluminum on aluminum and titanium on titanium, both of which are difficult metal pairs to lubricate. The superior lubricating qualities of these siloxanes were obtained at some sacrifice in oxidation stability, the continuous upper operating temperature decreasing from 400°F for the dimethyl silicones to 300°F for the methylalkyl types.

14. MODIFIED POLYPHENYL ETHERS

Properties of a new type of polyphenyl ether (the exact modification was not disclosed) were reported by McHugh and Stark (507). This family of fluids covered a viscosity range of 3 to 2000 cS or more at 100°F. Their viscosity-volatility relationship was much superior to that of the conventional polyphenyl ethers and approximated those of conventionally refined petroleum oils. Like other aromatic type fluids, these modified polyphenyl ethers, or C-ethers, had viscosity-temperature graphs that curved upward at low temperatures. Although their viscosity-temperature properties were greatly improved over those of polyphenyl ethers, they were inferior to those of diesters and super-refined oils. The lower viscosity fluids (below 10 cS at 100°F) had pour points of -50°F or lower. Surface tensions were high, being in the 45 to 50 dynes/cm range. These fluids are much less compressible than petroleum oils, diesters, silicones, and phosphate esters, a desirable property for hydraulic fluids.

The C-ethers had good thermal stabilities; their isotenscope decomposition temperatures of 720°F were somewhat below those of polyphenyls and polyphenyl ethers but above those of diesters, polyesters, and petroleum oils. They approached the polyphenyl ethers in resistance to ionizing radiation and were superior in this respect to lubricants of the nonaromatic type. Oxidation tests indicated that the C-ethers could withstand temperatures of 500°F; however, copper corrosion was observed. Subsequent tests showed that the oxidative corrosion of copper alloys decreased with decreasing copper content and became negligible in alloys containing less than 80 to 85 percent copper. None of the other common metals of construction were corroded by the oxidized oil.

Lubricity tests indicated that the C-ethers were much superior to polyphenyl ethers in lubricating ability. Wear-scar diameters of 52100 steel balls (Four Ball Wear Test), 10 kg load, 1200 rpm, at 400°F for one hour were in the same range as that for diesters and petroleum oils. Ryder Gear ratings, a measure of load-carrying capacity, were essentially constant over the viscosity range of 3 to 6 cS at 210°F. Gear ratings at 165°F were 3100 to 3200 pounds load per inch of gear tooth width (ppi), considerably higher than that of petroleum oils, diesters, or polyol esters of similar viscosity.

The preceding discussion reviews the new synthetic-oil developments. Some of the products were developed with the enhancement of a single property as the main objective. Frequently the improvement in one property was obtained at the expense of some other property or combination of properties. Many of the fluids are still in the experimental development stage, and some may never be available commercially. Unless the gain in overall properties is such as to satisfy a need at a reasonable cost, the limited demand will not justify commercialization.

V. PETROLEUM BASE LUBRICATING OILS

1. PETROLEUM OIL COMPOSITION

Petroleum lubricating and hydraulic oils are complex mixtures of hydrocarbons with small concentrations of organic compounds containing nitrogen, sulfur, and/or oxygen. It is not possible to make accurate predictions about the properties, lubricating characteristics, and service performance of such fractions unless much information is available about its chemical composition. The relative proportions of hydrocarbon types and the concentrations of sulfur, nitrogen, and oxygen containing compounds vary with the type of crude oil and also with the methods of refining. Refining methods are used to remove not only the nonhydrocarbon and polar compounds but also the less desirable hydrocarbons, e.g., olefins with poor oxidation stabilities, aromatics with low viscosity indexes, asphaltenes because they are precursors of sludge and varnishes, paraffins with high pour points, etc. (359, 416). Hydrogenation is being increasingly used as a refining step in the commercial production of petroleum fractions (92, 93, 432).

Although it is impossible to determine the exact chemical composition of a petroleum fraction, general methods have been used for characterizing the average proportions of hydrocarbon types, such as aromatic, naphthenic, and paraffinic (744). As more sophisticated methods of separation and identification have been developed, the analysis of petroleum fractions has become more specific (42, 47). Separation methods include: volatility, adsorption, absorption, thermal diffusion, and solvent extraction. Identification methods include: ultraviolet, infrared and mass spectrometry, nuclear magnetic resonance, and molecular weights.

King (434) has reviewed the advances made in the separation and identification of components and component types present in petroleum oils. Chromatography is becoming

an increasingly important method for the physical separation of components. Instrument methods are widely used for identification (47). Nonhydrocarbon compounds in petroleum have also been studied. Sulfur has been found free and also in combined form as thiols, sulfides, disulfides, thiophenes, benzothiophenes and in other heterocyclic rings (551). Nitrogen compounds present in petroleum include pyridines, quinolines, benzoquinolines, indolo- and carbazoloquinolines, hydroxy-benzene quinolines, phenothrolines, hydrocarbazoloamines, etc. (471). A variety of alcohols, phenols, carboxylic acids, and other carbonyl compounds have been identified as components in petroleum (366).

It is now well established that the high-boiling petroleum fractions contain paraffins, isoparaffins, cycloparaffins, aromatics, and mixed aromatic-cycloparaffins. The cycloparaffins include mono- and polycondensed structures as well as noncondensed polycycloparaffins. Aromatic components are also present as mono- and polycondensed rings and noncondensed polyaromatics. Mixed condensed and noncondensed aromatic-cycloparaffin structures are also present. In general, the rings contain alkyl side chains; the number of alkyl substituents is variable, as are their length and degree of branching. The concentration of the various types of hydrocarbons in lubricant fractions varies with the crude, methods of refining, and molecular weight of the fraction.

2. SUPER-REFINED PETROLEUM OILS

Because of the improvement in properties and performance of lubricating fractions by refining, the Pennsylvania State University Petroleum Refining Laboratory reasoned that further improvements would be attained by additional refining. Preliminary results have confirmed their premise (449). Exhaustive refining procedures were termed super-refining. Distillation was used to obtain narrow-boiling fractions. Such fractions showed only small changes in viscosity with evaporation losses. Good low-temperature fluidity was obtained by solvent dewaxing at temperatures as low as -75°F . This deep dewaxing, which removed paraffins and isoparaffins, resulted in products with viscous pour points. A variety of solvent systems (methylisobutyl ketone; methylisobutyl ketone-methylethyl ketone blends; toluene-methylethyl ketone blends; and toluene-acetone blends) were used in dewaxing procedures. It was found that the solvent system could be optimized for oil type and molecular weights so as to obtain oils with pour points closely approximating the dewaxing temperatures. The removal of unsaturates, polar impurities, and nonhydrocarbon compounds was accomplished by acid extraction, by all-out hydrogenation, or by a combination of the two methods. Water-white products were obtained by all three procedures (445, 447, 448). Super-refining techniques have been used successfully on paraffinic, naphthenic and aromatic type mineral oil fractions, but the paraffinic-type oils provided the best overall properties for wide range fluids. Super-refined oil fractions can be prepared covering the viscosity spectrum of lubricants. Super-refined petroleum fractions are composed of a variety of hydrocarbons with similar structures, namely, cycloparaffins with alkyl side chains. As the average molecular weights of the fractions increase, the number of naphthene rings in the molecules also increases.

Deep dewaxing, although able to reduce greatly the pour point of the oil, has an apparent adverse effect on V.I. The viscosity of the dewaxed fraction is slightly greater than that of its parent, but its V.I. is from 10 to 20 units less. This is understandable because the wax fraction removed is less viscous and has a greater V.I. than the original oil. Although the ASTM V.I. of the dewaxed oil is less than that of the original fraction, the former has the more desirable viscosity-temperature properties. This is due to its lower-than-predicted viscosities at low temperatures. At -65°F the measured viscosities of the deeply dewaxed oils are somewhat less than half that predicted by an extrapolation of the 210° and 100°F viscosities on the ASTM Viscosity-Temperature chart. Deviations from the predicted viscosities become less as the 100°F reference temperature is approached (447, 448).

Super-refined oils are much more responsive to antioxidants than are conventionally refined petroleum fractions. An antioxidant progressively increased the stable oxidation life at 347°F of an oil with each hydrogenation step rising from 30 to 90 to 140 hours after successive hydrogenations. Conversely, the stable oxidation life of a super-refined oil was decreased by the addition of some of the conventionally refined base stock. The better response of the super-refined oils to antioxidants is attributed to the removal of polar impurities and unsaturates by the exhaustive refining procedures (446, 447, 448, 449). Although the addition of small amounts of conventionally refined oils to super-refined ones decreases antioxidant effectiveness, blends of diesters and super-refined oils are approximately as responsive as the super-refined oil.

Since the super-refined oils are mixtures of hydrocarbons, they would be expected to be resistant to hydrolysis. Their thermal stabilities should permit a stable operating life under an inert atmosphere of ca. 50 hours at 700°F. At temperatures in the 600° to 650°F range they could be used for extended periods with little deterioration.

Super-refined hydraulic fluids are now commercially available in three viscosity and pour point grades (395). These grades are:

Viscosity at 100°F (centistokes)	Pour Point (°F)	Flash Point (°F)	References
15.41	-70	390	521
78.08	-30	445	
14.50	-40	340	561

Very viscous oils (250 to 4500 cS at 100°F) have also been prepared by super-refining paraffinic resins (421, 445). As their molecular weights are much greater than those of hydraulic fluids, they are less volatile and have higher flash and pour points. The more viscous products are recommended as shear-stable V.I. improvers for the lubricants and hydraulic oils.

Super-refining can also be used to upgrade synthetic hydrocarbons e.g., polyolefins, alkylated benzenes, isomerized wax, and hydrocracked naphthenes. When subjected to most (if not all) of the super-refining steps, these synthetic hydrocarbons are competitive in properties with super-refined mineral oils (447, 448).

3. AUTOMATIC TRANSMISSION FLUIDS

The automatic transmission is the most complicated mechanism in the modern automobile. Increases in the size of automatic transmissions have not kept pace with engine outputs, resulting in smaller oil capacities and demanding more mechanical work from smaller parts. This development has required the working fluid to operate at increasingly higher temperatures. Automatic transmission fluids have been under development for more than 25 years, beginning with the Oldsmobile semiautomatic transmission in 1937. Changes in designs, operating conditions, and materials of construction have been reflected by changing requirements for the operating fluid. Watt and Duckworth (759) have traced the development of General Motors automatic transmission fluids from 1937 to 1963, emphasizing the problems encountered and tests developed to determine pertinent requirements. A further complication is that different makes of automatic transmissions require fluids with different, and sometimes conflicting, properties. The conflicting property most difficult to reconcile is the frictional requirement; one type of transmission needs a fluid which permits clutch plates to engage quickly and firmly, while another type requires a fluid that allows the clutch plates to engage more gradually (25, 694).

Automatic transmission (AT) fluids conforming to the manufacturers' specifications are used as "factory fill" fluids and are generally available at their respective dealers. Service stations do not handle AT fluids that meet the different manufacturers' specifications, because of the variety of products required. Although most manufacturers' requirements could be built into a single fluid, it was necessary to compromise on the frictional and elastomer compatibility properties for service-station fluids. This compromise fluid conforms to the requirements of General Motors Type A, Suffix A, specification issued 1957 (120f, 694). The Type A, Suffix A, fluid can be added to all factory-fill fluids up to a concentration of about 30 percent without serious deleterious effects. "Lubrication" (25) reports that at the specific request of car manufacturers, two distinct types of AT fluids were made available at service stations in 1965. However, Automotive Industries (312) lists all 1966 automatic transmissions as using the Type A fluid.

Automatic transmissions place exacting demands upon the working fluid, and therefore a sophisticated formulation is required. Properties of interest in the modern AT fluid (25, 120f, 123, 495, 694, 759) are:

1. Adequate viscosity at the highest operating temperature;
2. Fluidity at lowest operating temperatures;
3. Excellent oxidation stability;
4. Good detergency;
5. Proper friction-reducing characteristics;
6. Compatibility with
 - a. Seals and elastomers,
 - b. Clutch plate materials;
7. Corrosion and rust prevention;
8. Resistance to foaming.

With the exception of the compatibility requirement with the materials of construction, which is primarily a function of the type of base fluid used, additives are required to enhance or impart the other properties demanded of the AT fluid.

To meet requirements for both the low-temperature fluidity and adequate viscosity at high temperatures, V.I. improvers and possibly pour-point depressants are required. Antioxidants are needed to impart the requisite stability and dispersants to prevent the precipitation of insolubles and sludges. The proper friction-reducing properties are obtained by antiwear or mild extreme-pressure agents. The most common antifoam additives are silicones. Corrosion resistance is generally attained by preventing oxidation of the oil to acidic materials. Rust protection afforded by metal salt type dispersants, particularly the "basic" materials, is adequate. These additives have been discussed in previous sections.

To obtain a good AT fluid, a critical balance must be attained between the base fluid and the additives (495). As many as a dozen different additives may be used in the formulation of an AT fluid. Additive compatibility may be a serious problem where many different additives are used. Additives alone cannot make up all of the deficiencies in a base stock; suitable petroleum fractions are a necessary ingredient for a good AT fluid. The base oil should have a low pour point, a low volatility, a high V.I., be responsive to additives, and be compatible with seal and clutch-plate materials. Physical properties of a good base stock are reported (120h) as:

Viscosity, 210°F	35-37 SUS
V.I.	100 min.
Flash Point, °F	330 min.
Pour Point, °F	-40

Suitable base stocks may be a single narrow cut fraction, but are generally a blend of two fractions (120h), a distillate fraction and a fraction of higher viscosity to improve lubricating properties.

Boner (120h) has given the composition of a number of AT fluids published in patents and in the open literature. These formulations included type of base stock used and the names and concentrations of the various additives. Additive "packages" for finished AT fluid formulations were also discussed (120h).

Specification requirements for AT fluid, Type A, Suffix A, are given in Table 8 to indicate the severity of service as well as the properties demanded.

Specification of the automotive manufacturers differ from the AT fluid of Type A, Suffix A, primarily as regards oxidation stability, frictional properties, and elastomer and seal compatibility (694). Watt and Duckworth (759) presented the opinion that automatic transmissions of uniform design requiring a single fluid are not probable. Therefore, AT fluids having different properties will be required for the various transmissions. It is also probable that the AT fluid requirements will become even more demanding.

Table 8
Specification—AT Fluid, Type A, Suffix A

Quality	Requirement
Miscibility	No separation or color change in cycling from 450°F to 5°F below pour point
Viscosity, SUS at 210°F	49 min
Viscosity at -10°F, centipoise	4500 max
Viscosity at -40°F, centipoise	64,000 max
Flash point, °F	320 min
Fire point, °F	350 min
Copper corrosion, 3 hr at 300°F	No blackening or flaking
Heating, 125 hr at 250°F	No sludge or deposits—Evap. wt loss 7.7% max
Rust prevention	Pass ASTM D 665 with distilled water
Compatibility, seals	Volume change +1 to +5%; hardness change 0 to -5
Odor	Must not be objectionable
Toxicity	No toxic components
Oxidation stability CLR L-39, 300 hr at 275°F	No sludge or varnish or adverse effects on transmission components
Non-chattering or squawking properties	Oldsmobile Hydra-Matic 2400 cycles and 2000-mile driving test
Durability	2400 cycles in Oldsmobile Hydra-Matic
Viscosity stability SUS at 210°F	46.5 min after 2400 cycles and performance tests
Frictional properties	Based on change in operational properties at beginning and end of driving test
Performance	Equal to or better than the reference fluid

Tests methods for AT fluid, Type A, Suffix A, include laboratory tests, and service-simulating and road tests using the transmission under consideration. Information on AT fluids is given by the SAE as J311a (655). The CRC Power-Transmission and Power-Steering Units and Fluids Group (176) is working to develop and standardize test methods for evaluating and specifying the properties of AT fluids.

Hydraulic transmissions of heavy-duty trucks, buses, etc., also require suitable working fluids. Although the AT fluids, Type A and Suffix A, give exceptional service, these applications do not require a fluid of such exceptional properties. The specification for Hydraulic Transmission Fluid, Type C-1 of the Allison Division of GMC, is typical of that required for heavy-duty torque converters (120e). Many heavy-duty motor oils of SAE 10W grade will meet the specification requirements.

4. CRANKCASE OILS

The SAE classification of crankcase oils (J300) is based on oil viscosity at the reference temperatures (655). For regular grade oils the reference temperature is 210°F, and for winter or W grade oils it is 0°F. Viscosity ranges of the SAE grade oils are given in Table 9.

Table 9
SAE Crankcase Oil Classification*

SAE Grade	Viscosity Range, Saybolt Universal			
	at 0°F		at 210°F	
	Min.	Max.	Min.	Max.
5W	—	4000 (872)	39 (3.86)	—
10W†	6000 (1307)	< 12,000 < (2614)	40 (4.18)	—
20W‡	12,000 (2614)	< 48,000 < (10,457)	45 (5.73)	—
20	—	—	45 (5.73)	< 58 < (9.62)
30	—	—	58 (9.62)	< 70 < (12.94)
40	—	—	70 (12.94)	< 85 < (16.77)
50	—	—	85 (16.77)	< 110 < (22.7)

Figures in parentheses are viscosities in centistokes.

*Reference 655.

† Minimum viscosity at 0°F can be waived provided the viscosity at 210°F is not below 40 SUS.

‡ Minimum viscosity at 0°F can be waived provided the viscosity at 210°F is not below 45 SUS.

Dashes indicate no requirement.

As different reference temperatures (0°F for winter and 210°F for regular grade oils) are used in the SAE viscosity classification system, it is possible for an oil to conform to two SAE grades, the regular and W grade. A high V.I. is a necessary requirement for such an oil. Increasingly large V.I.'s are required upon ascending the double grade series 5W-20, 5W-30, and 5W-40. Although it would be difficult to obtain a straight petroleum fraction that would conform to two SAE grades, polymer-thickened ones can be readily prepared.

The demands on both automotive and diesel crankcase oils vary with the type of service, sensitivity of the engine, fuel composition, and seasonal environmental factors. In order to cover the different crankcase oil requirements for both automotive and diesel engines, the American Petroleum Institute (API), in cooperation with the SAE (J303) and the ASTM, issued an oil-classification system (33, 655). Their 1956 revision has the following service grades.

GASOLINE ENGINES

Service ML — light and favorable use
Service MM — moderate to severe use
Service MS — severe to unfavorable use

DIESEL ENGINES

Service DG — light and favorable use
Service DM — moderate to severe use
Service DS — severe to unfavorable use

Oils for the more demanding service requirements are obtained primarily by the use of additives (18, 332, 407) and to a secondary extent by using refining procedures that produce more desirable base stocks. Emphasis has been placed on the formulation of oils for the more severe service requirements. In order to meet these requirements, the additives used normally include antioxidants, corrosion inhibitors, detergents, and antiwear agents. In general, the concentration of additives decreases as the service requirements become less stringent, and for light-duty oils, some additives may be omitted. Other type additives, e.g., V.I. improvers, pour-point depressants, antifoam agents, and metal deactivator-passivators may also be incorporated in crankcase oils. The functions, chemical species, and mechanisms by which additives function has been discussed earlier.

Unfortunately there are no reliable laboratory tests that can be used to evaluate adequately the performance characteristics of crankcase oils; hence, engine tests are required. The API system provides no method for determining the oil quality necessary for a given service. A test sequence for automotive oils for MS service has been standardized by ASTM from test procedures originally developed by the automotive engine producers. This sequence, which was revised in 1963 (44), includes tests for oil quality under certain test conditions. These are:

- I. Antiscuffing
- II. Low-temperature deposit and rusting test
- III. High-temperature oxidation test
- IV. High-temperature, high-scuffing, and wear test
- V. Insolubles, sludging, and screen-clogging test.

Tests I, II, and III were run in a 1960 Oldsmobile V-8 engine, IV in a 1962 Chrysler 361 cu in. V-8 engine, and V in a 1957 Lincoln-Mercury 368 cu in. V-8 engine. Engine Tests for Evaluating Crankcase Oils is given by SAE as J304 (655). All engine tests were run under carefully controlled conditions. The significance, repeatability, reproducibility, and suggested test modifications have been discussed in a symposium on automotive oils

(45) and by Christiansen and Brown (199). A new revision of ASTM test sequence is to appear in a forthcoming publication (43). The Coordinating Research Council and SAE are also active in the development of oil-test techniques for predicting the quality of crankcase oils (511, 655). Details of the engine tests required by government specifications are given in Federal Test Methods Standards No. 791a (287). A great variety of small and one-cylinder engines have been used to screen experimental oil formulations and to determine the quality of the oil under certain conditions of service (26, 711).

Pioneering work on engine tests for predicting the performance of diesel crankcase oils was initiated by the Caterpillar Tractor Company, before World War II. Since that time the number, variety, and severity of engine tests have increased. It has been reported (199) that the majority of diesel engine manufacturers rely now upon military-specification requirements as the basis for recommending crankcase oils for their equipment. The Coordinating Research Council has been active in developing oil-test techniques (511), and some of their test procedures are used in military specifications. These include the L series tests. Important military specifications for diesel crankcase oils are: MIL-L-2104B, "Lubricating Oil, Internal Combustion Engine (Heavy Duty)" (523); MIL-L-9000E (SHIPS), "Lubricating Oil, Internal Combustion Engine, Diesel" (529); MIL-L-10295A, "Lubricating Oil, Internal-Combustion Engine, Sub-Zero" (530); MIL-L-45199A (ORD), "Lubricating Oil, Internal Combustion Engine (High Output Diesel)" (536). The 2104B and 10295A oils are also used as crankcase oils for spark ignition engines. The latter oil is for service at subzero temperatures, down to -65°F .

Engine-test methods for diesel crankcase oils are also given by Federal Test Method Standards. As for automotive crankcase oils, a variety of engines are specified for determining the suitability of the oil for severe service in diesel engines. Engine tests are used to determine detergency under severe, normal and light operating conditions, supercharged conditions, under conditions of corrosive wear and deposit formation, and when operating on high sulfur fuels. Copper-lead-bearing corrosion resistance is stressed for Army oils and silver-bearing corrosion resistance for Navy oils. In addition to the diesel-engine tests for the Army 2104B and 10295A oils, the low-temperature deposit and rusting tests in a spark-ignition engine are required, since these oils are used in both types of engine.

Full-scale engine tests are expensive, and a number of different engines are required to determine the quality of the oil for a given service; thus the cost of qualifying an oil or evaluating a new oil formulation is expensive. It would therefore be desirable to develop a single engine that could be used to evaluate all the facets of oil quality. Such an engine would be difficult and expensive to design and build. If such an engine could be built, its characteristics for oil deterioration would have to be correlated with existing engines. Furthermore, it would have an uncertain useful lifetime, since engine design changes that cannot be predicted could make it obsolete within a few years. Emphasis has been placed on improving the repeatability and reproducibility of existing tests and in developing more discriminating test techniques for rating the quality of crankcase oils. It is felt (45) that a cooperative effort, in which the rating of test and reference fluids in the CLR Oil Test Engines would be primarily the task of the petroleum industry, with the automotive industry providing data on the reference fluids in full-scale engines and assisting appropriate groups in interpreting results, would be more fruitful.

There has been a significant increase over the past decade in the concentration of additives used in crankcase oils. This increase reflects both an increase in the severity of engine operating conditions and in the ability of the oil producer to supply crankcase oils that will function effectively for longer operating intervals between drain periods. The additive showing the largest concentration increase is the detergent (18, 199). Although metal salts of organic compounds constitute the larger percentage of dispersant additives, both the low molecular weight and polymeric ashless types are being used increasingly. Ashless detergents reduce combustion-chamber problems caused by the

metal of salt-type additives, valve burning in diesel engines, preignition, and octane-requirement increases in automotive engines. As the mechanisms of deposit formation in automotive and diesel engines are not identical, it is not surprising that the oil industry is developing separate oil formulations for diesel and automotive use (711).

Hall et al. (367) point out that although ashless dispersants reduce low-temperature sludge and varnish deposits in engines, rusting increased. Unpublished work of NRL indicates that ashless dispersants are less effective rust inhibitors than the neutral metal salt type. The excess alkalinity (see Section III-9, Detergents) present in many of the salt-type dispersants greatly increases their neutralizing power for acidic contaminants, and thus further increases their effectiveness as rust inhibitors.

Another problem in the crankcase-oil field is to define the relationship between oil viscosity and low-temperature cranking performance. Before the advent of polymer-thickened multigrade oils, a reasonable correlation existed between the extrapolated viscosity of the oil at 0°F (obtained by extrapolation from measured viscosities at 210°F and 100°F) and low-temperature cranking performance (227). The correlation failed when polymer-thickened oils were included in the program (227, 228, 505, 563, 672). This is understandable, since polymer-thickened oils are non-Newtonian liquids whose apparent viscosities vary with the shear rate. Apparent viscosities of the test oils, as determined by the engine test technique, CRC L-49-663, showed variation between engines (228). The engines did, however, rank the test oils in the same order. Since the engine-test technique is not suitable for routine viscosity determinations, a simple laboratory viscosity test method is desired.

Section B of Research Division VII of ASTM Committee D-2 is studying methods for determining the viscosities of non-Newtonian liquids; therefore, the SAE and CRC asked them to consider methods applicable to crankcase oils at 0°F. The results of their work (228, 746) showed that viscosities in simple capillary viscometers at low rates of shear did not correlate with the apparent viscosities obtained by the engine cranking test technique. The Feranti-Shirley cone-plate and the Forced-Ball viscometers more closely predicted the low temperature cranking performance of engine oils. Good correlation was also obtained with Mason Torsion crystal and Texaco High Rate of Shear Rotational viscometers but because of their complexity and limited availability, they were eliminated from consideration. In general, it was found that the best correlation between engine cranking characteristics and laboratory instrument viscosity was found at the highest shear rates investigated. Further work by Section B of Research Division VII of ASTM D-2 indicates that the Reciprocating Viscometer developed by Gulf gives results that correlate well with engine cranking characteristics. It is expected that standard laboratory test methods will soon be available for this purpose. As CRC (228) has recommended the elimination of the viscosity extrapolation procedure of SAE Handbook, J 305, it is not improbable that the viscosity limits of the W graded SAE oils will be modified to more accurately reflect the cranking characteristics of oils.

5. GEAR OILS

A great variety of types, designs, and sizes of gears are used in industrial equipment to transmit power (120a, 264, 515). Extremes of loading and speed are encountered in gear operations, and gears are made from such diverse materials as plastics, steel, ferrous alloys, and nonferrous metals. The mating parts of the gear may or may not be of the same composition. However, the great majority of gears are fabricated from steel and ferrous alloys. When the mating gear surfaces are separated by a continuous film of oil, hydrodynamic lubrication exists and wear is negligible. In hydrodynamic lubrication, the load-carrying capacity of the lubricant is related to oil viscosity (148). Thus, viscosity classification systems for gear lubricants are common (120c). Viscosities of gear lubricants may range from less than 2 cS at 100°F to greater than 500 cS at 210°F.

Increasing the loads on moving metal parts supported by an oil film decreases the film thickness. Metal-to-metal contact results in increased wear, galling, and eventually seizure. Additives are used in the oil to reduce friction and increase the load-carrying capacity of gear lubricants. Such additives have been discussed in Sections II-4 and II-5 and the general types are the following:

- Polar additives which adsorb on metal surfaces to form an oriented film able to reduce friction and wear and increase the load-carrying capacity. Examples are fatty alcohols, esters, acids, soaps, etc.

- Chemically reactive agents or extreme pressure (E. P.) additives which react with the metal surfaces to form inorganic films that prevent wear and galling and greatly increase the load-carrying capacity. Examples include compounds containing chlorine, sulfur, and phosphorus. Commercial E. P. lubricants frequently contain a combination of additive types, either as a mixture of compounds or as a single compound containing two or more of the active ingredients.

It is generally agreed (120b, 711) that gear wear proceeds by several mechanisms (see Section II-2):

1. Adhesive or galling wear
2. Abrasive and cutting wear
3. Corrosive wear
4. Fatigue wear.

In nonadditive type oils, load-carrying capacity or ability to prevent adhesive wear is primarily a function of oil viscosity (148). Therefore, the choice of viscosity grade for a gear application is a compromise between the lowest viscosity that will support the loads at the highest operating temperatures and the energy required to overcome the viscous drag at low temperatures, i.e., high lubricant viscosity. Furey and Appeldoorn (324) studied the effect of lubricant viscosity on metallic contact and friction in the transition zone between hydrodynamic and boundary lubrication. They found that higher viscosity oils had greater load-carrying capacities. The relationship was not linear but had the form $W = A\mu^2 + B\mu + C$, where W is load-carrying capacity, μ is the viscosity, and A , B , and C are constants. Normal bulk viscosity at atmospheric pressure and the test temperature were the important factors for Newtonian fluids. Pressure-viscosity and temperature-viscosity properties had secondary effects. The non-Newtonian behavior of polymer-thickened oils suggest that shear viscosity is the important factor in their load-carrying ability. Since viscosity effects are also apparent in additive oils, it is taken into consideration in selecting E. P. lubricants.

Abrasive or cutting wear results from wear debris and solid contaminants. Wear debris, a product of adhesive wear, is a manifestation that the lubricant is unable to support the loads developed on the gears and that a more viscous or more chemically active lubricant is required. Abrasive wear resulting from solid contaminants is not uncommon; it can be eliminated by cleaning the system and preventing the entrance of dust, dirt, and other abrasives. Air and oil filters can effectively remove wear particles and contaminants in circulating oil systems.

Corrosive gear wear may result from several mechanisms. Rusting takes place after leakage of water into the system or the condensation of water from humid atmospheres. Rust-preventing oil additives can inhibit or prevent the rusting due to fresh water. In marine applications, where contamination with sea water is nearly unavoidable, rusting and corrosion (accelerated by electrolytic action) may occur, and corrosion inhibition is more difficult. The reaction of E.P. additives with ferrous metal gear surfaces may be considered as controlled corrosion; here the wear rate is not excessive. However, certain E. P. agents designed for ferrous gears are so reactive that they will rapidly corrode many nonferrous metal gears.

A little-understood phenomenon is the fatigue that affects both gear and antifriction bearing wear. Mechanical and metallurgical factors such as tensile stresses, metal composition, presence of inclusions, dislocations, and other imperfections are important in controlling fatigue. However, the lubricant does play a role in increasing the fatigue life of the gears and bearings.

Rounds (634, 635) found that increasing lubricant viscosity increased life before fatigue failure. He speculated that molecular shape was also a factor. Since highly branched and very large molecules would not be expected to penetrate cracks as readily as small molecules, the crack propagation preceding fatigue failure would not progress as rapidly. Rounds suggested that nonpolar molecules penetrated cracks less readily than polar molecules. Thus, fatigue failure would occur earlier with a badly oxidized oil than with one that was stable to oxidation. Acidic oxidation products or additives, e.g., oleic acid or dialkyl phosphate, reacted with the metal surfaces at specific points to form corrosion pits that accelerated crack propagation, thus shortening life. Lubricants or additives that attacked the surface uniformly were expected to have little or no effect on fatigue. In fact, reactions that produce a uniform film able to prevent further attack on the metal can increase life before fatigue. Water in the lubricant may also have an adverse effect, (a) by penetrating cracks, and (b) by releasing hydrogen that may cause metal embrittlement. The causes of fatigue wear and failure are complicated, and not all of the parameters are adequately resolved; fatigue is initiated by stresses that cause changes and reactions in the metal (98, 552, 619, 740), but the course and kinetics of these reactions are influenced by the lubricant.

Other properties, beside film strength or load-carrying capacity, are required of gear lubricants if they are to be satisfactory for a specific application. These include:

1. Ability to act as a coolant or heat-transfer fluid
2. Stability
 - a. With respect to separation during storage or use
 - b. Satisfactory oxidation stability
 - c. Satisfactory hydrolytic stability
3. Freedom from excessive foaming
4. Ability to wet and adhere to moving parts
5. Compatibility, including
 - a. Noncorrosiveness to metal parts
 - b. Lack of attack on seals and elastomers
6. Inability to form stable emulsions with water
7. Satisfactory viscosity-temperature properties, i.e., sufficiently viscous at upper operating temperatures to support loads and should not channel or be so viscous at low temperatures as to consume excessive power
8. Viscosity stability, in that
 - a. Viscosity should not be degraded excessively when subjected to high shearing forces
 - b. Viscosity should not increase excessively during storage or use
9. Compatibility with other lubricants of the same types or specifications — an important military requirement

10. Provision of rust protection against action of water.

Gear-oil characteristics, grades, and specifications for a variety of applications are given by Boner (120d).

Lubricants for automotive and truck differentials and axles constitute a large and important segment of the gear-lubricant class. Five viscosity grades are given by the SAE (654) for this application.

The SAE classification, Table 10, does not indicate the suitability of a particular grade for a given type service. Straight mineral, synthetic, or additive oils of the requisite viscosity fall in the same grade.

Table 10
SAE J 306 Transmission and Axle Lubricant Classification*

SAE Viscosity Number	Viscosity Range				Consistency Must Not Channel at °F
	at 0°F		at 210°F		
	Min.	Max.	Min.	Max.	
75	—	15,000 SUS (3268 cS)	—	—	-40
80†	15,000 SUS (3268 cS)	100,000 SUS (21,786 cS)	—	—	-20
90‡	—	—	75 SUS (14.3 cS)	120 SUS (21.5 cS)	-10
140	—	—	120 SUS (25.1 cS)	200 SUS (42.9 cS)	+20
250	—	—	200 SUS (42.9 cS)	—	—

*Reference 655.

†Minimum viscosity at 0°F may be waived if viscosity at 210°F is not below 48SUS.

‡Maximum viscosity at 210°F may be waived if viscosity at 0°F is not greater than 750,000SUS.

Dashes indicate no requirement.

The American automotive industry has influenced the development of a number of new lubricants and additives that enhance or impart specific properties to oil. Extreme pressure lubricants for lubricating automotive hypoid gears are an outstanding example. Since different type gears are used in automotive and truck differentials and axles, the API and SAE J308-suggested Type Designations for gear oils (120d, 655) are:

1. Regular type
2. Worm gear type
3. Mild E. P. type
4. Multipurpose type.

It has become customary to add the letters E.P. after the SAE grade to indicate that it contains such additives. The designation "Multipurpose" was changed to API Service GL-4 in 1957. This lubricant is to provide satisfactory lubrication for hypoid gears and conventional differentials in sustained high-torque and/or high-speed service.

The Army has been active in the development of automotive and truck gear lubricants. Logistical considerations required that the number of lubricants be kept to a minimum (715), and therefore Military Specification MIL-L-2105A was revised in February 1962 as MIL-L-2105B Lubricating Oil, Gear, Multipurpose. This is a multipurpose gear lubricant suitable for axles, transmissions, transfer cases, winch-gear mechanisms, and steering-gear boxes. The basic requirements for 2105B were established by full-scale tests. It was determined that the E.P. activity requirements could be reduced through the use of chemical surface treatment of the gears without greatly impairing the high-speed, shock-loading protection. Recommendations for specification tests and requirements of 2105B were made by Gear Lubricants Group of CRC Motor Vehicle, Fuel Lubricant, and Equipment Research Committee. Tests on load-carrying capacity and extreme pressure characteristics of gear oils are determined by bench tests using the modification of CRC procedures (287). Only three viscosity grades -- 80, 90, and 140 -- are covered by MIL-L-2105B for logistical reasons. A gear lubricant for extreme cold applications is covered by MIL-L-10324A, Lubricating Oil, Gear, Sub-Zero.

Although the API Service GL-4 gear oil requires that it provide satisfactory lubrication of hypoid gears and standard differentials, no specifications are used to set forth its requirements. The various automotive producers have specifications for their factory-fill gear oils, but test methods, apparatus, and requirements differ from company to company (23, 120d, 120i, 120j, 287, 327, 396). It has been suggested that the automotive industry ask the ASTM to develop and standardize test methods in order to indicate to the petroleum industry the characteristics of gear lubricants needed (346). Such tests are under development. The petroleum industry would prefer that a single gear lubricant be adopted which would furnish outstanding performance in almost every type of service. This would obviate the necessity that filling stations stock a number of lubricants, with the attendant probability that "mix-ups" in servicing would occur. Automotive Industries (312) lists the gear oil requirements for the various 1966 passenger cars. Company recommendations include: hypoid or multipurpose, multipurpose, and extreme pressure, hypoid gear lubricants. Without exception, the SAE grade 90 is recommended for summer use and 75 or 80 for winter service. The "locking" or "limited-slip differential" available as an extra on most makes of cars requires a lubricant somewhat different from simple hypoid gear lubricant. This lubricant must prevent chatter of friction members used to lock and force the rear wheels to rotate together. An anti-chatter additive compatible with the E.P. additives is required (25).

Most gear lubricants have a petroleum oil as the base fluid. Boner (120g) has discussed the properties of petroleum oils used in the formulation of gear oils for a variety of applications. Additives used in the various type gear lubricants were also covered, as were methods used in physical (120i) and chemical (120j) testing of formulations.

VI. INSTRUMENT LUBRICATING OILS

"Instrument oil" comprises a vaguely defined class of lubricants. Instruments have greatly varying lubricant requirements, depending upon temperature range of operation, loads, speeds, metal combinations to be lubricated, and environmental parameters. In general, an instrument oil is a low-viscosity lubricant, usually 50 cS or less at 100°F. Although more viscous oils are sometimes included in this category, the majority of instrument oils are in 10 to 25 cS range at 100°F. Because of the small volume of such lubricants and the fact that in them are found the same additives as those required in other lubricants, not much attention has been devoted to the development of instrument oils. There are two distinct and different types of instrument oils: (a) spreading oils, and (b) nonspreading oils. Spreading oils are by far the most common, for they are used to lubricate journal bearings, antifriction bearings, and gears. Nonspreading oils are used to lubricate pivot bearings of watches, clocks, fuses and the like.

1. SPREADING OILS

World War II had an unprecedented impact not only on the design and production of a large variety of new instruments, but also on instrument lubrication requirements and practices. In order to assure greater accuracy of military instruments such as gyroscopes, bomb sights, computers, fire-control equipment, etc., speeds of rotation were increased and bearing tolerances and clearances were decreased. In addition, the operating temperature range was extended at both high and low temperatures. Manufacturers of such equipment refused to guarantee their product unless it was lubricated with the recommended oil. Thus, a great number of proprietary oils were added to the Navy supply system (560). Similar problems were encountered by the other services. There also resulted the ridiculous situation where identical equipment from different suppliers required different lubricants. Many of the proprietary lubricants required by equipment producers were unsuitable for military applications, the majority because of inadequate low-temperature properties (49).

Post-World War II instruments and small mechanisms have tended towards increasing compactness, especially military equipment. This miniaturization increased operating loads and speeds and reduced heat losses, with the result that operating temperatures were increased. As during World War II, the producer would not warrant his product unless the recommended lubricant was used. Approximately 200 different proprietary lubricants have been introduced into the military supply system (691) since World War II. Supply and logistic problems were such that the Assistant Secretary of Defense, Installations and Logistics, issued directives to eliminate some lubricants (249, 513). The number of proprietary lubricants was reduced by half by substituting military specification lubricants and by using the best of the proprietary lubricants for several applications. Service performance was equalled or improved by these changes. From a logistical point of view it would be desirable to have only one spreading type instrument oil for all military applications. The great variety of mechanical, optical, electric, and electronic components in use, as well as the required variations in loads, speeds, and temperature ranges, make it impossible to find a single lubricant with all the desired characteristics and properties. However, it is desirable to minimize the number of specified instrument oils.

Although the properties and characteristics of spreading instrument oils vary with the application, many properties are common to all applications and vary only in extent. Such properties of the oils are:

1. Ability to wet and adhere to surfaces to be lubricated
2. Adequate lubricating ability
3. Stability, i.e., no separation into phases or precipitation of additives during storage or use
4. Correct viscosity over operating range
5. Viscosity stability under shearing stresses
6. Stability to oxidation
7. Stability to hydrolysis
8. Compatibility with:
 - a. metals; b. plastics; c. elastomers; d. paints

9. Protection of ferrous metals from rusting
10. Low evaporation rates
11. Compatibility with and response to oil additives
12. Nontoxicity
13. Nonfoaming properties
14. Compatibility with other qualified products.

To maintain a continuous lubricant film between rubbing, sliding, or rolling parts, it is desirable that the lubricant wet and adhere to these parts. As most lubricating oils, petroleum and synthetic, wet and spread on clean metals (67, 318), any problem with inadequate spreading generally results from contamination of the oil or metal by polar organic compounds (213) which adsorb to form a low-energy surface. The surfaces to be lubricated should be well cleaned if a continuous lubricant film is desired. Polar additives from rust-inhibiting compositions used to preserve parts during storage prior to assembly are a frequent cause of nonwettability. Silicone additives or contaminants are another source of contaminating films that prevent spreading of lubricating oils (53).

Although complete spreading and wetting of moving parts by lubricants is desirable from a lubrication standpoint, uncontrolled spreading may sometimes cause trouble. An investigation of the performance of military servo and synchro motors taken from storage showed that few if any of these motors, after six months storage, could pass the life requirements of their respective specifications (537, 538, 540). Failure was due to lubricant loss through spreading rather than by evaporation, as previously assumed (299). Silicone-lubricated ball bearings are particularly susceptible to loss of lubricant by spreading, although the silicones are among the least volatile of lubricants. The loss of lubricant from the bearings can now be effectively controlled by the deposition of a fluorochemical barrier film on the plane faces of ball bearings (299). Servo and synchro motors with bearings so treated to prevent lubricant loss by spreading have greatly exceeded the specification life requirements (299). Other difficulties with uncontrolled lubricant spreading may be encountered in optical equipment, where the spreading lubricant film can fog lenses, prisms, mirrors, etc. Electrical contacts may also be fouled by a spreading lubricant film. Barrier films to control lubricant spreading offer promise of alleviating a variety of difficulties encountered with instrument oils.

Previously it has been pointed out that in hydrodynamic lubrication, load-carrying capacity is governed by sliding speed and oil viscosity. Additives to reduce friction and wear and to increase load-carrying capacity are available for instrument oils; these have been discussed in a previous section. Compatibility of active E.P. agents with certain synthetic oils should be determined before using such formulations. Of course, instrument-oil formulations should be fluid and homogeneous over the temperature range of application.

The modern equipment trend toward lighter weight, increasing compactness, and miniaturization has increased the demands on instrument lubricants. Many types of military equipment are required to start and operate at -65°F , and hence lubricants must have low freezing and/or pour points. In many instances, the power available to operate the mechanism is limited; therefore an oil with a low viscosity at -65°F (or -100°F) is demanded so that starting is almost instantaneous. Instrument miniaturization and modular construction has resulted in enclosed instrument packages of smaller size; consequently, heat losses through radiation and conduction have been decreased. Thus, higher operating temperatures are often demanded of the lubricant. Operating temperatures of 300°F are not uncommon, and in some applications above 350°F . Oils with small temperature coefficients of viscosity (high V.I.'s) are required for such applications.

Polymer thickeners or V.I.-improving additives may be used to produce such oils, but their use may result in deficiencies for certain applications. As V.I. improvers thicken the oil, base stocks with lower viscosities at the minimum operating temperature are required. In a homologous series of liquids, lower viscosity requires a lower molecular weight homolog; hence, the volatility will be increased. If a polymer-thickened lubricant is subjected to high shear rates in the mechanism, its viscosity will decrease, tending to approach that of the base oil, which may then be insufficiently viscous to support the loads.

An outstanding requirement for the lubrication of fine mechanisms is that the intervals between relubrication periods should be as long as possible; lifetime lubrication is frequently sought. Military equipment is often constructed with modular units having moving parts which are lubricated for life, or if not, the entire module is returned to a supply depot for relubrication and servicing. Examples of lifetime-lubricated equipment are the servo and synchro motors (537, 538, 540) that are important components of guidance systems, computers, range finders, and many other devices. Lifetime lubrication may impose stringent requirements on the oxidation stability and nonvolatility of the oil. In many applications only a few drops or milligrams of oil can be used to lubricate a bearing, in order to avoid increasing the starting torque required. Here the ratio of metal surface area to oil volume is quite large, and the catalytic effect of the metal on oil oxidation is significant. Although most instrument oil compositions contain anti-oxidants, the high metal/oil ratio imposes additional demands on the additive. Evaporation of the lubricant is also accelerated when it has a large surface area. The barrier-film technique, discussed earlier, would prevent uncontrolled spreading, thus reducing the surface area of the lubricant and its attendant evaporation rate. As the volume of oil is so small in such applications, cooling action of the lubricant is negligible and operating temperatures rise above those where bulk lubrication is used. Higher operating temperatures require better lubricant oxidation stability and adequate viscosity for satisfactory performance.

Since it is almost impossible to exclude moisture completely, as leakage or as a condensate, in many types of equipment, the oil should be stable to hydrolysis at operating temperatures. Hydrolytic stability is an inherent property of the fluid and cannot be enhanced by additives. Unfortunately, the converse is not true; both acidic and basic materials may catalyze the hydrolysis of esters, including the carboxylates, silicates, and phosphates. Additives that yield strong acidic products which catalyze ester hydrolysis are to be avoided in the formulation of compositions from such fluids. Since water may be present in lubricated mechanisms, it is important that the lubricant protect the lubricated metal parts from rusting. Metal carboxylates, sulfonates, and amine-acid complexes are commonly used rust inhibitors. Instrument oils must be compatible with the materials of construction; i.e., they must not corrode ferrous or nonferrous metals and alloys which they contact. Also they should not seriously degrade seals, elastomers, electric insulations, paints, and plastics in the system.

Since the lubricant and lubricated equipment often contact personnel, the lubricant should be nontoxic and should not have an objectionable odor. Foam stability can cause serious problems in certain applications; in addition to loss of lubricant by foaming, pump cavitation may result in an insufficient supply of lubricant to critical parts. Silicones, in a concentration of a few parts per million, are generally effective antifoam agents. However, they may cause spreading difficulties in applications where only a thin film of oil is used as the lubricant. An important military requirement is that all products qualified under a specific specification be compatible with each other.

A variety of base stocks are used in the preparation of instrument oil compositions. References 522, 524, 526, 527, 528, 531, 532, 533, 534, and 539 cover the specifications for some typical instrument oils. Symbols 2075 and 3042 oils of MIL-L-15016A (534) are refined petroleum fractions having viscosities 18 to 34 cS at 100°F, which are frequently used as general-purpose oils. Additives to depress the pour point and decrease

foaming are allowed. A low-temperature petroleum-base instrument oil, pour point -70°F , is covered by MIL-L-7870A (528). It contains an antioxidant and rust inhibitor. A polymer-thickened petroleum oil, pour point -70°F , is exemplified by MIL-L-644B (522). In addition to the V.I. improver, a rust inhibitor and antioxidant are needed to pass the specification requirements. Specification MIL-L-16958 (534) is for a petroleum oil containing an oiliness agent, an antioxidant, and an antirust agent. A dispersion of colloidal graphite in oil is covered by MIL-L-3572 (524). Synthetic-base instrument oils are covered in several specifications (526, 527, 531, 532, 539). MIL-L-6058A (526) and -11734A (531) relate to diester-base oils containing additives to improve oxidation stability and impart rust inhibition. MIL-L-6387A (527) is also a diester-base oil, but in addition to the additives used in the diesters mentioned previously, it contains a V.I. improver, and an antiwear and antifoam agent. A tetra alkyl silicate is covered by specification MIL-L-14107B (532) and a silicone by MIL-S-81087 (539). Additional instrument lubricants are covered by other military specifications and by proprietary compositions. For logistical reasons, the number of military instrument compositions must be kept to a minimum. The diversity of operating parameters, and the suppliers' insistence on guaranteeing the performance of their equipment only if operated with proprietary lubricants, make it difficult for the military to prevent the entrance of unnecessary instrument lubricants into the supply system.

2. NONSPREADING OILS

Nonspreading oils are widely used to lubricate equipment containing pivot bearings such as watches, clocks, fuse mechanisms, meters, and the like. It is important that the oil not spread from the pivot bearing to the escapement or hair spring, since the period would be altered, thus reducing accuracy. Early nonspreading oils were derived from animal and vegetable oils (porpoise jaw, black fish, olive, neat's foot, and bone oils) by various proprietary refining procedures, many of which were trade secrets. Reproducibility of these oils as regards spreading, oxidation stability (gumming and corrosion), and evaporation was a problem. Several manufacturers of watches initiated research to develop better oils. The Elgin National Watch Company fellowship at the Mellon Institute under Barker developed a number of nonspreading synthetic oils (64) that were reproducible and had improved properties. Methods for the laboratory examination of such oils were also developed (66). With the advent of the U.S. into World War II, it was realized that the available nonspreading oils were not suitable for use at the subzero temperatures encountered by aircraft instruments and controls. The Navy Bureau of Aeronautics arranged to support Barker's group on research, development, and production of nonspreading oils suitable for use down to -40°F . A satisfactory oil was developed, N22a (65), which is now covered by MIL-L-3918 (525). Improvements in this oil (525) are desired, particularly as regards fluidity and operability down to -65°F and stability at the higher operating temperatures.

Further development of nonspreading oils having specific characteristics has required an understanding of the laws governing liquid spreading. Research on the surface chemistry of the spreading of oils and other liquids on solids by Zisman and coworkers at NRL has resulted in an understanding of the various mechanisms involved in the spreading of liquids on solids.

A quantitative approach on spreading and wetting is best expressed in terms of Young's (788) definition of the contact angle (θ) between a drop of the liquid and a plane solid surface. When θ is not equal to zero, the liquid is nonspreading. When θ equals zero, the liquid completely wets the solid and spreads freely over the surface at a rate depending on the vapor pressure, viscosity, and surface roughness. Every liquid wets every solid to some extent; i.e., there is always some adhesion of a liquid to every solid. On a homogeneous solid surface, θ is independent of the volume of the liquid drop.

Wenzel (764) proved that the roughness (r) of a solid surface is related to the apparent, or measured, contact angle (θ') between the liquid and the solid and the true contact angle (θ) between the liquid and the solid surface, as follows:

$$r = \frac{\cos \theta'}{\cos \theta}.$$

Here the macroscopic roughness factor (r) is defined as the ratio of the true area of the solid to the apparent area. The effect of roughness cannot be ignored in practice, because surfaces having $r = 1$ are rare. Carefully machined or ground surfaces have values of r of 1.5 or more. Roughening the metal surface makes the apparent contact angle θ' less than the true contact angle θ ; thus, each liquid will appear to spread more when the metal surface is roughened.

Surface energy is an important concept in discussing wetting and spreading on solid surfaces. The surface free energy of liquids (excluding the liquid metals) is less than 100 ergs/cm² at ordinary temperatures. In contrast, hard inorganic solids have surface free energy from about 500 to 5000 ergs, the values increasing with increasing hardness and melting points. In contradistinction, most organic solids are much softer and have lower melting points, and surface free energies are generally under 100 ergs/cm²; examples are waxes and most solid organic polymers. It is convenient to refer to solids having high free surface energies as having "high energy surfaces" and solids having lower surface free energies as having "low energy surfaces."

Systematic measurements of the contact angles of a wide variety of pure liquids on various low-energy solid surfaces (89, 90, 91, 675, 793) and on high-energy solid surfaces (318) have revealed many interesting regularities. In general, a linear relation has been established between the cosine of the contact angle (θ) and the surface tension (γ) for each homologous series of organic liquids. This result led to the development of the concept of the critical surface tension of wetting (γ_c) for each homologous series of liquids; γ_c is defined as the intercept of the horizontal line $\cos \theta = 1$ with the extrapolated straight-line plot of $\cos \theta$ vs γ .

Figure 3 shows the critical surface tension of wetting (γ_c) for the n-alkanes on various low-energy surfaces. From the intercept of the graph in the figure, it is evident that γ_c is 18.5 dynes/cm for the family of n-alkanes on the surface of Teflon. Values of about 17 and 15 are obtained from curves B and C; that is, the introduction of perfluoromethyl groups as a side chain in the polymer reduces γ_c , the reduction becoming greater the higher the surface concentration of exposed CF₃ terminal groups. An adsorbed monomolecular layer of a perfluoro fatty acid (curves D, E, F) is an example of such a surface. Values of γ_c for such surfaces are therefore much lower than for surfaces comprised of only -CF₂- groups. The closer the packing of the aliphatic chains of the adsorbed molecules, the closer the packing of the exposed terminal CF₃ groups, and hence the lower the value of γ_c . The value of γ_c for a condensed monomolecular layer of perfluorolauric acid (curve F) is only 6 dynes/cm, and this surface is the least wetted by the alkanes (or by any other common liquid) yet encountered. It will be noted that of all the polymeric solids, the fluorinated polymethacrylate coating has the lowest value of γ_c (10.6 dynes/cm).

When $\cos \theta$ is plotted against γ for a variety of nonhomologous liquids, the graphical points lie close to a straight line or collect around it in a narrow rectilinear band. When rectilinear bands are obtained, the intercept of the lower limb of the band at $\cos \theta = 1$ is chosen as the critical surface tension, γ_c , of the solid. Although this intercept is less precisely defined than the critical surface tension of a homologous series of liquids, it is nevertheless an even more useful parameter because it is a characteristic of the solid only. The widespread occurrence of the rectilinear relationship between $\cos \theta$ and γ and the fact that these graphs do not cross one another has made it possible

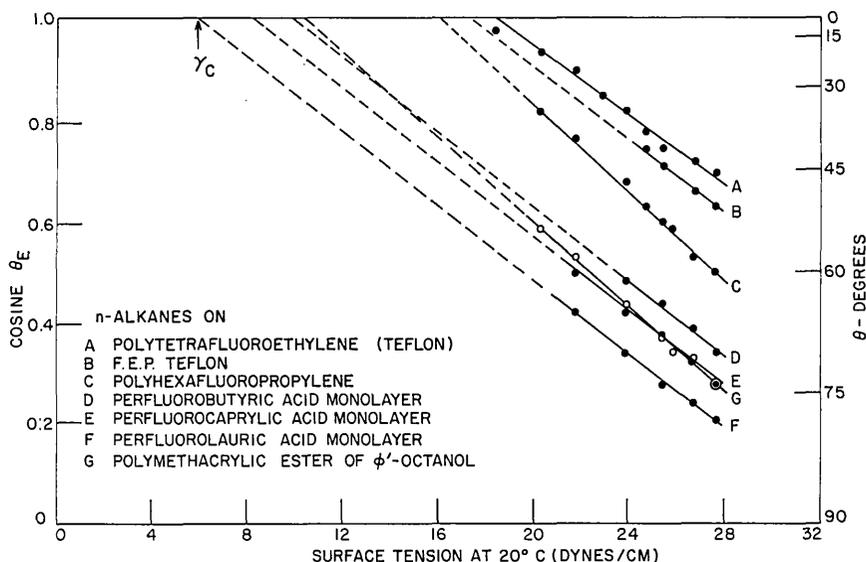


Fig. 3 - Critical surface tension of wetting

to use γ_c to characterize and compare the wettabilities of a wide variety of low-energy surfaces. In Table 11 are presented values of γ_c obtained from studies of the contact angles of a number of well-defined, low-energy, solid surfaces (675). In the first column is given the chemical constitution of organic radicals comprising the surface of the solid arranged in the order of increasing values of γ_c . Surfaces of the lowest energy are comprised of close-packed $-\text{CF}_3$ groups. Of the hydrocarbon surfaces, the one having the lowest value of γ_c (and hence the least wettability) is that comprised of close-packed $-\text{CH}_3$ (methyl) groups. A less closely packed arrangement, as in condensed adsorbed monolayers of high-molecular-weight fatty acids or amines, is characterized by a value of 24 dynes/cm.

The preceding background on the wettability of low-energy surfaces is very helpful in explaining the spreading of liquids on high-energy surfaces. Three classes of pure liquids are known to be inherently nonspreading on high-energy surfaces. The first class, the autophobic liquids (375), are exemplified by tri-*o*-cresyl phosphate and octyl alcohol. Each autophobic liquid is nonspreading because the first molecules of liquid to adsorb on the solid form a monomolecular film whose critical surface tension of wetting is less than the surface tension of the liquid. In short, each liquid is unable to spread upon its own adsorbed film. The second class of nonspreading pure liquids is comprised of numerous esters which, although able to spread completely on metal surfaces, are unable to spread on glass, silica, and sapphire because the ester hydrolyzes immediately upon adsorbing on the surface of these hydrated solid surfaces (318). Of the two products of the hydrolytic reaction, the one having the greater average lifetime of adsorption remains to coat the surface with a close-packed monolayer and so block any progress of the hydrolysis reaction. If this protective monolayer has a critical surface tension of wetting which is less than the surface tension of the liquid ester, nonspreading results; i.e., the ester is unable to spread upon the adsorbed film of one of its own hydrolyzed products. In the third class of nonspreading liquids, the surface tensions are so high and the adhesional energy so low that the energy of adhesion is less than that of cohesion. Liquids, like some of the chlorinated diphenyls, belong to this class.

Turning from pure liquids to mixtures, there are many ways by which the addition of a solute can make a liquid nonspreading on a high-energy surface. Any solute which is

Table 11
Critical Surface Tensions (γ_c) of Some Low-Energy Surfaces

Surface Constitution	γ_c (dynes/cm at 20°C)
Fluorocarbon Surfaces	
—CF ₃ *	6
—CF ₂ H*	15
—CF ₃ and —CF ₂ — (ratio 1 to 2)	16.2
—CF ₂ —CF ₃	18.5
—CH ₂ —CF ₃	20
—CFH—CF ₃	22
—CF ₂ —CH ₂ —	25
—CFH—CH ₂ —	28
Hydrocarbon Surfaces	
—CH ₃ (single crystal face)	22
—CH ₃ *	22-24
—CH ₃ (monolayer of polymethylsiloxane)	24
—CH ₂ —CH ₂ —	31
—CH— (phenyl ring edge)	35
Chlorocarbon Surfaces	
—CClH—CH ₂ —	39
—CCl ₂ —CH ₃ —	40
=CCl ₂ *	43

*Close-packed adsorbed monolayer.

able to adsorb on a high-energy surface to form a monolayer having a critical surface tension of wetting less than the surface tension of the liquid will prevent the liquid from spreading on that surface. Where the liquid involved is an oil, the solute is said to make the oil become "oleophobic" to the solid surface, and the solute is called an oleophobic additive (95, 96, 317, 675, 793). If the liquid surface tension is below 24 dynes/cm, the oleophobic additive must be a fluorocarbon or silicone derivative. If it is above 24 dynes/cm, a fatty acid or other paraffinic polar compound will do, and as the liquid surface tension becomes higher, the more readily can one use a branched-chain or cyclic hydrocarbon derivative as the polar solute.

In preparing nonspreading clock oils, it is obvious that there are many chemical routes. However, in practice there are severe limitations imposed because of other physical and chemical requirements of a clock oil. In general, the larger the contact angle of the oil, the less the spreading tendency. The adhesion energy W_{adh} of a nonspreading liquid on a solid is given by the classic Dupré relation (268):

$$W_{adh} = \gamma(1 + \cos \theta) + f_{sv}.$$

Here the term f_{sv} is negligible for nonvolatile liquids exhibiting nonzero contact angles (792). Therefore, the maximum adhesion of the droplet of oil occurs when γ is as large and θ is as small as possible. All of the useful clock oils have values of γ above 35 dynes/cm at 20°C and values of θ varying from around 5 degrees to less than 20 degrees.

The existence of oleophobic additives explains why many of the early clock oils were derived from porpoise jaw, black fish, bone, and olive oils, since such substances are rich in fatty acid esters whose slight hydrolysis releases fatty acids and alcohols capable of serving as oleophobic film-forming compounds. The NRL investigations have shown that there are numerous classes of oleophobic additives besides the saturated fatty acids, and, incidentally, have proved that pure oleic acid is not oleophobic to many common oils. The principal problems in obtaining nonspreading properties by the use of oleophobic additives are (a) the limited solubility in many oils, (b) the necessity of using very low concentrations of the additive so that θ will not be large and the adhesion poor, and (c) when θ is kept small enough to be below 15 degrees, the additive concentrations necessary are so low that the adsorption of the active ingredient on the walls of the containers may result in a significant decrease in oleophobic properties.

Synthetic clock oils can readily be found among the aromatic esters of aliphatic alcohols or acids (318); some have high enough surface tensions to be autophobic, and many are nonspreading because of their hydrolytic products. The introduction of aromatic rings in the molecular structure always increases the slope of the viscosity versus temperature curve, and hence decreases the temperature range over which the oil can be used. The difficulty is evident in the work of Barker et al. (64, 65, 66) and in the more recent work of O'Rear (576) and Gisser et al. (599). Singleterry et al. (67, 213) in a study of the control of oil spreading showed that by the proper choice of the additives, oils could be made nonspreading. However, an additive that makes one oil nonspreading may cause violent spreading in another. This anomalous spreading phenomenon is produced by surface-tension gradients resulting from adsorptive depletion of additive along the edge of the drop. Effective nonspreading additives include silicones, fluoroesters, amine-organic acid salts, high-molecular-weight organic acids, alcohols, or amines, and some oil-soluble soaps.

An unexpected result of the NRL study of spreading and wetting was to dispel an old widely held belief that a good lubricating liquid wets better and adheres more to a bearing surface than a poor lubricant. The ability of liquids to spread on metals has no necessary relation to their lubricating properties (793). Some liquids like tricresyl phosphates, which have exceptionally good boundary-lubricating properties, do not spread on clean metals; other liquids, like the dimethyl silicones, have very poor boundary-lubricating properties yet spread freely on all clean metals. The basic reason is that the molecular structural requirements for good spreading ability are very different from those for good boundary-lubricating properties (795).

The previously reviewed investigations of spreading and wetting make it possible to give a simple and fundamental explanation of the "epilame" treatment of Woog (779, 780) which uses a close-packed adsorbed monolayer of a higher fatty acid, such as stearic acid, to prevent oil spreading; such a film has a value of γ_c of 24 dynes/cm. Any oil or other liquid having a surface tension γ at 20°C greater than 24 would therefore be

nonspreading on such a monolayer. One can improve greatly on the "epilame" treatment by applying the knowledge of the laws of wetting. A methyl silicone resin coating on a solid surface can be prepared having a value of γ_c as low as 24 dynes/cm (792, 794). Such a coating is as effective as the stearic acid "epilame," but is more durable, since it is not readily dissolved by common cleaning solvents. "Epilame" films of fluorinated polymers, Teflon, FEP Teflon, and perfluoroalcohol ester of polymethacrylic acid (88) are also effective. Because these films have such low values of γ_c , their contact angle with the oil will be so large and the adhesion of the liquid to the coating will be so small that a slight jar is likely to detach the oil drop. This difficulty can be overcome by laying down the coating as a circular ring around the bearing to be lubricated (88). Since the nonspreading oil feature is obtained by the surrounding ring of resin, it is no longer necessary to consider nonspreading as an essential requirement of the oil. Hence, it is possible to employ one of the many available spreading-type lubricating oils which may have more desirable properties for the application under consideration.

VII. GREASES

The definition of a grease until recently was "A semisolid or solid combination of a petroleum product and a soap, with or without fillers, suitable for certain types of lubrication." Synthetic lubricating fluids, developed during and since World War II, offered a great variety of new liquid lubricant bases for the production of greases. Greases have been prepared from essentially all of the new synthetic lubricants. In addition to new base fluids, a great number and variety of gelling and thickening agents have been developed and used in the production of lubricating greases. These new technologies have necessitated a new definition for lubricating greases to cover the much broader scope of lubricating liquids and thickening agents. A grease is now considered to be a solid or semisolid lubricant consisting of a thickening agent in a liquid lubricant.

Grease lubrication has advantages over oil lubrication for certain applications (121, 277, 278). Probably the greatest advantage of grease over oil lubrication is the much longer interval between relubricating periods. In fact, many mechanisms are lubricated for their useful life with greases. Grease-lubricated bearings can operate at higher temperatures than those lubricated with oil, since the grease adheres to and does not flow away from the bearing surfaces as rapidly as oil. Grease also acts as a seal, preventing the entrance of dirt, dust, and other extraneous material into the bearing. Probably the major disadvantage of lubricating grease over oil is its greater viscosity and starting torque, particularly at low temperatures when the power available is limited.

Greases can be prepared with varying hardnesses, and they are classified according to their consistencies as measured by their worked penetration (ASTM Method D217). In 1963 (13) several softer grades were included in the classification, which is shown in Table 12. Like the SAE crankcase oil-classification system, the NLGI grease-classification system gives no indication as to the suitability of a grade for an application other than its rheological property.

Boner (121) in his excellent review on greases covers the state of the technology up to 1954. We shall emphasize the progress that has occurred since then. Greases have been prepared from just about all of the synthetic fluids covered here and those described in Ref. (361). Many of the greases prepared from the newer synthetic fluids have had no application. However, it was demonstrated that grease-type materials could be prepared using known thickening agents.

Thickening agents are generally divided into three categories or types:

Table 12
NLGI Grease Classification

NLGI Grade No.	Worked Penetration at 77°F (ASTM D217)
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

1. Soap type
2. Complex type
3. Nonsoap type.

Soaps derived from fatty acid salts of practically all metals (121) have been investigated as possible thickening or gelling agents for greases. It was found empirically that some metal soaps did not effectively gel petroleum oils. The inability to correlate the parameters of soap-solvent systems has resulted in a large body of poorly organized information. Pilpel (596) has reviewed the properties of organic solutions of heavy metal soaps and greases made from them. He emphasized that trace amounts of additives and impurities affect properties of soap-oil systems and that correlations based on properties of pure chemicals are impossible. Physical properties of organic soap solutions were reviewed

with emphasis on micellar theory. Soap-oil systems may be classified into two types -- micellar dispersions and crystalline dispersions. The first type, or oil-soluble soaps, is exemplified by the branched chain carboxylates and petroleum sulfonates, which are mixtures of branched-chain isomers and homologs. This type of soap is not useful in preparing greases because of its high solubility and limited gelling ability.

Metal soaps of straight-chain carboxylic acids generally give crystalline dispersions in nonpolar solvents and hence are frequently used as thickening agents for the production of lubricating greases. The solution of crystalline soaps in nonpolar solvents (117) first involves the swelling of the crystal lattice. As the critical solution temperature is approached, the swollen soap disintegrates or swells without limit. In a study of lithium stearate-hydrocarbon systems, Cox (222) showed that at least three major phase transitions in the solid state of the soap occur as the grease is heated. He also observed that the phase transition, waxy to liquid crystal, was a function of the molecular weight of the oil. Dropping points of lithium soap greases have been observed to be a function of oil viscosity within a given oil family (22). Suggitt (717) confirmed Cox's findings about lithium stearate transitions, and in addition he found that lithium soaps of certain higher carboxylic acids may have as many as four transitions in the solid state. Phase transitions were nearly independent of soap concentration. Suggitt (717) concluded that in lithium stearate-hydrocarbon systems, the phase diagram is essentially that of the soap diluted by an inert fluid.

More recent work at NRL by Bolster and Little (117) showed that the solvent influences the critical solution temperature of soaps. Their data suggest that if the grease dropping point is taken as a measure of the final solid-state phase transition, then the solvent exerts a parallel effect on both the critical solution temperatures and the last solid-state transition. They were able to show that the dropping point was a function of the solubility parameter (381). Dropping point has been observed to be characteristic for each type grease, but it has no general significance as to maximum operating temperature (254) of the grease. By using a calibration curve of grease dropping point versus the solubility parameter of known solvents, they could calculate the dropping point of the same soap in other solvents. This method will give useful information about greases prepared from new synthetic fluids. Although the method is strictly applicable only to pure solvents, it is possible to estimate the solubility parameter of commercial cuts of petroleum oils. Calculated dropping points of lithium stearate-petroleum oil fractions using estimated solubility parameters agreed quite well with the experimentally determined values. The applicability of the method to solvents of high polarity has not been determined; however, nearly all lubricating fluids used for the preparation of greases are liquids of low polarity. The introduction of polar groups into the soap-oil system

may cause unusual phase behavior (756a). Thus, the introduction of water or polar additives may have a significant, but as yet unpredictable, effect on the structure and characteristics of soap greases.

Acid chain length, configuration, and structure have an important bearing on the properties of the soap derived from it. As has already been mentioned, soap phase transitions in greases are related to fatty-acid chain length (717). It is important that soaps used in the production of greases be of uniform composition, otherwise the greases may vary in property from batch to batch of acids. Gas chromatography (188) has proven a useful method of maintaining close control of the fatty-acid components used in grease production. Mixed metal soaps are also used for grease production. The structure of grease derived from two different soaps is usually similar to that of the grease prepared from the predominating metal soap. But modifications of normal structure are sufficiently common so that it is not possible to predict the structure accurately. If more than two metal soaps are used, the system is very complicated and predictions are not possible.

It is well known that the particle size and shape of the thickener will affect grease properties. The formation of grease thickeners by reactions "in situ" or by precipitation from hot solutions is a crystallization process involving crystallization and growth. The rates of the reactions are proportional to the diffusion rate of the crystallizing molecules and the degree of supersaturation, and inversely proportional to the surface free energy of the nuclei. Panzer (582), after making some simplifying assumptions, derived crystallization equations in which nucleation and growth rate could be expressed in terms of: E = interfacial free energy between embryo of nucleus and supersaturated solution; S = supersaturated ratio; and T = temperature. He considered the effects of (a) temperature, (b) thickener concentration, (c) oil viscosity, and (d) oil composition and surfactants. Factors affecting interfacial free energy far outweigh variations in temperature or supersaturation. Thus, the introduction of surfactants or polar additives can radically change the properties of a grease derived from a given soap. This agrees with conclusions of Tausch (730). Panzer's equations gave excellent qualitative agreement with experimental data reported in the literature, and they should be useful in indicating what changes should be made in grease formulation and production to achieve a desirable thickener particle-size distribution or shape.

The structural skeleton of soap greases consists of crystallites of higher fatty-acid soaps. Much has been learned about the skeleton structure of greases using electron photomicrography. Vinogradov and Sinitsyn (755) reviewed the papers on the electron-microscope investigation of greases through 1960. They considered the various techniques used by investigators for preparing specimens for study: suspensions, smears, sectioning, aerogels, and embedding. These investigations established that the dispersed-soap phase in most cases consisted of ribbons, needles, or rod-shaped soap crystallites. Electron photomicrographs of dispersed phases are shown (121, 755). Structural skeletons of greases may be formed by highly anisometric particles and particles of symmetric shape. This result shows that the most important factor in the building of the structural skeleton is not the shape of the dispersed-phase particles, but their size and ability to aggregate.

Correlations of the effects of various factors on grease structure have been summarized (755). Water stabilizes calcium greases and promotes the formation of fibers 400 to 500 Å in diameter. The addition of calcium acetate and stearic acid promotes crystallization of the calcium soap as flat ribbons. Glycerine and certain polyesters promote the growth of sodium soap fibers, whereas petroleum resins and high-molecular-weight polymers inhibit fiber growth. In the presence of free alkali, soap crystallites were quite small as compared to those formed in neutral media. Free acidity had little effect on fiber size or shape. Raising the viscosity of the petroleum oil greatly increases the length-to-width ratio of lithium soap fibers. The influence of both the soap anion and

cation on structure has been studied with the electron microscope; pertinent references are given by Vinogradov and Sinitsyn (755). In general, very rapid cooling results in broken soap fibers.

Mechanical shearing breaks down the grease structure; the soap fibers decrease mainly in length. Sodium soap fibers on prolonged shearing split axially. Sodium and lithium soap fibers are more stable to shear forces than those of calcium soaps. The recrystallization of sheared soap fibers on resting of the greases depends upon the nature of the soap particle; thus no generalizations can be made. Both oxidation and radiation produce considerable breakdown in structure of the dispersed soap phase. Therefore, nonsoap thickeners have received the major emphasis in the preparation of greases for extreme temperature and radiation environments.

By an electron-microscope study of serial sections of very thin soap thickeners, Wilson (772, 773) was able to reconstruct their three-dimensional space structures. Information was obtained on the state of aggregation of the soap fibers, and possible mechanisms for network formation indicated. The lithium-calcium soap fibers had a tendency to associate in bundles, but the association was weak. There were relatively few junctions between fibers. Lithium 12-hydroxystearate fibers were associated more strongly, and there were a fairly large number of junctions between fibers. However, there were a number of fiber ends from which very fine fibrils had grown in such a way as to suggest the possibility that they were active centers of crystallization. Fibers of the calcium-lead complex thickener had a large number of junctions; more than two fibers may have been involved in certain junctions.

Rooney and Bird (629) described the preparation of carbon replicas for electron-microscope studies. Electron micrographs of the carbon replicas gave more contrast and revealed greater detail of the soap fiber than those obtained by direct examination. Criddle (229) suggested that the particle-size counter technique be used in conjunction with the electron microscope to obtain a better picture of particle size distribution of thickeners in greases. The electronic counter emphasizes the larger particle sizes, whereas the electron microscope emphasizes the smaller. He found that each grease had a characteristic particle-size distribution and that the average size increased with increasing thickener concentration. Wiberly et al. (766) reported that infrared techniques gave useful information on the state of grease thickeners during processing and also on the effect of additives on grease structure.

Sisko and Brunstrum (686) suggested that information as to the size, shape, concentration, and dispersion of particles in the disperse phase of a grease could be obtained by a study of the permeability of the continuous liquid phase. From Darcy's Law, they derived an equation for permeability,

$$B = k \frac{d \log h}{dt} .$$

Plots of $\log h$ versus time were linear, as predicted. Exploratory studies indicated that permeability could be a useful tool in grease research. Eubank et al. (155, 281) showed that grease permeability was characteristic of the structure of the thickener particles for both soap and nonsoap thickeners and obeyed Darcy's flow equation. They concluded that permeability represented the areas of the largest pores through which essentially all flow occurred. Less than 25 percent of the oil in place in a grease was susceptible to flow under the force gradient used. This result was interpreted to mean that each fiber was surrounded by a relatively thick layer of lubricant bound to it by forces large enough to impede flow.

The Volds (756b) presented the idea that the structure of soap greases could be assembled from building blocks joined either corner-to-corner or face-to-face. The type

of assembly had a pronounced effect on grease properties: bleeding, penetration number, softening, etc. Different amounts of energy were involved in each type of assembly. Differential thermal analyses of two lithium-base greases whose preparation differed only as to the rate of cooling showed energy differences which gave preliminary confirmation of their new idea.

Complex greases are those prepared by mixing the soap with a low-molecular-weight salt of an acid or base. This class has been further divided into (a) greases in which the soap and additive may be mixed in any proportion and whose association is an adsorption phenomenon, and (b) greases in which the thickener is a chemical combination of soap and additive. Some investigators (14, 461) have offered x-ray diffraction evidence that new compounds were formed on heating a grease derived from a soap and its acetate. Panzer (583) studied the diffraction patterns of (a) calcium oleate and calcium acetate, and (b) barium oleate and barium acetate, before studying the complex greases prepared from them. He showed that calcium acetate forms at least two hydrates, three anhydrous modifications, two chemical compounds with acetic acid, and a compound with acetic acid and water. Published x-ray data on calcium soap-acetate complex greases can be accounted for by the presence of the starting materials and the modifications mentioned above. Evidence was also obtained that barium acetate formed chemical compounds with water or acetic acid. It was concluded that the soap and acetate did not form chemical compounds. The evidence suggested that strong adsorption interactions between the soap and acetate, developed during the preparation of the grease, accounts for the properties of these complex greases rather than chemical reactions, as had been previously reported. Complex-type greases amount to more than half of the grease produced (121). Because of their improved properties, complex greases are suitable for a variety of applications as multipurpose greases (461, 598).

Nonsoap materials have been extensively investigated as grease thickeners, primarily because of their inertness to oxidation and radiation and their high melting points (40, 41, 169, 226, 263, 285, 352, 422, 461, 482, 499, 506, 518, 519, 562, 583, 736). Diverse materials have been used as gelling agents, including organic pigments, organic bases and derivatives, polymers, carbon blacks, clays, metal salts, and others. As new synthetic-lubricant fluids have become available, greases have been prepared from them using a variety of gelling agents. The inability of certain of these agents to gel some fluids led to investigations of the mechanism responsible for gelation. These studies have shown that coupling agents (518) are required to assist the oil in wetting natural clay and silica thickeners and in preventing breakdown of the structure by preferential wetting of the thickener by water. To facilitate the dispersion of treated bentonite or "Bentone" thickeners and subsequent gelation, low-molecular-weight polar organic compounds (alcohols and ketones) were used as dispersion aids (286). Granquist et al. (347, 422) concluded that electrostatic effects were important in the role of a dispersant in the gelation of hydrocarbons, and they advanced a mechanism based on ionic double-layer theory. Further work on coated bentonite suspensions in substituted benzenes in the absence of a dispersant led them to attribute the stability to a combination of dielectric solvation and double-layer formation.

Chessick et al. (195, 196, 198, 786) tried to organize and systematize the information on nonsoap thickeners. The influence of particle size, shape and solubility were studied relative not only to the thickening action, but also to the properties of the resultant grease. Flocculation of solids (polar and nonpolar) in both polar and nonpolar liquids was attributed to attractive and repulsive forces at the solid-liquid interface. It was concluded that flocculation may result from primary (van der Waals) attractive forces, primary and secondary, or from primary and tertiary attractive forces. Secondary attractive forces were defined as those due to an adsorbed film of one or more monolayers on the solid particle, and tertiary forces were those due to additives such as triethanolamine, ethylene diamine, citric acid, etc. Reduction or deflocculation is a result of steric hindrance, adsorbed lyosphere, and entropic repulsion or double-layer effects. Martinek

and Klass (500) rejected the flocculation mechanism of Chessick (195, 196) where individual silica and other inorganic particles are joined through water bridges to form a porous structure. Their rejection is based on the evidence that (a) there is a quick regeneration of structure after shearing; (b) dilution of the grease with oil does not destroy the structure even after shearing; (c) silica thickeners containing no physically adsorbed water form stable grease structures. They contend that chemically bound water, i.e., the silanol content of the silica surface, is of primary importance. They proposed that the double-layer repulsive forces were applicable in nonaqueous systems and were sufficient to prevent sedimentation, and therefore concluded that interparticle distance, surface potential, and conductivity of the medium were of major importance in the development of nonsoap greases.

Chessick and Christian (197) studied organic nonsoap thickeners, principally the arylureas. A variety of liquid substrates were gelled with them, and their results led to conclusions about the properties of the reactants and products which govern particle growth and stability. Some of the conclusions are similar to those governing the growth and properties of soap crystallites. More recently, Traise (736) discussed the chemistry of polyurea grease thickeners. Arylurea thickeners are generally prepared in situ by reacting an aryl isocyanate with a primary amine. The dispersion was heated until it acquired the requisite properties. It was postulated that the urea dissociation and disproportionation to the amine and isocyanate is followed by random recombination and the attack by the free amine on urea molecules to give polymer chains. Polyurea greases were prepared from both petroleum oil and DC-550 silicone fluid. Changes in the particle size of the polyureas on heating were followed by electron microscopy. Other polymeric materials have been reported as grease thickeners, notably polyethylene (512) and polytetrafluoroethylene (516). The latter grease, which was derived from perfluorotrialkylamine, was developed because of the need for a lubricant inert to missile fuels and oxidizers.

Greases are non-Newtonian fluids; that is, their viscosities are not independent of the shear rates. Non-Newtonian materials are further subdivided into classes: plastic, pseudoplastic, dilatant, thixotropic, and rheopectic. A definite minimum stress or force must be applied to a plastic before it will flow. A pseudoplastic fluid has no yield point, but its apparent viscosity decreases with increasing shear rate. At very high shear rates pseudoplastics exhibit Newtonian behavior. A dilatant fluid increases in viscosity with increasing shear rate. The apparent viscosity of thixotropic and rheopectic fluids depends not only on the magnitude of the shear rate but also on the length of time during which the shearing forces are applied. Thixotropic fluids increase and rheopectic fluids decrease in viscosity with increasing shear times. Upon removal of the shearing stresses, the fluids tend in time to revert to their original viscosities. Since the viscosity of a non-Newtonian fluid is dependent upon the shearing forces acting upon it, apparent viscosity determinations at several shear rates are required to characterize it as regards type and to obtain its apparent viscosities over the shear rates encountered in service. In addition to non-Newtonian behavior, greases exhibit viscoelastic properties. Viscoelastic properties exist when the shear rates are sufficiently high to produce non-Newtonian effects. An enormous amount of work has been expended on studying the rheological properties of greases. Flow equations for greases have been derived from both empirical and fundamental approaches and correlations attempted between rheological properties and composition (77, 78, 157, 158, 159, 160, 230, 273, 282, 283, 308, 309, 310, 326, 362, 363, 364, 365, 377, 392, 460, 500, 520, 553, 566, 586, 616, 631, 685, 687, 743, 763, 784).

Oxidation characteristics of grease are of interest in relation to storage stability and service properties. It has been shown that soap-base greases are more labile to oxidation than the soap or oil (343, 559). It was postulated that grease oxidation is catalyzed by the soap, probably by adsorption of inhibitors from the oil onto the soap crystals. The catalytic effects of soaps on oxidation were found to be in the order lithium > sodium

> potassium > barium > magnesium > calcium > aluminum. Any excess base present will retard oxidation, and excess acid will accelerate oxidation. No correlations between oxidation stability and service performance have been obtained, but relationships between storage stability and oxidation tests have been advanced. More work on the oxidation mechanisms of both soap and nonsoap type greases is needed for a better understanding of grease performance.

Godfrey (339) observed that the friction characteristics of soap greases varied with the nature of the soap and temperature. He suggested that differences in the frictional characteristics of a soap grease below their melting points was a function of the shear strength of solid soap film. Frictional characteristics above the soap-melting points was due to chemisorbed films. Since soap greases have lower frictional properties than the base oil, the reduction in friction was attributed to the soap. Frictional characteristics of greases prepared from inorganic thickeners such as silica, bentonite, calcium carbonate, and calcium hydroxide did not decrease on heating. Wear characteristics of oxidized soap greases, as measured in the Four Ball Wear Tester, varied with the nature of the soap and degree of oxidation (559). Variation in wear with different soaps was attributed to the chemical nature and surface characteristics of the soap. The oxidation product causing wear was the alcohol-soluble fraction which was a mixture of carbonyl compounds.

The use of grease for the lubrication of military equipment is increasing (173). Current policies are to eliminate nonspecification items and to combine specifications so as to reduce the number of items in the supply system. Calhoun (173) lists the current Military Grease Specifications and gives the volumes purchased for certain periods. Although considerable progress has been made in understanding the parameters that contribute to grease formation and in controlling the variables in grease manufacture, it is not yet possible to correlate grease structure and composition with service performance. For example, grease bleeding cannot be related to type and concentration of soap, oil viscosity, temperature, or pressure (174). The final criterion is the performance of the grease in actual equipment. Thus, the indiscriminate consolidation of specifications based on the similarity of grease properties could lead to performance difficulties with some equipment.

The Department of Defense research program on greases includes that at Rock Island Arsenal on:

1. Permeability-coefficient relations to porosity as influenced by thickener concentration, particle size, shape, and structure
2. Phase changes of soap thickeners with temperature
3. Grease oxidation stability
 - a. Dynamic and static tests
 - b. Mechanism studies
 - c. Identification of oxidation product adversely affecting wear characteristics
4. Effect of grease composition and shear rates on chemical stability
5. Additive effectiveness and compatibility — role of acidity and basicity on corrosion inhibition
6. Resistance of grease lubricated metal combinations to fretting.

Pittman-Dunn Laboratory program includes:

1. Instrument greases
2. Additive compatibility — interaction of rust inhibitors with thickeners.

Marine Engineering Laboratory program includes improved shipboard greases:

1. Factors contributing to noise
2. Limits of bearing size and speeds
3. Lifetime grease lubrication
4. Effects of vertical versus horizontal bearing mountings on grease lubrication.

Air Force Materials Laboratory program includes:

1. Evaluation of grease for Air Force applications
2. Contract research
 - a. American Oil Co. — high-temperature stable greases suitable for use at 10^{-11} torr
 - -65 to 400°F type greases
 - 65 to 900°F type greases
 - b. Gulf Oil Corp. — high-temperature greases for high-speed ball and roller bearings
 - c. Lehigh University — basic factors in the formation and stability of nonsoap greases
 - d. Dynamic Science Corp. — rheology of silicone fluids thickened with boron nitride

The Bureau of Naval Weapons program includes evaluation of greases for various applications.

The Department of Defense program on greases includes:

1. Fundamental research on the relationships between grease composition, properties, and structure
2. The empirical evaluation of greases for military applications.

The Department of Defense research program reflects the state of knowledge on greases. Although knowledge on the factors affecting grease properties and structure is increasing, the final criterion of the suitability of a grease is its satisfactory performance in the equipment to be lubricated.

VIII. GENERAL TRENDS

The general military trend toward reducing the size of motors and mechanisms and increasing their power is expected to continue. To a lesser extent this trend will be evident in many areas of industrial effort. This trend will result in increased operating temperatures, speeds, and loads. As a consequence, lubricants having improved oxidation stabilities, lower evaporation rates, and higher load-carrying capacities will be required to meet the more demanding operating requirements. The development of improved lubricants and bearings will be aided by advances now taking place in our understanding of elastohydrodynamic and quasi-hydrodynamic lubrication.

The adhesion theory of friction has recently been greatly revised, but the basic concept of friction and wear resulting from adhering-surface asperities has been reaffirmed. Additional information is needed to determine more accurately the real area of contact, mode of asperity deformation, and role of junction growth. A more complete understanding of the influence of the boundary films in limiting junction growth may be expected. Recent advances in decreasing the boundary friction of polymer solids by the incorporation of surface-active materials will be given increasing attention. The use of reactive gases to lubricate metals through their reaction only at friction-induced "hot spots" to form protective films will also receive much attention.

Solid-film lubricants are being used more frequently for a large variety of applications. Graphite, MoS_2 , and polytetrafluoroethylene (PTFE) are the most widely used materials. Graphite has the highest service temperature in air but is ineffective in high vacuum or at cryogenic temperatures. Molybdenum disulfide and PTFE are particularly suitable for use in near vacuum. Of the many lamellar solids investigated as potential dry-film lubricants, MoS_2 , appears to be the best. Interest in lubrication of space vehicles will continue unabated and can be expected to stimulate further research on solid-film lubricants. Binders for solid-film lubricants will be developed with improved ability to adhere at higher temperatures. Ball-bearing retainers and gears will be fabricated from composite materials which contain a metal matrix and a solid lubricant. New ceramics and cermets designed for use as high-temperature bearing materials can also be expected.

Petroleum oils are expected to continue to be the major source of lubricants. Advances in petroleum refining will make possible the large-scale production of base stocks having more uniform and better characterized compositions, and greater freedom from the less desirable hydrocarbons and polar impurities. Such fractions will be more responsive to the action of additives such as antioxidants.

Although progress is being made in understanding how the various lubricant additives function, much more needs to be learned about the mechanisms. Interactions with other additives and with different types of base fluids also need further attention. The trend toward operating temperatures above 400°F requires the development of new types of antioxidants. Synergistic combinations of antioxidants still appear to offer a fruitful field; however, large gains in maximum operating temperatures can not be expected by the use of combinations of presently used antioxidants.

Because of the numerous special-purpose oils which must be stocked to care for present military and industrial uses, multipurpose oils are needed which will not sacrifice essential properties. These oils would help simplify present military logistical problems and decrease industrial costs and inventories. Particular attention needs to be given to lubricants for instruments and small mechanisms. The use of fluorocarbon barrier films around bearings will assist greatly in narrowing the variety of such oils now used.

The inadequacy of laboratory and bench tests for determining and rating lubricant properties continues to retard the development of new and improved lubricants. Because of the number and complexity of mechanisms and reactions involved in lubrication and lubricant deterioration, it does not appear probable that simple laboratory tests can be developed that will satisfactorily rate lubricant properties.

Although the volume of synthetic lubricants will be comparatively small as compared to petroleum oils, their variety, industrial importance, and critical military applications will continue to grow. Reliable rules and generalizations are available to guide the synthesis and development of promising organic lubricating liquids having specific properties. It should be remembered that the structural requirement for the optimum in a specific property may be diametrically opposite to that required for another desirable property. Compromises to obtain a liquid (or mixture) with the best combination of properties requires knowledge about the operational and environmental parameters. For example, a number of synthetic oils are stable or can be stabilized against oxidation at temperatures up to 400°F. If the applications also require oils with high V.I.'s and small fluidities at subzero temperatures, the number of candidate oils are considerably reduced. Synthetic oils having these properties include certain silicones, polyolefins, carboxylate esters, silicate esters, and perfluorinated liquids.

An oxidation stability requirement of 500°F greatly restricts the number of candidate oils. The more promising materials are certain stabilized silicones and the perfluorinated liquids. A relaxation of the V.I. and subzero fluidity requirement would allow the consideration of aromatic carboxylate esters, silicate esters, aromatic hydrocarbons, aromatic ethers, and resonance-stabilized heterocyclic structures and derivatives. An operational requirement of 600°F would eliminate the carboxylate and silicate esters from consideration. Of the candidate oils for consideration at 600°F only the stabilized silicones and perfluorinated liquids have high V.I.'s and low pour points. At 700°F, thermal stability becomes of increasing importance and is limiting for certain synthetic organic compounds. Information is needed on the oxidation stabilities of resonance-stabilized synthetic oils at 700°F. It is unlikely that purely organic compounds will have the requisite oxidation stabilities at temperatures above 700°F to be considered for bulk lubrication. Possibly they could be used in a single-pass lubrication system. At temperatures above 700°F, solid lubricants, metallo-organics, and inorganic compounds will have to be considered.

Since World War II great strides have been made in developing new nonsoap thickeners for the preparation of lubricating greases from both petroleum and synthetic oils. More information is needed as to how additives, impurities, and fluid types influence the formation, structure, and stability of the thickener matrix. To reduce the number of greases in the supply system, multipurpose greases are desired. Since such greases will probably contain a variety of additives to enhance certain properties, information is urgently needed about additive interactions and their effects on grease properties and performance.

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13. ABSTRACT <p>The progress made during the last decade in advancing the knowledge of the science and application of lubricants is reviewed and summarized. Advances have been made during this period in understanding the fundamental mechanisms operable in friction, wear, and lubrication. The adhesion theory of metallic friction has been extended to include high polymers, hard oxides, and brittle materials. The mode of deformation, real area of contact, and the role of junction growth between sliding solids has received more attention. Systematic studies of adhesive and abrasive wear have increased the understanding of the wear process. Considerable progress has been made in the development of solid-film lubricants.</p> <p>New synthetic liquid lubricants, having unusual physical properties, have been prepared, studied, and evaluated for special applications. Emphasis has been placed on synthesizing lubricants which are stable at increasingly higher temperatures.</p> <p>Although the mechanism by which additives enhance or impart special properties to liquids is now better understood, much more needs to be learned about the interaction among the many types of additives compounded in a modern lubricating oil. Frequently an additive improves one property at the expense of another. Progress has been made in developing new nonsoap thickeners for the preparation of greases from both petroleum and synthetic oils.</p> <p style="text-align: right;">(Continued)</p>			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Lubrication Friction theory Wear theory Boundary lubrication Hydrodynamic lubrication Lubricant properties Lubricant additives Synthetic lubricants Greases Solid-film lubricants Automatic transmission fluids Crankcase oils Gear oils						

ABSTRACT (Continued)

New environmental conditions and more extreme operating requirements have created many new lubrication problems. Lubricants may be subjected to high vacuum, radiation, cryogenic or burning rocket fuel temperatures. Attention is called to areas in research and development where solutions are needed.