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INTERDISCIPLINARY APPROACH TO LIQUID LUBRICANT TECHNOLOGY

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NTERDISCIPLINARY APPROACH TO LIQUID LUBRICANT TECHNOLOGY

Proceedings of a NASA-sponsored symposium held
January 11-13, 1972, in Cleveland, Ohio

Edited by P. M. Ku
Southwest Research Institute

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Foreword

THESE PROCEEDINGS, as well as the proceedings from previous symposia, are the result of a program attempting to combine an interdisciplinary subject with interdisciplinary lecturers and audience. The objective of such a combination was to apply a new approach to the solution of unresolved problems in the fields of lubrication, wear, surface damage, fretting, and fatigue. The publication of the proceedings of these symposia has provided extremely useful reference material for all those with an interest in these problems, whatever may have stimulated such interest. Before the program can be considered a success, however, one must study the results. For example, have the basic scientists applied their specialized knowledge and skills to the problems? In general, the present answer to this question appears to be in the negative. Perhaps, however, the basic scientists have been motivated to start work along these lines. Time is required to judge the continued interest and fruitfulness of such efforts.

Since motivation is all important in determining effort in any particular area, one must study the motivating factors. These factors (requirements) include (1) an abiding interest in the problem, possibly from an intriguing presentation; (2) a reasonably favorable prognosis for success in application of one's research efforts in this area; and (3) financial support for such work. With the three symposia presented to date, it is believed the first of these requirements has been successfully accomplished. The second and third requirements have, however, apparently not been met to such an extent that many basic scientists have shifted their labors to the new field. Perhaps time will show that some have, in fact, picked up the new work and are making progress toward successful accomplishment of some of the tasks. Until such time, we can only state that intriguing problems have been brought to light for the scientific community to see.

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Preface

THIS PUBLICATION presents the proceedings of the fourth and, by current plan, the last interdisciplinary lubrication conference sponsored by the National Aeronautics and Space Administration (NASA). This conference series grew out of a realization that lubrication is a highly complex and multidisciplinary subject and that satisfactory solutions to many advanced lubrication problems require the joint efforts of lubrication scientists and engineers, systems design and development engineers, as well as specialists in many basic sciences. Such a synthesis of talents did not exist in a real sense 6 years ago when the conference series was being planned and, despite improvements, is now still more the exception rather than the rule. In any case, it was felt that one of the prerequisites to effective cooperation was an effective dialog, not only between the lubrication profession and the related scientific and engineering professions but also among those within the lubrication profession itself.

To stimulate the interdisciplinary dialog and also keep the deliberations within reasonable bounds, it was decided to deal with the subject matter in a series of meetings, primarily in the form of coordinated symposia. These symposia would differ from the conventional types of meetings principally in two respects. First, they would emphasize the critical evaluation of the state of understanding and needed research in a planned and comprehensive manner, rather than the presentation of individual research papers. To accomplish this end, strong reliance would be placed on invited lectures, which would be aimed at covering the various topics in both breadth and depth to provide suitable starting points for subsequent discussions. Special attention would also be given to the selection of the lecturers, not only for their expertise in their respective fields but also for their general interest in the related disciplines. Second, these symposia would emphasize an interdisciplinary approach and the active participation by all attendees. Meaningful and provocative discussions would be considered just as important as the lectures. Accordingly, attendance would be by invitation only. The audience would be limited to a manageable size, composed ideally of 25 percent basic scientists, 50 percent lubrication scientists and engineers, and 25 percent systems design and development engineers. To encourage and facilitate discussions, preprints of the invited lectures would be mailed to all preregistrants approximately 1 month ahead of each meeting, with a special solicitation for discussions to be submitted either in advance or shortly after the meeting. Moreover, at least as much time would be allotted at each meeting for the presentation of the discussions as for the lectures. All written discussions received after each meeting would be forwarded to the lecturers for closing remarks. The final proceedings of each meeting, including the lectures, the discussions, and the lecturers' closures, would then be assembled, edited, and published.

The first meeting of the series, a symposium held in San Antonio, Tex., on November 28–30, 1967, was devoted to a broad and critical appraisal of the level of understanding and needed research in the area of sliding friction and wear under unlubricated and boundary lubrication conditions.[1] The second meeting was a workshop held in Cleveland, Ohio, on November 19–21, 1968, which again emphasized unlubricated and boundary-lubricated sliding friction and wear but attempted to focus attention on some selected theoretical and practical problems by discussing in small working groups their implications and possible methods of attack.[2] The third meeting, held in Troy, N.Y., on July 15–17, 1969, was a symposium concerned with the lubrication of heavily loaded machine elements in a combined rolling and sliding situation.[3]

This volume records the proceedings of the symposium on liquid lubricant technology, held at the NASA Lewis Research Center on January 11–13, 1972. Among the 126 participants were 17 from Great Britain; 3 from Canada; 2 each from France and the Netherlands; and 1 each from Israel, Italy, Norway, and West Germany, representing a total of 22 percent international participation. There were 11 invited lectures, 4 of which were given by British specialists, who accounted for a 36-percent international participation. These lectures, along with 60 discussions, which include an international participation of 45 percent, as well as the lecturers' closures, are published herein.

The NASA interdisciplinary lubrication conferences were organized under the guidance of a Steering Committee, which has attempted to evaluate the contributions of each meeting held and make recommendations to NASA regarding the desirability of any followup meetings. The Committee held a meeting at the end of this last symposium, at which the

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[1] Ku, P. M., ed.: Interdisciplinary Approach to Friction and Wear. NASA SP–181, 1968, 486 pp.

[2] Bisson, E. E.; and Ku, P. M., eds.: Friction and Wear Interdisciplinary Workshop. NASA TMX–52748, 1970, 86 pp.

[3] Ku, P. M., ed.: Interdisciplinary Approach to the Lubrication of Concentrated Contacts. NASA SP–237, 1970, 589 pp.

majority of the members, based upon their own personal reactions as well as their contacts with the conference participants and others, expressed satisfaction with the concept of bringing high-caliber multidisciplinary talents together for periodic, coordinated deliberations on some facets of lubrication not adequately provided for by other types of meetings. It was also felt that the proceedings of these conferences have been of excellent quality and have become valuable references not just for the experienced scientists and engineers, but particularly for the less experienced who desire authoritative guidance in both breadth and depth. As to the desirability of additional meetings, it was felt that a dialog had started, and time should be allowed for the dialog to be transformed into action before taking further steps. Accordingly, specific recommendation regarding a meeting for the immediate future was deferred.

Speaking as one who has been largely responsible for the conduct of the NASA interdisciplinary lubrication series since its inception, my own feelings have been somewhat mixed. Taken as a whole, I believe these meetings have provided an effective forum for lubrication scientists and engineers and systems design and development engineers to meet and discuss many problems of mutual interest. However, they have not succeeded in bringing about a genuine dialog with basic scientists. Perhaps the achievement of such a dialog must take time, and the long-range impact of the venture cannot be measured by short-term accomplishments. Nevertheless, one cannot but feel that some other technique might have produced better results. In any case, it appears to me that if this conference series should be reactivated in the future, a change in orientation and organization is desirable.

In thus concluding the NASA interdisciplinary lubrication conference series, I should like to record my personal indebtedness to the members of the Steering Committee, who have helped in a very substantial way in planning the conferences and in reviewing the invited lectures.

This conference series was started in 1967 at the request of G. C. Deutsch, Director of Materials and Structures Division, Office of Aeronautics and Space Technology, NASA Headquarters. Over the years, it has received constant support from E. E. Bisson, Associate Chief, Fluid System Components Division, NASA Lewis Research Center. A great deal of the burden of reviewing the invited lectures has been assumed by the staff of the Lewis Research Center, whose reputation in lubrication research is widely recognized. To these and other NASA personnel who have rendered valuable assistance in the past 6 years, I offer my sincere thanks.

It is clear that the most important ingredient of any technical conference is the participants, whose interest and support are absolutely crucial. I would therefore like to thank, on behalf of the Steering Committee, all the lecturers and discussers of this and the previous conferences for their generous gifts of time and energies. Their sharing of knowledge with others and their thoughts on what remains to be learned are in essence timeless. These proceedings constitute a tangible record of their contributions.

P. M. Ku
San Antonio, Tex.

September 1, 1972

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Liquid Lubricants—Functions and Requirements

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This is a broad review of the present state of liquid lubricant technology. It considers the limits of present knowledge, especially in the boundary regime, and some of the factors, such as colloid behavior, viscoelastic effects, and relaxation times, whose contributions have not yet been fully assessed. Some specific applications problems and some of the lubricant requirements that have not yet been met are also discussed.

THE PURPOSE OF THIS LECTURE is to set out in very general terms what liquid lubricants are for and what their requirements are for industrial and aerospace applications. There is very little I can say that will not be said better and in much more detail in the specialist lectures which are to follow.

As in most fields of technology, the greatest expertise tends to reside in the suppliers rather than the users. In many areas this is no problem because, for example, the user of a plant rarely needs to do the stressing or fatigue calculations. But the users of lubrication include plant designers and others who do need to understand lubrication technology. Unfortunately their knowledge is often not adequate, and there is a wide gap in understanding between the experts and the general industrial engineers. The main object of the British tribology campaign in recent years, and of organizations such as ours, has been to bridge this gap, but there is no doubt that it is still one of the most important practical problems in lubrication.

Like all attempts to isolate particular areas of technology, the restriction of this symposium to liquid lubricants is a necessary but artificial one. Liquid lubricant technology has no meaning except in association with other factors such as wear, compatibility, sealing, and ultimately the whole of machine design. So while we restrict our discussion primarily to liquid lubricants, we should keep continuously in mind the environment in which they have to operate.

PRIMARY FUNCTIONS OF A LUBRICANT

The primary function of a liquid lubricant is, of course, to lubricate, that is, to reduce friction and wear, but even this simple and conventional statement merits some analysis. In fact, very often what we want to avoid is neither friction nor wear, but seizure and/or structural failure. We would be prepared to put up with considerable friction and wear if we could be sure that nothing more catastrophic would occur. Liquid lubricants, properly used, reduce the tendency to seizure and structural failure. It may be of secondary importance that they do so by reducing friction. The second point is that it is not always necessary to reduce both friction and wear. Rather, we may wish to reduce wear but not friction, as in lubricated clutches, or friction but not wear, as in some grinding and polishing operations.

Liquid lubricants are a nuisance and will only be used as long as the improvement they produce is sufficient to offset their disadvantages. Unlubricated metals tend to gall and score in sliding, and wood usually wears rapidly and exhibits uneven friction. Traditional materials of construction usually benefited from the use of liquid or semiliquid lubricants, and so it became normal to use them. Even so, a desire to get rid of liquid lubricants is no new development. Bowden and Tabor (ref. 1) quote a clockmaker in 1717 who introduced lignum vitae roller pinions "which move so freely as never to need any Oyl."

In the past 30 years, a vast range of new structural and coating materials that are capable of operating without liquid lubricants has appeared, and the use of liquid lubricants is no longer the only way of reducing seizure, friction, and wear. Detailed consideration of dry or solid lubricants is outside the scope of this conference, but it is important when considering liquid lubricants not to consider them in isolation and to bear in mind that they are in competition with other materials and techniques.

But if all liquid lubricants are a nuisance, some are more of a nuisance than others, and we should also bear in mind that their use will be markedly affected by handling and supply difficulties, as well as by their functional behavior.

It would probably be true to say that in the majority of applications the prime function of the lubricant is to minimize both friction and wear at the interface between surfaces in relative motion. It performs this function by interposing a distinct phase between the interacting surfaces. The properties of this phase determine the behavior of the lubricant, and therefore its suitability for the specific application.

This is, to my mind, an important concept if we are to define accurately the functions and requirements of lubricants. It is the properties of the intermediate phase as it exists in operation between the interacting surfaces that are important. The properties of the lubricant in the can are only important insofar as they can be correlated with the properties in the operating bearing.

There are two classes of interphase, and the considerations that apply to them are quite distinct. The simplest class includes those cases in which the interphase is a continuous fluid film that carries the whole of the bearing load. The film is not broken by any solid-solid contact between the separated machine elements. In other words, there is full fluid film separation. There are several conditions in which full fluid film separation can occur, such as hydrostatic, hydrodynamic, and elastohydrodynamic (EHD) and the special cases of squeeze films.

The more complex class arises where the lubricated surfaces are close enough together for the surface asperities and interfacial effects to have a significant influence on the lubrication behavior. In this case it is an oversimplification to call the interfacial system a phase because it will normally include at least four distinct phases, each of which contributes to the behavior of the system. This is the situation normally described as the boundary regime.

SECONDARY FUNCTIONS OF A LUBRICANT

Before going on to a more detailed consideration of these two types of systems, and the requirements they impose on the lubricant, it may be useful to consider the secondary functions of liquid lubricants. These are the functions that lubricants are usually expected to perform, but which are not inherently part of the lubrication process.

The first of these secondary functions is the removal of surplus heat. This is so important a factor, and a requirement that is so commonly required of liquid lubricants, that it might almost be considered a primary function. The requirement is in itself easy to define as the highest available specific heat and thermal conductivity. It is only when these targets are in conflict with the other required properties that a compromise must be made, and the heat-transfer properties will then normally be considered of secondary importance. Removal of heat is one of the ways in which liquids help to avoid seizure and mechanical failure, regardless of whether they reduce friction or wear at the same time.

The next secondary function is that of scavenging wear debris and other contaminants from the bearing and insuring that they are not deposited in critical zones. It is only in inherently dirty lubrication systems, such as those of internal combustion engines, that this function becomes important in the formulation and selection of lubricants, and it is then achieved by the use of detergent or dispersant additives. It is more common to accept the dispersant properties of the selected lubricant and to optimize the removal of contaminants by design of the oil flow and use of filters.

Finally, it is common to expect lubricants to protect bearings and systems against corrosion. This requirement has probably arisen largely because of the very effective corrosion prevention that has been provided over the past hundred years since petroleum-based lubricants became widely used. There is no obvious reason why the lubricant should protect against corrosion, but many designers now find themselves in difficulty when they are obliged to use lubricants that are not effective in corrosion prevention.

But a hard-and-fast definition of primary and secondary functions is dangerous and unnecessary, and there are many situations where the positions are reversed. An electrical coolant or refrigerant may be expected to act as a lubricant for a pump or valve, and a cutting fluid may be primarily required to cool the tool and workpiece and to remove swarf and only incidentally to lubricate the tool-stock interface and the circulating pump.

There are a few other functions that the lubricant may occasionally be required to perform, such as electrical insulation. In the special case of greases, an important function may be to seal the bearing against ingress of contaminants or loss of lubricant.

FULL FLUID FILM LUBRICATION

The dominant property of a lubricant in full fluid film lubrication is its viscosity. The viscosity of an oil is normally quoted by the suppliers in Redwood seconds, Saybolt universal seconds, degrees Engler, or, increasingly, in centistokes. The Redwood and Saybolt systems are slowly becoming less common, and it appears to be both Institute of Petroleum and American Society for Testing and Materials (ASTM) policy to standardize on kinematic viscosity. Even so there will still be complaints from engineers, who wish to use absolute viscosity in centipoises. The adoption of the International System of units (SI) is bringing strong pressure for the replacement of centistoke and centipoise by square meters per second and pascal seconds. More important than this is the fact that it is normal to quote the viscosity on the basis of a measurement made at low shear rate and at pressures close to atmospheric, but there are several factors that significantly alter the effective viscosity of the lubricant in operation in the load-carrying zone.

Pressure-Viscosity Relationship

There is no need to go into detail about the effects of pressure on viscosity. It is only in the EHD regime that pressure-viscosity effects are of great importance, and equations such as that of Dowson and Higginson (ref. 2) for cylindrical contacts and Archard and Cowking (ref. 3) for spherical contacts give a very useful prediction of the film thickness, taking account of the pressure-viscosity coefficient. There are, however, a number of remaining problems, and it may be useful to remember them when considering the minimum film thickness in an elastohydrodynamically lubricated contact.

In practice, the effect of surface asperities is likely to be of considerable importance because it is conventional to predict the effectiveness of EHD lubrication by relating the calculated minimum film thickness to the combined effective surface roughness. Where the two are of similar magnitude, the local film thickness near an asperity will vary considerably from the calculated value.

In a thin film of liquid with a very high effective viscosity, high stress concentrations can be transmitted from an asperity to the counterface without physical contact, but this will be offset by distortion of individual asperities as a result of the high local pressures. In other words, asperities may be expected to generate a second order of EHD effects. At the 1967 symposium, Fein and Kreuz (ref. 4) gave a useful description of this condition, called microelastohydrodynamics.

Such factors will be further complicated by the occurrence of shear in the lubricant film. Dyson (ref. 5) has shown that in thicker EHD films the film thickness is not sensitive to shear, but where asperity heights are significant this is probably no longer true (refs. 4 and 6). It seems likely that behavior in the high-pressure zone will be non-Newtonian and that there will be significant viscoelastic effects when shear occurs. It is also interesting to speculate what time-dependent factors may affect the local film thickness. The time for one asperity to pass another may be of the order of nanoseconds, and this is likely to be significant in relation to the relevant relaxation times. Lamb (ref. 7) has shown that the relaxation times at atmospheric pressure are of the order of 10 psec for saturated hydrocarbons to a nanosecond for monoaromatics. These times increase with pressure at the rate of approximately 1½ decades per 1000 bars.

Because of the variety of possible situations, these effects can only possibly be described in statistical terms for model geometries, but one practical problem is to decide whether we need to apply any safety factors in predicting the effectiveness of EHD lubrication. Some experimental work[1] has indicated that under laboratory conditions, if the predicted film thickness is greater than the sum of the surface roughnesses, there will be no damage. In other words, no safety factor is required. On the other hand, Tallian (ref. 8) discussed the various failure modes in rolling-contact bearings in relation to the EHD film thickness-to-roughness ratio ξ_0 where

$$\xi_0=\frac{h_0}{(\sigma_1^2+\sigma_2^2)^{\frac{1}{2}}}$$

and showed that all forms of damage can occur at values of $\xi_0>1$. In particular, surface fatigue can be significant at values of ξ_0 up to 1.5.

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[1] Hirst, W.: Private communication.

In general, EHD behavior is controlled by the lubricant viscosity and viscosity-pressure coefficient under inlet conditions. The presence of shear introduces factors of microelastohydrodynamics, traction, and temperature change for which other rheological properties such as viscosity-temperature coefficients at high temperatures and pressures will be important.

Viscosity-Temperature Relationship

The variation of viscosity with temperature is also a subject that is well studied and well understood, and the oil property most often quoted after its nominal viscosity is probably its viscosity index (V.I.), or some other viscosity-temperature relationship. Again the relevant viscosity measurements are usually made at low shear rate, and this raises special problems where a high V.I. is obtained by the use of polymeric V.I. improvers. In fact, the introduction of multigrade motor oils has probably led to more misunderstanding than any other lubricant development. Even after 20 years it is still common for users to believe that their viscosity increases, or at worst remains constant, as the temperature rises.

Perhaps the biggest difficulty in estimating the effective viscosity is to decide what the relevant temperature is. It is possible in theory to calculate the temperature profile through the loaded zone and thus to assess accurately the effective viscosity, but in practical operating bearings, the uncertainty is likely to be of the order of tens of degrees Celsius. With a V.I. of 100, this represents a viscosity error of more than 100 percent, and there is therefore a natural tendency to add a safety factor to the calculated required viscosity. The use of a more viscous oil will lead to higher friction torque, higher heat generation, and hence lower viscosity, so that this, like many features of journal bearings (ref. 9), tends to be self-optimizing.

In this situation, the industrial lubricant classifications of BSI (B.S. 4231) and the ASTM (ASTM D–2422), which are based on kinematic viscosity increases of 50 percent from one grade to the next, provide an adequate range of lubricants. Most users will now look forward to the time when commercial mineral oils are actually sold in accordance with these classifications.

Viscosity—Shear Rate Relationships

The assumption of Newtonian behavior is made in almost all calculations involving hydrodynamic lubrication and in all calculations involving EHD lubrication, but the use of lubricants known to be non-Newtonian is increasing. There are in addition some other known problems involving loss of viscosity at high shear rates. The non-Newtonian lubricants include greases, oils with polymeric V.I. improvers, thickened or thixotropic oils, and, in some circumstances, emulsions. Furthermore, even Newtonian liquids become non-Newtonian or viscoelastic under conditions of rapidly changing stress, when, for example, the time of application of the stress is shorter than the relaxation time (ref. 7).

The one widely recognized property of liquids containing dissolved polymers is that at low shear rates they have an effective viscosity which is a function of both solvent and solute, but that as the shear rate is increased the apparent viscosity decreases, ultimately to that of the solvent alone. This effect is also obtained with certain liquids with long-chain molecules even when there is no dumbbell distribution of molecular weight. Figure 1 shows the change of viscosity with shear rate for a silicone of medium viscosity.

To cope with this situation for polymer solutions, it has been conventional to calculate the minimum film thickness for such lubricants on the basis of the base oil viscosity (if known), and to assume that any error involved would lead to an underestimate of the film thickness and thus to a useful safety factor.

In fact, of course, the behavior of non-Newtonian fluids is not as simple as this. In a rotary viscometer with either concentric cylinder or cone-and-plate geometries, there is a known tendency for non-Newtonian fluids, including greases, to migrate to zones of lower shear rate. By analogy, the same tendency must arise in plain thrust and journal bearings. The im-

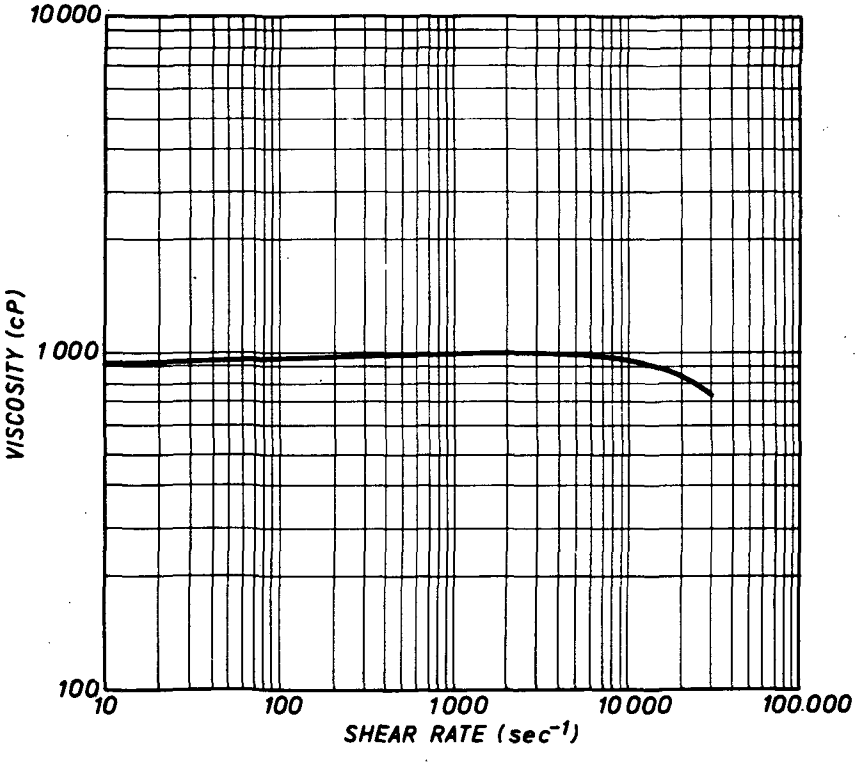

FIGURE 1.—Viscosity versus shear rate for a 1000-cs silicone.

portance of the effect will depend on the aspect ratio of the bearing, but the tendency must be to a reduction in film thickness.

Figure 2 is taken from a paper by Dyson and Wilson (ref. 10) and shows the variation of film thickness with time in a two-disk machine for a typical mineral oil and for the same oil containing 5 percent of a typical polymeric V.I. improver. The final film thickness for the V.I.-improved oil is little more than half that of the base oil. The authors showed the same effect for a series of greases and ascribed it to partial emptying of the inlet zone by the phenomenon of migration to a region of lower shear rate.

Finally, there is the problem of shear stability, involving loss of viscosity as a result of shear. This apparently has two components. The first is a temporary loss that has been ascribed to molecular orientation and that is usually recovered in less than a second. The other is a permanent loss that must be chemical and that has been ascribed to rupture of long-chain molecules followed by stabilization or recombination in less viscous structures. The chemical nature of this latter phenomenon is supported by the marked influence of increased temperature in increasing the rate of viscosity loss.

The same phenomenon occurs to a lesser extent with plain high-viscosity mineral oils, but it can also be obscured by thickening of the oil in practical systems.

Thus for non-Newtonian lubricants there are several phenomena that

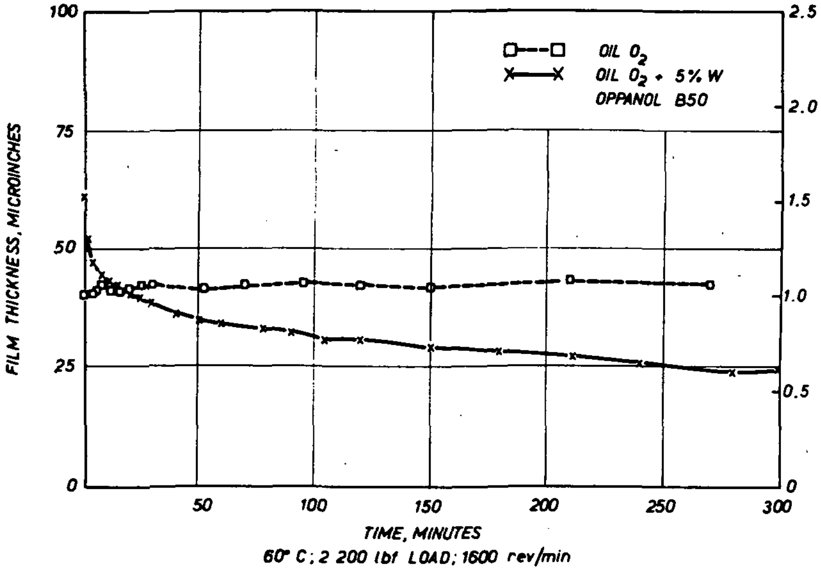

FIGURE 2.—Effect on film thickness of the addition of 5 percent polyisobutylene to a 140-cs oil.

adversely affect their effectiveness. The advantages of V.I.-improved hydraulic fluids and multigrade oils in particular are much less apparent, and a review by Hollinghurst and Singleton (ref. 11) did little to clarify the situation. Obviously there are practical benefits such as reduction of leakage, and presumably there are advantages in squeeze film situations. This whole problem, however, needs clarification.

BOUNDARY LUBRICATION

The study of boundary lubrication has probably not completely recovered from the effect of the advent of EHD theory, which led some workers to suggest that boundary lubrication did not even exist (ref. 12). However, in the same reference, Tabor deduced the reality of boundary lubrication and suggested a useful definition as—

> that type of lubrication which cannot be attributed to the bulk viscous properties of the lubricant (whether the system is operating under hydrodynamic or elastohydrodynamic conditions) but arises from a specific solid-lubricant interaction.

Almost every author who writes about boundary lubrication supplies his own definition, but I do not propose to try to improve on this one. I would only challenge the phrase "a specific solid-lubricant interaction," which implies that a single phenomenon may be dominant. This may be true under laboratory conditions, and especially with the simplified models with which Dr. Tabor works so elegantly, but any practical boundary lubrication system involving steel-on-steel or ferrous-on-nonferrous surfaces, with commercial lubricants in an uncontrolled atmospheric environment, is enormously complex.

Incidentally, the above definition implies that boundary lubrication is necessarily associated with the presence of a liquid lubricant, and this seems to be common usage, in spite of the fact that there are many common features in boundary-lubricated (liquid), dry lubricated, and unlubricated systems. In general, we should perhaps think in broader terms about boundary lubrication to insure that we are not placing any artificial limits on our thinking, but in the context of a symposium on liquid lubricants, the usual interpretation is satisfactory.

It is surprising that such systems have not attracted the sort of scientific effort that is expended on high-energy nuclear physics. Their complexity makes nuclear physics look childishly simple, so their scientific challenge should be much greater, while the potential gains to mankind of a better understanding of them are also likely to be greater.

Because boundary lubrication as such is not the subject of a paper in this symposium, it may be useful to consider briefly the various phenomena that can occur when moving surfaces interact in the presence of a liquid lubricant under conditions in which interfacial effects are significant. Figure 3 shows diagrammatically some of the features that may be in-

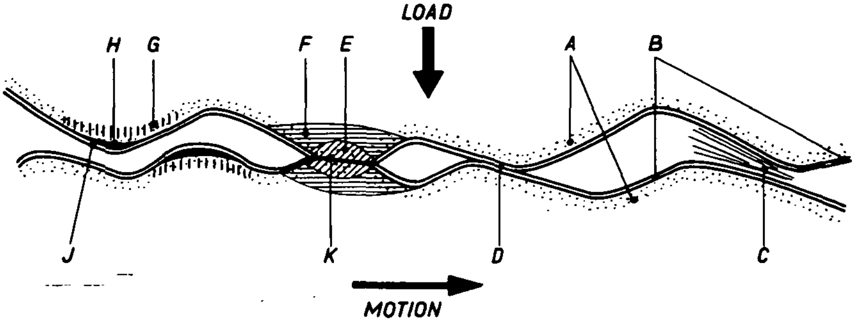

FIGURE 3.—The boundary system. *A:* Enrichment of oxygen and other "contaminants" near metal surfaces; *B:* adsorbed films of boundary lubricant; *C:* viscosity increase adjacent to metal surfaces; *D:* adsorbed films carrying load between asperities; *E:* plastically deformed tip of asperity; *F:* elastic deformation of substrate; *G:* residual stress in asperity after plastic deformation; *H:* work-hardened tip of asperity; *J:* chemisorption on abraded surface after contact; *K:* local high temperature at asperity contact.

volved. Even this is a simplified model because it ignores factors such as metal transfer between surfaces, the competition between reagents for both stable and freshly exposed surfaces, and the possible occurrence of special activation phenomena such as exoelectrons.

It is a natural consequence of this complexity that the study of boundary systems tends to be fragmentary. For really fundamental study, the systems have to be simplified to the point where the relevance of the results to practical systems is often difficult to establish. For practical studies, as in the development of new antiwear and extreme-pressure (EP) additives, the theoretical basis is weak, and even the relevance of the empirical tests that are used is open to question. In fact, the only justification for most of these studies is that they seem to work.

Of the different phenomena highlighted in figure 3, the one that has been most hotly disputed is item *C*, the increase in viscosity which has been described in the vicinity of bearing surfaces. The long series of studies of "thick" lubricant films in oils containing polar molecules, ranging from Hardy (ref. 13) to Fuks (ref. 14) and Cameron (ref. 15), was reviewed in 1969 by Hayward and Isdale (ref. 16), who ascribed all the evidence to the presence of particulate contaminants. More recently, Smith and Cameron (ref. 17) have produced further strong evidence for the existence of order in a solvent containing a long-chain fatty acid to a distance of 2100 Å in an experiment at room temperature. The effect is ascribed to the formation of soaps by reaction between the acid and the steel surface, followed by the entrainment of solvent to produce a pseudogrease structure. If this explanation is correct, then the reaction kinetics of the soap formation and the stability of the agglomerated soap molecules will repay further study.

There are obvious objections to the hypothesis that reaction between free fatty acids in solution and the metal surfaces can lead to soap films that are more than monomolecular in thickness. One objection is that under certain sliding conditions, sufficient to disrupt the greaselike structure but insufficient to abrade or scuff the mating surfaces, there should apparently be a disturbance of the equilibrium, resulting in very rapid continuing solution of metal and formation of soap. Such a process should be easy to demonstrate and should in fact have been known already in practical bearing systems. The amounts of soaps that have been detected in wear debris (ref. 18) do not appear to be as great as would be implied by the ready formation of the multimolecular layers postulated by Cameron.

There is some evidence from spectrographic oil analysis programs that part of the "wear" metals can exist in true solution in the lubricant, even when the lubricant is a plain mineral oil. This requires the formation of some form of organometallic compound, and because of the widespread occurrence of fatty acids, the formation of soaps is an obvious possibility. On the other hand, iron soaps are generally insoluble in common solvents, and some form of micellar dispersion may be a more likely mechanism.

The presence of oxygen and/or water appears to be necessary for the formation of iron soaps (ref. 19). The contribution of oxygen to the action of other additives is less clear. It has long been taught that most chemical reactions will only occur in the presence of very small quantities of such things as oxygen or water, which act as promoters or catalysts. On the other hand, Fein (ref. 18) has suggested that atomically clean metals react with almost anything they contact and instanced the case of adhesion of insoluble metals under space conditions. It is open to argument whether this adhesion is really analogous to chemical reaction, but Morecroft (ref. 20) has shown that octadecane, butane, and decoic acid all reacted to give hydrogen, methane, and carbon monoxide when in contact with clean iron surfaces. It is generally accepted that freshly exposed clean metal surfaces are in a highly reactive state, but this condition is sometimes believed to be a transient one. Clearly this is another aspect of surface behavior that could usefully be clarified.

It should therefore follow that the best antiwear or EP additives for use in high vacuum or inert atmospheres will differ from those that are effective in the presence of oxygen. There does in fact seem to be a tendency for spacework to use those additives that are likely to act by adsorption rather than chemisorption. Where oxide replenishment is critical, a possible technique is to incorporate an oxidant in the lubricant (ref. 21).

The overall effort on the development of new antiwear and EP additives is very large but almost entirely empirical. There have been many excellent papers by workers like Allum and Forbes (ref. 22) showing the variation of antiwear and EP performance with the elemental and structural composition of additives, but without more fundamental work on the surface chemistry, the prospect of radically new techniques or even of significant improvements is not very great.

At the 1967 symposium in San Antonio, Godfrey (ref. 23) emphasized the physical aspects of boundary lubricant films and concentrated on the strength and rupture of sorbed and reacted films. The general assumption was that a uniform (usually monomolecular) film forms on the whole of the available surface and that it is the integrity of this film which prevents metal-to-metal contact, the film being ruptured only when very high normal or tangential stresses arise.

This mechanism may well apply to adsorbed films of the so-called mild EP additives such as vegetable oils, fatty acids, and soaps, but the work of Forbes (ref. 24) with electron probe microanalysis of wear scars has indicated that this is not the case with the more powerful chemisorbed additives. Forbes infers that where smooth sliding is occurring the concentration of additive is low, but that there is an increased concentration on torn or otherwise damaged parts of the surface. The implication is that reaction takes place preferentially at freshly exposed surfaces and that the product of reaction insures a nondisruptive operation until the damaged area has been smoothed, when the additive concentration will again be low.

There is, of course, a great deal of evidence for such preferential reactions at freshly exposed surfaces. One possible example is that described by Moore (ref. 21) in which lithium nitrite acted as an oxidant in greases for use in a helium atmosphere. Nitrites are traditionally reducing agents, rather than oxidants, and their oxidizing action in this application requires temperatures very much higher than expected or the existence of some alternative activation mechanism.

While it is generally accepted that freshly exposed surfaces have a high reactivity, the effect and importance of this in specific wear situations is less easy to predict. Rozeanu (ref. 25) demonstrated an abnormal surface potential on fresh fracture surfaces, and it would be interesting if a similar technique could be applied to freshly worn surfaces.

The energy considerations as a whole in the boundary regime are poorly understood, even by the specialist, while the nonspecialist, perhaps because of their complexity, tends to disregard them completely. There have been some very elegant researches on surface tension and free energy such as those of Zisman (ref. 26), although even these have not received the degree of application that they appear to deserve. But there is a need for much better understanding of the dynamic energy situation. The suggestion has been made that some completely unsuspected energy conditions occur at sliding contacts, apart from the neglected exoelectrons (ref. 27), but whether this is so or not, this is clearly an area of potentially interesting and valuable research.

It is interesting to trace the changes that have taken place in the interpretation of the term "boundary lubrication." Originally the distinction was made between hydrodynamic and boundary lubrication, and it was assumed that where hydrodynamic pressures were insufficient to account for satisfactory lubrication, the effect was due to the presence of (probably uniform) adsorbed films. The subject of lubrication was therefore divided, with hydrodynamic lubrication being the concern of the engineer, and boundary lubrication that of the chemist.

With the development of a satisfactory EHD theory, much that was previously considered to be boundary lubrication became also the concern of the engineer. Boundary lubrication was still associated with the existence of uniform sorbed films (ref. 23), but the question was asked (ref. 28) whether the physical adsorption of Hardy and Langmuir was the important mechanism, or whether the action was chemical, producing reaction products giving a form of rheodynamic or EHD lubrication. Tallian (ref. 8) described partial EHD effects in which much of the load is transmitted through an EHD film, but asperities penetrate the film and contact each other. His comments seemed to support the rheodynamic view, but use of the phrase "a boundary film" implied the assumption of a uniformly sorbed layer.

The comments of Fein and Kreuz (ref. 4) interpret the boundary regime in purely microelastohydrodynamic and microrheodynamic terms, and in doing so provide a basis for a reintegration of the work of engineers and chemists. The assumption of more or less uniform sorbed films is still made, but if Forbes' inference (ref. 24) is correct then a modification of Fein and Kreutz's analysis to take account of preferential sites for adsorption and chemisorption may well give an excellent qualitative description of boundary lubrication.

In 1967 both Tabor (ref. 12) and Fein and Kreutz pointed out some of the remaining uncertainties requiring clarification, and it would be interesting to know whether any answers to their questions have yet been supplied. Perhaps boundary lubrication would be the best theme for a future interdisciplinary symposium.

STABILITY FACTORS

So far I have discussed some of the behavioral aspects of a lubricant that enable it to perform the lubricating function. It is also important that the lubricant continues to perform satisfactorily for as long as necessary. This introduces additional physical and chemical stability requirements that are sometimes in conflict with the requirements of lubrication itself.

Chemical Stability

Chemical stability of a lubricant is normally considered under four separate headings: thermal, oxidative, hydrolytic, and compatibility, although two or more of them may be jointly involved in a specific situation.

Thermal stability is probably best defined as the resistance of a material to chemical change induced by change in temperature in the absence of any other reagent. In practice, there is a tendency to include the external influence of common materials such as bearing materials, and to say, for example, that "the thermal stability of the diesters is reduced by steel" (ref. 29).

There is, however, a great deal to be said for considering all such external influences under the heading of "compatibility."

If we then consider thermal stability in accordance with the above definition, it is essentially a single-phase problem, and it is possible to predict the rate of degradation, and therefore the rate of change of some relevant physical parameter, as a function of temperature and time. It follows that it is only necessary to define the maximum acceptable change in that parameter, and the maximum temperature limit can be established at which the required life will be obtained. This limit is thus an inherent property of the lubricant and represents an absolute limit on its capability under ideal conditions where all external chemical factors are excluded.

There are many base oils whose thermal stability is adequate to permit operation at over 300° C, and even mineral oils may be sufficiently stable up to 250° C. In practice the temperature limit is reduced by the presence of minor unstable constituents or catalysts. It is rarely possible to exclude other reagents, so it is only under unusually well-controlled conditions that the operating temperature is limited by thermal stability.

Oxygen is the external reagent that is most commonly present in lubricated systems, so oxidative stability will usually be a more important practical limitation than thermal stability. Oxidation is more complex and more difficult to predict than thermal degradation because it is essentially a two-phase problem. Although the actual oxidation of lubricant molecules may be by dissolved oxygen, the overall rate of oxidation will often be controlled by the rate of replenishment of oxygen, usually from the gaseous state. The replenishment will in turn be controlled by the partial pressure of oxygen in the ambient atmosphere, the contact surface area between lubricant and atmosphere, and the rate of flow of both phases.

It follows that it is not possible to predict the lubricant life under oxidizing conditions with any accuracy for a given lubrication system. Two methods are used to obtain a useful prediction. Where oxidation is likely to be a dominant factor in lubricant life and where the performance of the lubricant is critical, as in an aircraft engine, it will probably be considered necessary to carry out expensive qualification testing to insure the required performance.

In less critical systems, or as a supplement to full-scale system testing, bench-type oxidation tests may be used, but these suffer from the natural consequences of a two-phase test, that direct extrapolation of the results can rarely be made from the test to the proposed application, and that it is not generally possible to correlate different types of test. They do, however, have some value in giving comparative ratings for different lubricants.

The oxidative stability of mineral oils and diesters can be improved enormously by the use of antioxidant additives. This is unfortunately less true with synthetic lubricants and especially those for use at elevated temperatures. The discovery of effective high-temperature antioxidants for silicones and polyphenyl ethers would render them much more attractive and could have a marked effect on the temperatures considered practicable for many industrial lubricant systems.

Hydrolytic stability resembles oxidative stability because it is often difficult or impossible to avoid the presence of water in a lubricated system and the ensuing reactions will be effectively two phase. However, hydrolytic stability is not often a limiting factor in the performance of lubricants. Most base oils are relatively unaffected by water, although esters will generally be slowly hydrolyzed at higher temperatures, and silicate esters are readily hydrolyzed. Water is likely to be more important in its effects on bearing materials and certain additives.

In general, the subject of compatibility between lubricants and other materials is too broad and complex to be considered here. The extent of the problem generally depends on the amount of experience that exists in the use of a specific lubricant. Thus the compatibility problems with vegetable and mineral oils are so few and so familiar that they have virtually ceased to be problems. With synthetic lubricants the selection of compatible materials is more restricted.

The influence of chemical stability factors on the operating life of various lubricants is shown in figures 4 and 5, which are based on an original diagram by Fowle (ref. 29).

Apart from the chemical stability of the base oil, it is equally important that the various additives continue to perform their functions during the required working life. In the case of additives that act other than by chemical reaction, such as V.I. improvers, the overall life of the lubricant is not likely to be limited by the chemical stability of the additive, but there are others, such as antioxidants, EP additives, and corrosion inhibitors, whose action is partly or wholly chemical.

With these latter additives, there is a conflict between the chemical reactivity required for effective operation and the chemical stability required for long life. The solution lies in providing high enough concentrations of the additives, but there are other restrictions on the amounts that can be used, and in practice it is possible for the effective life of the lubricant to be limited by depletion of additives, especially at high operating temperatures. The same conflict between the requirements of chemical stability and chemical reactivity is undoubtedly a major reason for the general lack of success in developing chemical additives for temperatures over 200° C.

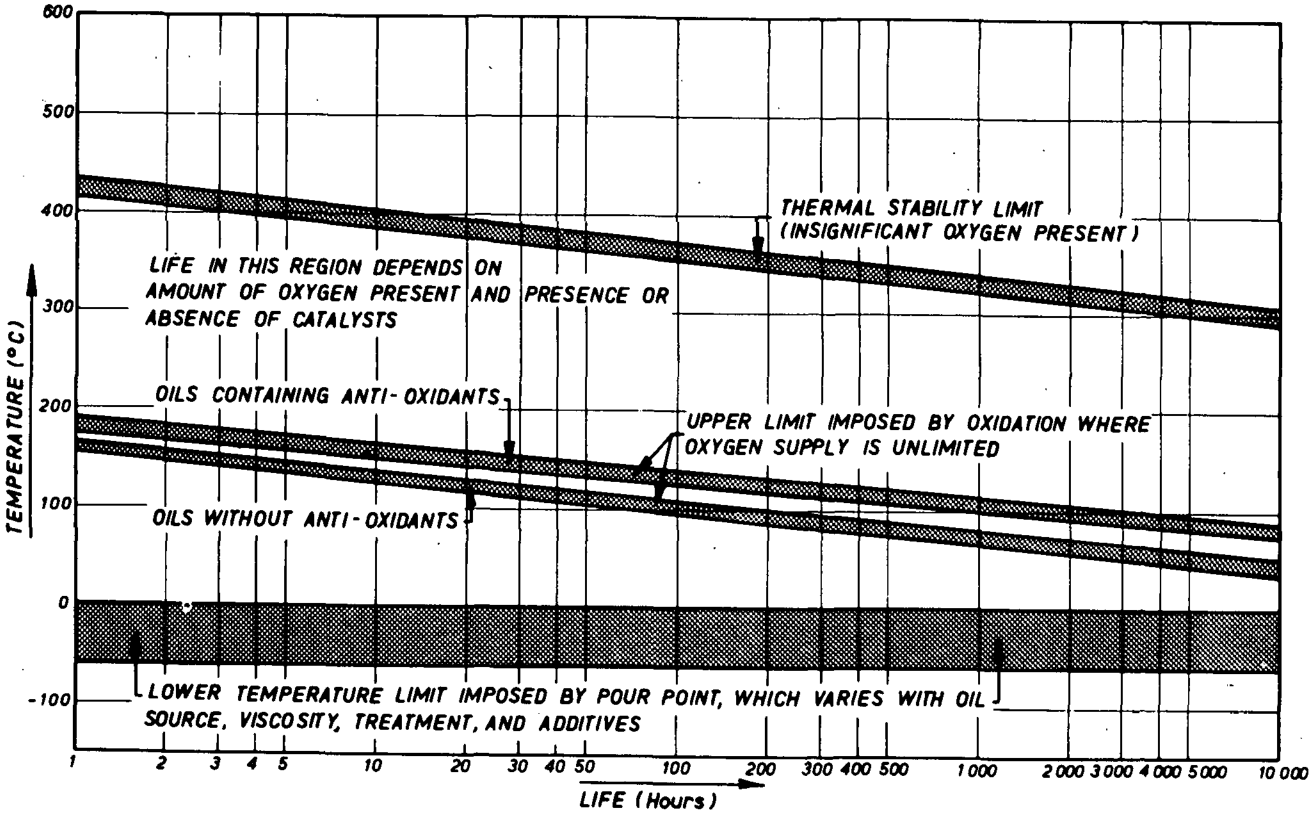

FIGURE 4.—Temperature limits for mineral oils.

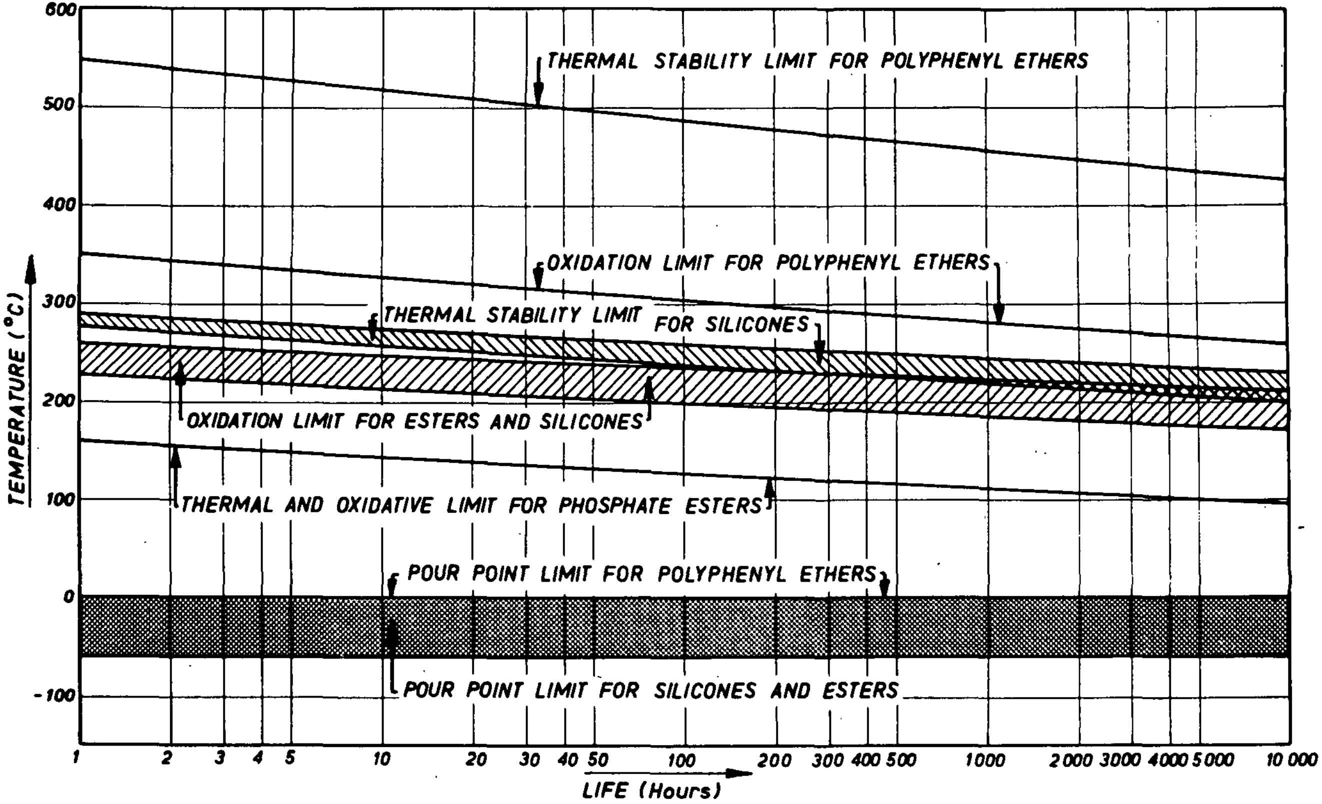

FIGURE 5.—Temperature limits for some synthetic oils.

Physical Stability

The three physical factors that lead to loss of effective lubrication are evaporation, creep or spreading, and the breakdown of emulsions or other dispersions.

Under *normal atmospheric conditions, loss of lubricant by evaporation* is negligible. Vapor pressures, even of light spindle oils, are usually less than 10^{-3} torr, so even under high airflows and in high-altitude aircraft, the rate of loss is low. For space and other high-vacuum applications, volatility is, of course, critical and is further considered under that heading.

Loss of lubricant by creep or spreading is a very important phenomenon wherever the quantity of lubricant present is very small. Major progress in understanding this problem has been made by the U.S. Naval Research Laboratory (ref. 26) in work aimed at the development of improved instrument lubrication. The two general solutions to problems of oil spreading are the use of oleophobic additives and the use of barrier films. Use of the latter constitute the best general solution to the problem because they do not impose any further constraint on the selection of lubricant, and their use is increasing in advanced-technology applications such as military aircraft and space.

There are many other industries in which loss of lubricant by spreading limits the operating life, including miniature electric motor bearings in a wide range of consumer goods. For such applications the introduction of an additional step into the production process to apply barrier films is generally considered uneconomical, and there may be a potential market for improved nonspreading oils capable of withstanding loads and operating temperatures higher than those usually required of instrument oils. The temperature is particularly important because it is at higher temperatures that the loss of lubricant is most serious.

The breakdown of a stable disperse system is also technically a physical change, but it may be commonly caused by either chemical contamination or heat. Greases are the best known lubricant dispersions, and numerically more bearings are lubricated by grease than by oil. Traditional soap greases vary in their resistance to attack by chemical contaminants, while the more recent clay-thickened greases generally have improved resistance. The greatest protection against attack on greases is provided by the nature of their application. In most bearings the bulk of the grease transfers to the covers or other surrounding areas, where by virtue of its high viscosity it provides an effective seal against ingress of contaminants to the critical bearing surfaces. This situation has a retarding effect on any attack on the grease itself, except by the most powerful solvents.

Breakdown of a grease by temperature is a well-recognized phenomenon expressed as the drop point. This is the temperature at which a grease changes from the solid or semisolid to the liquid state, and it is characteristic of soap-based greases that after heating above the drop point they will not on subsequent cooling fully recover their consistency and performance. Many non-soap-thickened greases do not demonstrate a true drop point, but show a gradual increase in penetration over a broad temperature range. It is sometimes claimed that such greases can be heated over their softening temperatures and will fully recover their properties on cooling, but many users have found to their cost that this is not always so. The behavior may depend on the amount of shearing that can occur in the softened condition, but whatever the cause, a clear explanation would be of considerable value to users and might help to restore a certain amount of lost confidence in the suppliers. The complexity of the temperature limits on greases is shown in figure 6.

In recent years emulsions have become increasingly important in lubrication. They include metal-cutting oils, metal-rolling coolants, and fire-resistant hydraulic fluids. The greatest volume use is in the form of dilute oil-in-water emulsions, but there is a growing use of water-in-oil or invert emulsions.

The stability of the various emulsions varies with the proposed application. For certain metal-rolling operations, the emulsion is relatively unstable and is intended to separate in use to give a small volume of neat lubricating oil and a large volume of cooling water. In general, however, a lubricating emulsion is intended to remain stable in use.

The thermal stability of emulsions is generally good, and they will remain stable until the temperature approaches the boiling point of the water phase, but all of them are susceptible to the effect of contamination. Because of the way in which they are used, hydraulic fluids are not normally exposed to contamination, except as a result of microbiological growth.

Contamination by foreign or tramp oil will sometimes break an emulsion by extracting the dispersed oil droplets into the free oil phase. Any contaminant that interferes with the stabilized surfactant will also lead to phase separation. For example, ionic surfactants are susceptible to interference from electrolytes.

Microbiological Attack

All petroleum, vegetable, and animal oils and some synthetics are susceptible to microbiological attack by bacteria and fungi that feed off of these oils. The effects of attack include degradation of base oil, depletion of additives, production of corrosive and emulsifying agents, and blocking of filters and jets by solid organic debris.

Spores of the organisms can remain viable for long periods in dry oils, but their germination and growth require the presence of free water. Growth therefore takes place at the oil-water interface and can be prevented in most systems by keeping the lubricant clean and dry. Often

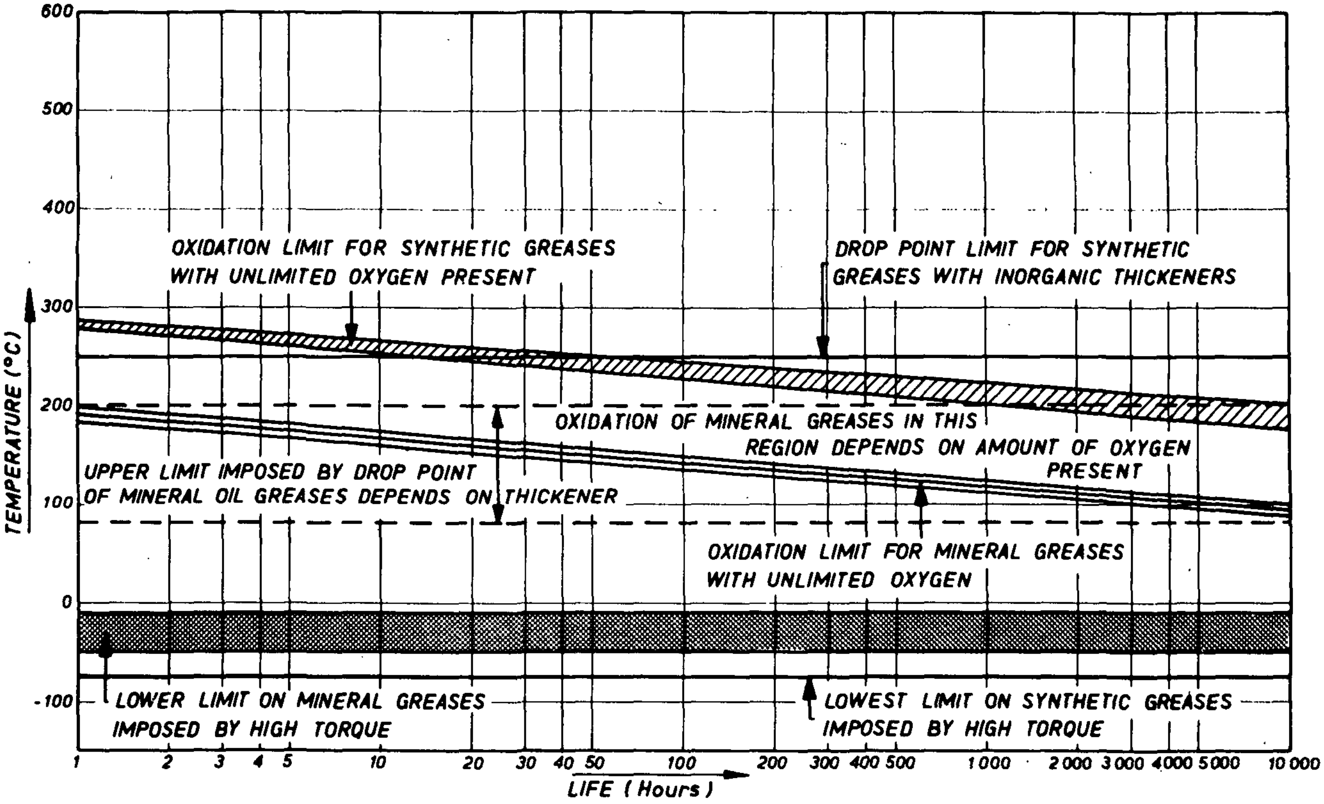

FIGURE 6.—Temperature limits for greases.

condensation cannot be completely eliminated, but it appears that there is an induction period in the initiation of growth, and if condensation water is removed frequently, serious growth will not take place.

By their nature oil-in-water and water-in-oil emulsions are particularly liable to microbiological attack, and system cleanliness alone will not prevent infection. It has therefore become common practice to use biocides in emulsion systems that are exposed to aerial contamination and heat, although their use has not become general in fully enclosed hydraulic systems.

CURRENT REQUIREMENTS IN LIQUID LUBRICATION

There is a tendency to discuss lubricant requirements in terms of the broad range of industries for which they are intended: aerospace lubricants, automotive lubricants, metalworking lubricants, industrial lubricants, and so on. These, however, are marketing classifications, not technical ones.

The real targets of lubricant development need to be defined in relation to specific mechanisms, and the mechanisms in turn will define the required viscosity, load-carrying capacity, required temperature range, stability, volatility, compatibility, and so on.

Because aerospace requirements are in many respects more stringent than those of other industries, large effort has had to be put into the development of aerospace lubricants and some of the advances in other industries have derived from fallout from aerospace programs. It may be a further consequence that advances have been less rapid in some fields where the requirements are very different from those of aircraft and space.

It would not be possible even to touch on all the current requirements for liquid and semiliquid lubricants, but it may be useful to consider the present state of development in a few specific areas.

Aircraft Lubricants

It is common to combine aircraft and space requirements in the term "aerospace," but in fact the requirements of atmospheric and space vehicles are almost completely different. Space lubrication is therefore considered separately. The class of aircraft lubricants is itself very diverse, and the requirements of subsonic commercial aircraft are completely different from those of supersonic or hypersonic military aircraft.

The lubrication of subsonic aircraft has presented no great difficulties in recent years and is based largely on esters for engine oils, airframe oils, and greases. The search for satisfactory fire-resistant hydraulic fluids has been met by phosphate esters, which are adequate for low-temperature applications now that the main compatibility problems have been solved. Efforts have been made to obtain greater standardization of lubricants within specific aircraft and between different aircraft, and this has led to the widespread use of multipurpose greases such as MIL–G–23827A and MIL–G–21164B. For turbine engines, the search for standardization was a major factor in the introduction of MIL–L–23699A, as a potential replacement for both MIL–L–7808 and D. Eng. R.D. 2487, but to date all three seem to be still in use.

For high-performance military aircraft there has also been a search for increased standardization, but this has not been dominated by the overall need for economy, as is the case with commercial aircraft. At the same time there has been a continuing need to cope with higher and higher temperatures. The overall picture during the past 30 years has therefore been one of lubricant standardization within a certain temperature range, followed by the development of a new lubricant for higher temperatures, followed by a fresh standardization phase to cover the wider temperature range, and so on.

This trend can be well illustrated with respect to aircraft greases. Until 1950 there was a high level of standardization on soap-based mineral oil greases. As temperature requirements rose during the 1960's, there was a general adoption of diester-based greases, of which three different ones were in general use in 1960: a general-purpose grease (MIL–G–3278), an EP version (MIL–G–7118), and a low-temperature type (MIL–G–7421). For compatibility and stability reasons, these never completely supplanted mineral greases, for example in wheel bearings.

The upper temperature limit for the diester greases was approximately 130° C, and a further standardization step during the 1960's led to a general-purpose EP diester grease (MIL–G–23827) with a temperature range from −73° to +130° C to replace the previous three. By this time, however, the high-temperature requirement had risen, and this led to the introduction of a more complex mixed-base grease (MIL–G–25760) usable from −40° to +175° C.

The latest standardization step favors the use of greases based on synthetic hydrocarbons (MIL–G–81322), usable from −60° to +175° C and therefore capable of replacing MIL–G–23827 and MIL–G–25760 in most applications. Because the compatibility problem of esters has been removed, this grease is also capable of replacing most, if not all, of the remaining mineral-base greases.

During the late 1950's, a limited need arose for greases up to 230° C. This need was met by silicone greases (MIL–G–25013). The need has since become more general, but the restricted performance of silicones has prevented their more general use. There is therefore a current need for a general-purpose grease for the temperature range from −73° to 230° C, but it is likely to be some time before this need is met.

A similar need has existed for high-temperature hydraulic fluids suitable to 200° C as compared with the 135° C (occasionally 150° C) limit of current petroleum-based fluids (MIL–H–5606), but this need has been in conflict with the search for fire-resistant hydraulic fluids. A chlorinated silicone usable to 200° C and with a high degree of fire resistance was used successfully in certain British military aircraft but did not find general acceptance. As a result the present trend is to use synthetic hydrocarbons for high-temperature systems and phosphate esters for fire resistance in low-temperature systems. There is therefore an outstanding need for a good high-temperature, fire-resistant hydraulic fluid.

The civilian supersonic transport aircraft shares the military need for high-temperature lubricants, although in this case they must also be economical in use. For the Concorde, the greases are similar to those in military use for 175° C, and the same dilemma of high temperature versus fire resistance led to the original selection of a silicate ester fluid with fire resistance not very much better than that of mineral oils.

Piston Engine Lubricants

It is often said in the petroleum industry that research on lubricants cannot be justified on the basis of lubricant sales, as most lubricants do not generate sufficient income. The justification is said to lie in their influence on fuel sales. Whether this is true or not, it is interesting that significant problems still exist in the lubrication of piston engines, where both the volume of oil sales and the volume of associated fuel sales are very large.

The subject of V.I.-improved multigrade oils has already been discussed in some detail and will not be repeated here, except to say that the advantages and disadvantages of such oils need to be more clearly demonstrated.

Concurrent with the widespread use of multigrade oils in spark-ignition engines has come the worrying appearance of a light-colored emulsion, referred to as mayonnaise. "Worrying appearance" is a more accurate term than "problem," as there seems to be no evidence that it has had any deleterious effects on engine performance.

The mayonnaise is a 70-percent water-in-oil emulsion (ref. 30) that may appear in static areas such as rocker covers and filter bodies and occurs with the use of effective polymeric dispersants such as polybutyl succinimides. These dispersants are desirable for engine cleanliness, so there is no obvious cure from the viewpoint of oil formulation, although there is probably scope for some compromise. On the other hand, the formation of the emulsion only occurs if crankcase ventilation is poor, so it should be possible to control it by improved design.

A more serious problem in recent years has been the thickening of diesel engine lubricants used in long-distance, high-speed road transport. This thickening has in some cases progressed to a greaselike consistency and has caused bearing and pump failures because of failure of the lubricant to flow properly.

The thickening has been attributed (ref. 31) to the accumulation of insoluble material derived from combustion soot. It was shown that the amount and type of dispersants used in the oil can have a marked effect on the degree of thickening, but the problem has not yet been eliminated. The generation of soot from inefficient combustion is associated with the difficulty of timing the fuel injection in a high-speed engine, so improved injection control should lead to a reduction in the thickening.

The most serious tribological problem in piston engines is probably that of scuffing (ref. 32) of piston rings and cylinders or liners. Scuffing is associated with a local temperature rise, a reduction in oil-film thickness and an increase in metal-to-metal contact, leading to a further temperature rise, and so on. The resulting surface damage appears to have a critical level, beyond which further surface degradation, and ultimately seizure and structural failure, are very rapid. Where chronic scuffing problems occur in a specific engine type, a cure can usually be obtained by modifying the cylinder cooling, increasing the oil flow, and especially by controlling the surface finish. Attempts to improve the situation by oil formulation have been generally unsuccessful; but this is the subject of continuing effort.

Lubrication in Metalworking

The term "metalworking" is here used in its most general sense to include metal cutting or machining and hot or cold forming. It therefore includes a range of operating conditions that is far too broad to be sensibly covered under one heading, but it is conventional to consider it as a single category, and it includes a number of topics that are of interest in liquid lubricant technology.

Although metalworking lubrication represents a very large application of liquid and semiliquid lubricants, it tends to be ignored in publications or conferences dealing with the general subject of lubrication, especially when they deal with the more theoretical aspects. It also follows, of course, that there are specialized conferences and publications dealing with metalworking lubrication (ref. 33). In this symposium it appears that no detailed consideration will be given to metalworking lubrication, but it is important to remember that this is a major area of liquid lubrication, and that in spite of the specialized operating conditions that occur in metalworking, the same general phenomena of hydrodynamic, EHD, rheodynamic, and boundary lubrication apply.

The special conditions include high contact pressures, large amounts of plastic deformation (even in metal cutting), and the extent of generation of freshly exposed metal surface. The dominant friction and wear mechanism is adhesion, and where effective fluid film separation cannot be maintained, powerful boundary lubricants such as sulfurized fatty oils, sulfochlorinated oils, and chlorinated waxes are used.

There are several current topics of interest, but the one that has probably caused the greatest concern in recent years is that of toxicity. Because of their mode of application, machine-tool operators are generally exposed to contact with cutting fluids, and careful attention has been paid for many years to possible physiological effects. These can include skin infections such as dermatitis caused by organisms carried in infected fluids or toxic effects of certain additives.

More recently there has been serious concern about the carcinogenicity of cutting fluids (ref. 34), which has caused a number of deaths of operators, in most cases many years after exposure had ended. The carcinogens were probably related to the known polycyclic aromatics, and it is possible that by the time the problem became recognized, their occurrence had already been significantly reduced by improved refining techniques. The best solution to all such physiological problems is to reduce the degree of exposure by extraction systems, shielding, protective clothing, and barrier creams. It is difficult, however, to persuade operators to use these techniques when the effects do not become apparent for years.

There have been a few elegant analyses of lubrication in metalworking operations, but in general only the simplest geometries have been adequately described, and it has usually been necessary to make a number of simplifying assumptions. For example, the cold rolling of flat metal strip is essentially a simple two-dimensional system for which many different analyses have been performed, but in every case a simplifying assumption has had to be made, for example, that plane sections through the workpiece remain plane (ref. 35), that the coefficient of friction between roll and workpiece is constant (ref. 36), or that no roll flattening occurs (ref. 37). These assumptions are all more or less invalid under certain rolling conditions, but more important for the lubrication technologist is the fact that they prohibit useful deductions about lubricant selection and formulation.

Hot-forming operations impose severe lubrication conditions, and the development of a stable liquid lubricant for 1000° C would revolutionize the industry. Vegetable oils are currently being used in hot rolling and continuous casting of steel, and it is staggering that with nominal oil-film thicknesses usually of the order of 25 μm (ref. 38), rapeseed oil used in continuous casting has been reported (ref. 39) as emerging still in liquid form with the steel billet from the mold nozzle.

In continuous casting the technical performance of rapeseed oil appears to be quite satisfactory, and it is presumably only the price that has led to a search for petroleum-based alternatives (ref. 40). In hot rolling it is much less certain that the performance of current oils is adequate, and where satisfactory lubrication has been achieved, it appears to be critically dependent on lubricant quantity and mode of application. For hot hydrostatic extrusion of steel, no satisfactory pressurizing fluid and lubricant exists, and the only practical material at present seems to be molten glass, with its usual associated handling difficulties.

Space Lubrication

Although a great deal of work has been done on solid or dry lubricants for space applications (ref. 41), their use in space does not seem to differ greatly from their use in terrestrial applications. Thus solid lubricants are used in certain low-speed applications where the torque is not limiting, such as for snubbing blocks, expansion joints, self-alining housings, and so on, but the important rotary load-carrying bearings such as despin bearings tend to be conventional deep-groove or angular contact ball bearings with oil or grease lubrication.

The lubricants themselves appear to be quite conventional apart from their low vapor pressure and consist of petroleum-based oils or greases fortified with mild EP additives. Such exotic lubricants as the perfluorinated ethers are, as in terrestrial applications, only used where temperature or oxygen compatibility render them necessary.

Vapor pressures of the lubricants are commonly of the order of 10^{-7} torr, so that under the full space vacuum of 10^{-13} torr there would be a rapid loss of lubricant by evaporation. In practice the main bearings are enclosed in chambers from which loss of lubricant molecules is effectively retarded by simple labyrinth seals. The chamber therefore represents a closed system in which the liquid lubricant is in equilibrium with its vapor at the vapor pressure. There is, nevertheless, a steady loss of lubricant from the bearings, and the dominant problem is to maintain sufficient lubricant for effective operation. The available torque is usually low, and the frictional torque in the bearings increases with the quantity of lubricant. There are therefore objections to the use of an excess of lubricant in the bearing on assembly, and there is also a risk that the surplus would drain away during launch.

The technique adopted is to lubricate the bearing initially with a very small quantity of oil or grease and to provide for replenishment. One type of reservoir consists of porous cages or other porous elements providing a continuous capillary path to the bearing surfaces, and with this type the lubricant flow is presumably by capillary and surface migration. The other type of reservoir is either a porous element or a cup that is separated from the bearing by an open gap. The one design criterion for this type of reservoir is that there must be a direct optical path from the surface of the lubricant in the reservoir to the bearing. The assumption is usually made that lubricant molecules escaping from the reservoir will travel in a straight-line path and those which impinge on the lubricant in the bearing will be retained because of the surface tension.

This argument is open to debate. The rate of loss of molecules from the liquid surface will depend on the exposed surface area, the surface tension, and the temperature. All of these factors will favor loss from the bearing rather than from the reservoir, and there should therefore be a continuing lubricant deficit in the bearing. The fact that the technique works in practice implies that another phenomenon may be controlling lubricant supply, and a possible mechanism is that droplets from a disrupted surface in the reservoir move under free fall until they strike the bearing surface. If this is in fact the operative mechanism, it raises some interesting questions about the internal currents in the lubricant reservoir in the absence of convection or other gravity-controlled movements and about the energy and nature of surface disruption.

One simple design feature that will assist the transfer of lubricant from reservoir to bearing is to provide a small amount of reservoir heating. This is done with a few existing satellites, although it is not yet standard practice.

The performance of bearings in space is not yet sufficiently reliable. For Applications Technology satellites there has been limited success in achieving 2 or 3 years' life; but the life of 7 to 10 years that is required of Applications satellites cannot yet be guaranteed.

Sealing

Seals are an important and integral part of liquid lubricant technology, and in many industries seals cause more difficulties and expense than bearings. Many of these difficulties involve packed glands or O-ring seals used for process fluids rather than lubricants, but in many cases where a liquid is retained by a dynamic seal, the liquid is required to provide adequate lubrication of the seal and the counterface.

Wherever flexible seals are used, the seal profile will be influenced by the pressures developed in the sealed liquid, while the pressures will in turn be affected by the seal profile. This is therefore a classic EHD situation, and for certain cases the EHD conditions have been analyzed (refs. 42 and 43). Because of the low modulus of the elastomers, the hydrodynamic pressures developed are low, and the increase in viscosity of the fluid is not usually significant.

For many process fluids the viscosity is not high enough to provide full fluid film separation, and there is a high degree of surface contact. The performance of the system then falls into one of three categories, depending on the nature of the sealed fluid, the nature of the elastomer, the material and surface finish of the counterface, and the temperature and pressure profiles. The three categories are—

(1) *Satisfactory boundary lubrication.*—In many cases this can be predicted on the basis of the known properties of the fluid, as with many edible oils and other food products, but in other cases the reason for satisfactory operation is not at all clear. There is in any case a natural reluctance in industry to spending much effort in establishing why something works.

(2) *Steady wear of the seal until leakage becomes unacceptable.*—This is the normal process when lubrication is inadequate, and the system

is usually optimized empirically by control of seal material, shaft material, and surface finish, use of a lubricant where possible (e.g., a smear of a silicone grease on the seal face), or change to a different seal design.

(3) *Wear of the seal counterface.*—This is often the most intriguing, and exasperating, process. A hard, high-quality, expensive shaft may be rapidly worn by a relatively soft, cheap, and easily replaced elastomeric seal. In most cases the cause is found to be some form of corrosive wear, and the solution is to surface the shaft with a material offering better protection against corrosive attack.

The actual restraining force on the sealed liquid is believed to be due to its surface tension in the annular gap (fig. 7). It follows that where the surface tension is low, the restraint is weak and there will be a tendency

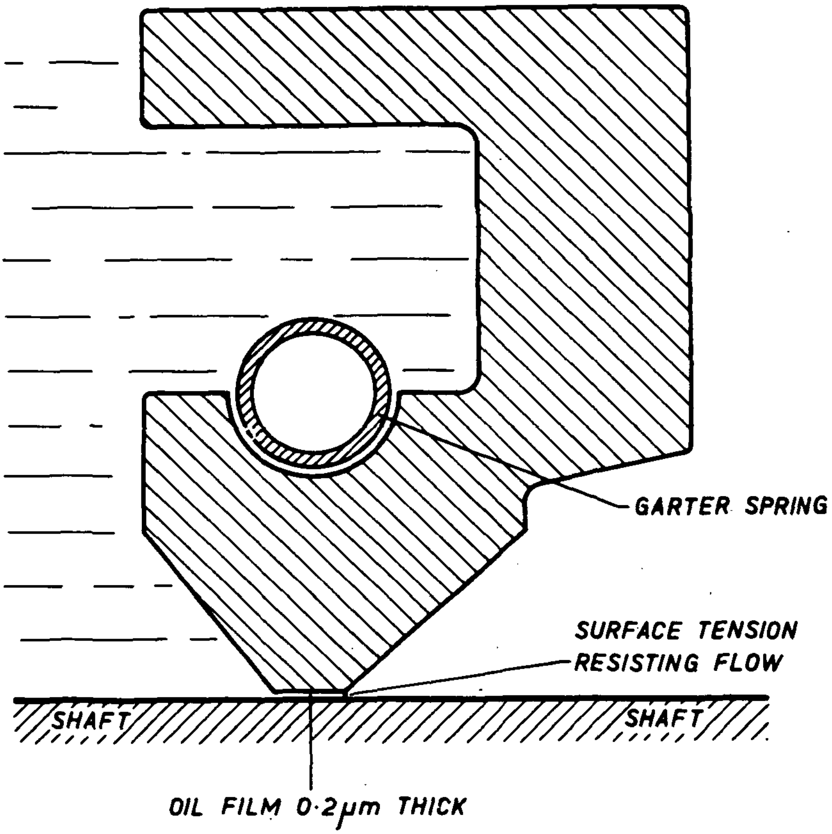

FIGURE 7.—Cross section of an elastomeric lip seal for oil sealing.

to leakage. This will occur with surfactant solutions or if the seal is separating similar fluids or fluids whose interfacial tension is low.

Problems with mechanical seals and process fluids arise most often from corrosive wear or low surface tension. The corrosive wear problem is again usually solved by selecting seal face materials to give adequate corrosion protection, but the problem of low surface tension may require multistage sealing or the use of an incompatible barrier liquid.

Sealing of lubricants is usually by means of elastomeric lip seals of the general type shown in figure 7. The simple unsupported lip is capable of restraining up to 15 psig or slightly higher pressures, while a supported version may provide adequate sealing up to 100 psig. Lubrication of the seal face is hydrodynamic, and the film thickness is usually of the order of 0.0001 in. The mechanism by which a hydrodynamic film is maintained under a simple lip seal has not been satisfactorily explained since there is no apparent wedge action, and it has been ascribed to the effect of imperfections on the surface of the shaft.

The sealing action of a lip seal is again due to the surface tension in the meniscus, and anything that tends to disrupt the meniscus will lead to leakage. This situation is self-perpetuating because while leakage is taking place, the small annular meniscus cannot re-form. There have therefore been a number of recent developments in which modified profiles of lip seals are designed to produce a positive pumping action to drive fluid back into the pressure side and re-form the required meniscus form. These modified profiles include angular ribs or single helices, which are effective only in one direction of shaft rotation, and double helices or raised elements that are effective in both directions of rotation (ref. 44).

The temperature limits for adequate sealing of lubricants are those of the available elastomers. Difficulties arise above 180° C, which is the limit for satisfactory performance and reasonable service life with silicone or fluorosilicone rubbers.

High Temperatures

Some of the factors controlling the maximum useful temperature of lubricants have been discussed in connection with chemical and physical stability, and approximate limits imposed are shown in figures 4 and 5. These limits are for the fairly conventional lubricants that are liquid at or near normal temperatures, but there are other less conventional materials that are usable as liquid lubricants in higher temperature ranges, some of which are listed in table 1.

There is a general shortage of viscosity data for such liquids. Rowe (ref. 45) has given useful information on viscosity-temperature characteristics and coating properties of glasses for use in metalworking, but there appears to be little or no information available about the pressure-viscosity characteristics or viscoelastic behavior. The viscosities of the molten

TABLE 1.—*High-Temperature Liquid Lubricants*

Lubricant	Temperature range, °C	
	Minimum	Maximum
Lead glass	750	1400
Low-melting borate/silicate glass	900	1600
Silicate glass	1000	1600
High-melting borate/silicate glass	1350	1650
Alkali phosphate/tetraborate	600	1100
Sodium chloride/silica	850	1450
Potassium sulfate/silica	1100	1600
Potassium chromate/magnesia	1050	1450
Sodium/potassium eutectic	0	850
Bismuth/lead/cadmium eutectic	100	650
Sodium	150	750
Bismuth/tin eutectic	150	1400
Lead/tin/cadmium eutectic	160	700
Tin/30-percent lead	190	1200
Tin/zinc eutectic	210	800
Lead/antimony eutectic	255	1100

metals and salts tend to be low, and silica and magnesia (ref. 46) have been used as thickeners for molten salts.

Molten glasses are used as lubricants for many hot metal forming operations, including drawing, forging, and extrusion. The wide range of glasses available together with their relatively good viscosity-temperature characteristics make it possible to select a satisfactory glass for a given application. Their thermal stability is good, and their boiling points are high, while their chemical inertness helps to avoid problems of compatibility. The biggest practical problem with molten glass is the difficulty of removing it completely from the surfaces after use.

Molten salts have been known for many years as potential lubricants for hot metalworking operations but have not been favored since the introduction of molten glasses. They suffer from several disadvantages when compared to glass because of their lower viscosities, lower thermal and oxidative stabilities, and higher reactivities. They have two advantages that justify some continuing interest in their use, and these are their easier removal after use and their easier recovery for reuse.

Liquid sodium and sodium/potassium eutectic are used in hydraulic systems in reactors, and the theoretical upper temperature limit in such systems is controlled by the system pressure required to prevent boiling.

In practice, limitations are imposed by the reactive nature of the liquids and the difficulty in maintaining surface conditions on the bearing faces that will provide acceptable friction and wear behavior (ref. 47). Their high reactivity with oxygen and water makes it impossible to use them except in completely enclosed and inert systems.

For all liquid lubricants, conventional or unconventional, use at high temperatures is limited by decrease in viscosity. The actual minimum acceptable viscosity depends on the nature of the bearing system and on the specific design, but the achievement of satisfactory lubrication becomes very much more difficult as the viscosity falls toward 1 cp. This means in practice that even when thermally stable liquids can be obtained, full film separation is difficult to achieve, and there is a greater need for effective boundary lubrication, which is in its turn more difficult to provide at high temperatures.

Fire Resistance

The development of lubricants with improved fire resistance has been the subject of tremendous effort during the past 15 years, and their use is rapidly growing in the aviation, mining, electricity generation, steel, and other industries. As a result of this effort a wide variety of fire-resistant fluids is now available, but their wider application is retarded by two problems: the assessment of fire resistance and the design of equipment for their effective use.

In assessing the fire resistance of a fluid, two basic steps are necessary. The first is to define the conditions that are most likely to expose it to ignition. These may include contact with a flame, contact with an electrical or incandescent solid spark, or contact with a hot surface. Each of these ignition sources may be associated with variations in oxidant supply and heat flux. The ignition tendency of a fluid may be affected by its own premature thermal degradation products and therefore by the rate of increase in temperature.

The second step is to design or select a test procedure that will give a satisfactory simulation of the risk condition, and the resulting tests suffer from duplication and poor correlation. The simplest situation is that of the various flashpoint tests, all of which assess the temperature to which a liquid must be raised in order for its vapor to be ignited by contact with an open flame. There are currently five distinct flashpoint tests in general use for petroleum products: the Tag, Abel, Cleveland open cup, and Pensky-Martens open and closed. They are now being joined by a new type of test based on the Seta-Flash. Fortunately the results obtained by these different tests will rarely differ by as much as 10° C, but even this can cause serious problems with insurance companies and excise departments.

Theoretically the spontaneous ignition temperature of a lubricant should be easy to assess in a reliable and meaningful way because such a test involves only the application of heat to the lubricant in an inert vessel in an excess of air. Unfortunately the ignition tendency is strongly affected by the distance from a solid surface, so lower and lower spontaneous ignition temperatures are measured as the test vessel changes in size from 160 ml to 1 liter to 1 cu ft. An even more complex situation arises when the test simulates sparking or arcing or contact with a hot manifold or molten metal.

As a result of the plethora of ignition tests simulating different conditions, each tending to flatter some fluids and denigrate others, it has been very difficult to make an objective comparison of different fluids for different applications.

The design of equipment to use fire-resistant fluids has been slow, and in the early days it was usually demanded (ref. 48) that fire-resistant fluids should have properties similar to those of the mineral oils they replace. This imposed a serious restriction on the development of fire-resistant fluids, which has only slowly been lifted. Equipment designed specifically for use with fire-resistant fluids is now becoming available, but there is still a shortage of design data and of information about the relevant physical properties of the fluids.

The fluids themselves fall into two categories. The synthetic fluids such as phosphate esters, chlorinated diphenyls, halocarbons, and halogenated silicones have inherently good resistance to ignition, and their initial thermal decomposition products tend to suppress combustion. Apart from their high or very high cost, their greatest technical problems lie in compatibility, especially with elastomers and other nonmetallic materials, but also with many metals. Data are usually readily available on viscosity at various temperatures, volatility, thermal conductivity, specific heat, and chemical stability, and some form of antiwear or load-carrying capacity data, but information about bulk modulus, pressure-viscosity coefficient, non-Newtonian behavior, and shear effects is usually incomplete.

The other class of fire-resistant fluids consists of aqueous solutions or emulsions, which depend for their fire resistance on the cooling effect of the high specific heat and latent heat of vaporization of the water and on the blanketing effect of the steam that is produced. Compatibility problems with such fluids are not serious, apart from the need for adequate rust prevention. The available data are usually similar to that of the synthetic fluids, but for the emulsions it is also important to understand the emulsion stability and the behavior of the emulsion in thin films and under shear.

ACHIEVEMENTS, FAILURES, AND POSSIBILITIES

Perhaps the greatest practical achievement in liquid lubricant technology has been the extension of conventional lubrication techniques to meet more and more rigorous operating conditions. Petroleum-based lubricants have been used at temperatures from −70° to over 300° C, and at pressures from 500 bars to space vacuum and in zero gravity, while machine sizes have grown to over 50 MW for prime movers and over 500 MW for generator sets. At the same time, the operating life of both lubricants and machines has grown steadily longer. With more exotic lubricants, such as polyphenyl ethers and liquid sodium, but with the same conventional design techniques, the temperature limit has risen to over 600° C.

A second achievement has been a better theoretical understanding of the behavior of liquid lubricants in bearings, especially with the development of a satisfactory EHD theory. So far this better understanding has only helped us to understand more clearly the techniques we were already using. Obviously the application of this theoretical knowledge will have helped to refine some existing and new designs and to avoid a certain amount of prototype development effort, but in my experience it is not possible to point out one important application which could not have been developed without a knowledge of EHD theory.

The same might be said, but with less force, about our improved understanding of squeeze films, and there do seem to be some instances where an ability to make a reasonable prediction of squeeze film effects has led to successful designs that might not otherwise have been attempted.

But when we look for radically new and important concepts in liquid lubricant technology, the picture is less flattering. The most important new trend has probably been the widespread use of externally pressurized bearings and, to step outside the field of liquid lubricants, the extension of hydrodynamic and hydrostatic techniques to gas bearings. These developments have involved a great deal of high-quality engineering work on optimization and on manufacturing and metrology, but the basic concept of external pressurization is very pedestrian.

On the other hand, less pedestrian techniques such as magnetohydrostatic bearings, magnetohydrodynamic bearings, and magnetic levitation, in spite of satisfactory development of the theory and demonstration of their effectiveness in many different configurations, have received so little practical application as to be generally considered as fascinating toys rather than practical engineering techniques. Probably a major cause of their general lack of acceptance is that it is often easier to provide external pressurization than to provide a powerful magnetic field.

Foil bearings may come closest to the definition of a radically new and practical technique. They represent a clear innovation and have been well described and analyzed. In addition, there have been some interesting and useful practical applications.

A new development that is of considerable theoretical interest is the demonstration by Tabor (ref. 49) and Roberts (ref. 50) of short-range repulsive forces due to electrically charged double layers on solid surfaces. The magnitude of the repulsive force increases as the separation distance decreases, rising to approximately 10^5 N m^{-2}, or 1 atm, at a separation of

5 nm (50 Å or 0.2 μin.). Uniform separations of this magnitude are not normally found with practical engineering surfaces, but the load-carrying capacity and reduction in friction provided by this mechanism must be of importance in the action of many body fluids.

Another fascinating recent innovation has been the development and successful analysis[2] of the oscillating hydraulic squeeze film bearing in which a load-carrying capacity can be developed between two parallel plates immersed in a fluid when one of the plates is made to oscillate in the direction normal to the gap. It is not clear whether any practical applications of this system have yet been made, but it has been considered as a potential technique for use in gyroscope bearings.

Crystal balls are notoriously unreliable devices, but if one can pick a field in liquid lubricant technology that would repay more intensive study, it might be that of emulsions. In fine emulsions the stabilizing forces, and therefore the resistance to distortion and disruption, can be quite powerful, so significant effects in shear and load-carrying capacity can be expected to occur. In concentrated emulsions the effect of shear is apparent simply as an increased non-Newtonian viscosity, but in dilute emulsions the resistance to shear depends critically on the size of the gap in which shear is occurring and its relationship to the droplet size distribution. The repulsive forces due to charged double layers must also have interesting implications for emulsions.

The important point about emulsions is that they give scope for quite accurate tailoring. In lubricant technology so far, the tailoring has been for fire resistance, high or low emulsion stability, viscosity, corrosion protection, and so on. It may be that with a better understanding of their behavior under boundary conditions, we may be able to provide a new, and helpful, contribution to boundary lubrication.

This has been a kaleidoscopic view of the present state of liquid lubricant technology as seen by the prejudiced eyes of one professional bystander, and some aspects will have been overstressed while others have been understressed or completely overlooked. But it is equally true of lubricant technology itself that some aspects have been overstressed while others have been understressed or overlooked. The field is a broad, complex, interdisciplinary one, and it is natural that individual interests, including financial interests, will have determined the directions of progress. For example, if some large part of the effort that has been devoted or lubricant additives had been diverted to fundamental surface physics to colloid physics, the present state of lubricant technology would be quite different.

I have said earlier that there have been considerable achievements in

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[2] Kauzlarich, J. J.: Hydraulic Squeeze Bearings. Trans. Amer. Soc. Lubric. Eng., in press.

liquid lubricant technology, but to see how far we fall short of the optimum it is instructive to consider the lubrication of animal or human joints. For mammals alone, the size of joints ranges from the phalangeal joint of a pigmy shrew at a 0.2-mm diameter to the neck of a blue whale at a 300-mm diameter. The maximum sliding speed, at about 2 msec^{-1} (400 ft/min), is rather higher than would be recommended for a grease-lubricated plain bearing. The pressure, at 2 $\mathrm{MN\text{-}m}^{-2}$ (300 psi), is near the limit for grease or oil at such speeds, while the maximum *PV* product at 1.5×10^6 $\mathrm{N\text{-}m^{-1}\text{-}sec^{-1}}$ (50 000 psi-ft/min) is in the range where external oil pressurization would probably have to be selected for the specified oscillation amplitudes and frequencies.

The friction is very low, and the system has great flexibility to cope with varying design requirements. Most important is the fact that the operating life is only rarely less than that of the complete machine, except for one type of machine that is now tending to be retained beyond its normal replacement life.

The great fascination of animal joint lubrication is the way in which so many different lubrication techniques contribute to the overall performance, and it has been said[3] that all known lubrication techniques are present in the action of synovial fluid. Roberts[4] has recently suggested that the repulsive forces of charged double layers also contribute to the lubrication of joints, but in view of the magnitudes of the pressures involved, this would appear to be a small-scale contribution.

Of course, if the lubrication of animal joints is a remarkable process, it is also fair to point out that biological processes are self-optimizing (ref. 51), and this process has benefited from something like 10^7 iterations. Mutations are only retained when they are beneficial, and in our own man-made liquid lubricant technology it is the very success obtained that has suppressed the rate of advance in less vital directions. There can be little doubt that as the environment changes, mutations will arise in our technology to cope with them.

But there is one serious change in our environment that can be forecast with certainty and which will inevitably revolutionize our technology, unless we take steps to reverse present trends. By far the greater part of lubrication is based on petroleum, and petroleum reserves are limited and nonrenewable. It would be unproductive to join in the guessing game about when they will expire: the only certain thing is that without conservation they will expire.

The economists talk glibly about "alternative sources of energy when fossil fuel stocks are exhausted," but for us this ignores two vital problems. The first is that the so-called fossil fuel stocks are in fact raw ma-

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[3] Unsworth, A.: Private communication.

[4] Roberts, A. D.: Nature, in press.

terial stocks, from which we can decide to make energy or lubricants or other materials. The second problem, which follows from this, is that if petroleum reserves are allowed to expire, we will immediately lose most of our lubricants and will be forced to base our future on vegetable oils.

This situation has, of course, already arisen with the supply of sperm oil. It may be a matter of opinion whether it is important to save the sperm whale from extinction. It is not a matter of opinion that sooner or later we must have an alternative to sperm oil, or that if the sperm whale does become extinct we, as lubricant technologists, will be largely responsible. In other words, we share the general dilemma of mankind in that we have to start learning to live within our means.

ACKNOWLEDGMENT

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DISCUSSIONS

E. D. Brown, Jr. (General Electric Co., Silicone Products Division, Waterford, N.Y.)

Dr. Lansdown's introductory paper, as he says, must emphasize and touch lightly. We cannot fault him for his priorities. Each specialist would have his own. He did, however, miss a golden opportunity to make two pleas that need hearing. The first is for order and direction in our studies, and the second for a continuing bank of cooperative knowledge. Many of us have hoped that this conference would evolve into this.

No one doubts the essential need for basic theoretical study nor the certain requirement for pragmatic problem solving, but with very little difficulty we could find ourselves in the same ridiculous position as the theoreticians and engineers of the 18th century. At that time theoreticians and textbook authors assumed and based all calculations on a universal 0.1 coefficient of friction for all lubricated surfaces. Even simple calculations would have shown them that one railroad journal would have operated at white heat and required more power than the locomotive could produce. Fortunately, engineers paid no attention and continued to design rolling stock even before Beauchamp Tower and Reynolds enunciated the hydrodynamic theory. One could say, as Dr. Lansdown said about the EHD theory, that then and for many years after, "it is not possible to point out one important application which could not have been developed without a knowledge of EHD theory." Theoretical studies have always preceded to guide and followed to explain. Without them the hit-or-miss pragmatic approach would consume more time than it does now. We need the study of the gray area between the two extremes and have within this group the means of making such a study in each of the areas Dr. Lansdown covered.

Our group can even set priorities in each area. Two examples will suffice. In Dr. Lansdown's discussion of metalworking fluid, he obviously recognized the problems and might as well have spoken bluntly and told us what some of us have learned through bitter experience. The absolute controlling factors of cost and congressional acts governing employee exposure to hazardous materials puts three-quarters of the available technology "on the shelf," or paradoxically requires deep theoretical study. Which way to go? Perhaps an interdisciplinary group can tell us, and here we have the backing of a complete computerized bank of available knowledge.

We are all familiar with the second example, aircraft lubrication. In various countries at various times, people have come to grips with this gray area in a number of ways. Directed research, contracted research, pragmatic on-the-spot problem solving have all been tried, each with a reasonable degree of success. From this experience we should have learned that, within limits, any individual problem yields to sufficient study. Dr. Lansdown himself showed that once a manufacturer knows what he must work with, reasonable designs with reasonably sound theoretical backup result. The limit-extending function of basic research continually changes the picture. The rarity of spectacular breakthrough emphasizes the need for continued interdisciplinary surveillance and evaluation.

We should consider establishing a clearinghouse of ideas and problems, a quick sounding board for unconventional ideas, a reservoir of information available on a day-by-day basis, and even a translation service to convert the language of metallurgy, for example, to the language of chemistry and the language of fundamental study to the language of real machines. We have a major opportunity to reduce the number of problems Dr. Lansdown reports, simply by uniting our scattered knowledge.

N. Glassman (Naval Ship Research and Development Center, Annapolis, Md.)

The author has presented a very useful and stimulating review of the subject. He has recognized that the scope of the subject is of a size requiring careful limiting statements of what is being presented and therefore leaving to the reader the understanding that there is more to the subject. However, if it is assumed that these proceedings will enjoy the same stature as reference sources as those of the previous NASA symposia, then there is a risk that the reader's view of the liquid lubricant world may assume a bias not intended, particularly if the reader does not have guideposts to some of the areas not presented. Accordingly, the purpose of this contribution is primarily to indicate an area—marine lubrication—that deserves the attention of researchers, machine designers, and liquid lubricant manufacturers, and then to make some comments on some of the items presented in the paper.

The author notes that it would not be possible even to touch on all current requirements for liquid and semiliquid lubricants, but considers it useful to examine the present state of development in a few specific areas. The areas selected are aircraft lubricants, piston engine lubricants, metalworking lubrication, space lubrication, sealing, high temperatures, and fire resistance. This is a diverse collection and contains much of general and specific interest, but it also could leave the reader with the impression that these are the most important areas.

This possible outcome could stem from the author's suggestion that aerospace requirements are more stringent than those of other industries and that some advances in other industries have been derived from the fallout of aerospace programs. I agree that if one wants to fly high at speeds exceeding those of sound and operate in a fairly hard vacuum, that a strong case for the relative stringency of aerospace requirements can be made. But what of those who must operate machinery in a marine environment without the benefit of frequent maintenance, using systems that may not be overhauled more frequently than once in every 3 years, made of materials with marginal compatibility with liquid lubricants (e.g., copper alloys in certain marine hydraulic systems), and where the likely ingress of sea-water contamination into the lubrication system is high? In assessing the relative stringency of the marine lubrication area, consider the requirements for hydraulic fluids as set forth by McQuaid (ref. 52) and McQuaid and Keller (ref. 53) for the power transmission, machinery lubrication, and environmental protection of deep submersible vehicles. In such vehicles most of the machinery is placed outside the pressure capsule because of vehicle available space and weight requirements. Thus reliable vehicle performance is critically dependent on the liquid lubricant to perform all of its normally required functions from the surface to the greatest depth of the ocean (from 0 to 20 000 psi and from 150° to 28° F) and an additional function of producing an external environment for equipment instead of either air or sea water. Further examples to support a position of relatively high stringency for the area of marine lubrication are cited in a paper by King and Glassman (ref. 54). These include corrosion inhibition of machinery vapor spaces, countering the effects of sea-water entry into hydraulic systems, the need to provide quiet bearing lubrication, and providing suitable means for lubricant purification. That the area of marine lubrication is a challenging one and capable of providing rewards to the liquid lubricant research and development community as well as to those who must operate in the marine environment is illustrated by the following. Brown (ref. 55) described the development of a new class of hydraulic fluids that can provide satisfactory system performance in the presence of up to 10-percent sea-water contamination. Schatzberg (ref. 56), using a planetary four-ball machine, showed that the reduction in rolling-contact fatigue life by sea-water contamination of the lubricant could be inhibited by lubricant additives, and Felsen et al. (ref. 57) provided further information on the importance of chemical effects in the rolling-contact fatigue life and failure distribution performance of a wide range of lubricating fluids in actual ball bearings. Hopefully the foregoing comments will accomplish the desired goal of drawing attention to the area of marine lubrication.

Returning to specific items in the paper, consideration should be given to listing power transmission requirements among the important commonly occurring secondary functions that liquid lubricants are required to perform. The question of which is the more important liquid function in the hydraulic systems, i.e., lubrication or power transmission, is frequently determined by failed pumps or inoperative valves; however, at pressures in excess of 3000 psig, lubricant compressibility becomes an important factor in system response and then the choice between liquids becomes a matter of relative power transmission effectiveness.

The inference that hydrolytic stability is not often a limiting factor in the performance of lubricants is true in the general sense of the frequency of occurrence of the effect in all classes of lubricants. However, it can be misleading with respect to those cases where its occurrence is important to system success or failure. For example, in the case of fire-resistant aromatic phosphate esters used in certain hydraulic systems, an increase in fluid neutralization number value to greater than 0.3 mg KOH/g can result in measurable system copper and zinc corrosion and is a cause for the removal of the fluid from the system. Water contamination levels in excess of 0.3 percent also are associated with this corrosion. The system bulk oil temperature is approximately 120° F, although the temperature rise of the fluid passing through some of the pump parts may reach approximately 250° F. Also, recently it has been found that hydrolytic instability may be important in the selection of antiwear petroleum-base oils for electric-hydraulic winch applications. Here the effect of hydrolysis is not to decompose the base petroleum oil but rather to decompose some of the additives used and to increase the copper corrosivity of the additives with resultant increase in pump rubbing component wear.

The concept that hydraulic fluids are not normally exposed to contamination except as a result of microbiological growth in the author's discussion of the stability of emulsions may be misleading. While the mechanical engineers design hydraulic systems with the hope that they will keep contamination (dirt and water) out, experience shows that the designers frequently fail and significant amounts of dirt and water are found in the systems without the need for a microbiological factor to cause system operating problems. This certainly is the case in marine applications.

The author mentions water in passing with respect to chemical reactions in the boundary lubrication regime. How important water can be at relatively low concentration levels to satisfactory ball bearing performance is illustrated in the papers by Schatzberg (ref. 56) and Felsen et al. (ref. 57).

With respect to improved fire-resistant lubricant development, the list of industries exerting effort should include national and local governments and the marine industry. The list of ignition conditions should include heated air, i.e., compression ignition. For the effective use of fire-resistant fluids, the problem is not so much the design of new equipment but rather the cost of changing existing designs to accommodate material-fluid compatibility requirements. Where material compatibility was achievable for fluids such as the aromatic phosphate esters and the water-glycol blends, reliable service has been obtained with the desired reduction in the fire and explosion hazards (refs. 58 and 59).

The problems cited in fluid fire-resistance definition and measurement are true in a general sense if one accepts the idea that there should be only one universal test to permit an objective comparison of all liquids. In practice, a consumer will analyze his machinery system and its use, define the likely hazard(s), build a model to simulate the sensitive areas of the system, e.g., a quick-opening valve leading to a dead-end section of a pressure gage, demonstrate how conventional fluids would be ignited, and then use the model to evaluate fire-resistant fluid candidates. Following this, attempts would be made to correlate simpler fire-resistance tests with the behavior of the fluids in the model. That this approach is reliable is illustrated by the history (ref. 60) of the development and experience with two military specifications for fire-resistant hydraulic fluids (refs. 58 and 59).

Because it is an area where researchers can find a challenge, mention also should be made of the relatively poor angular contact ball bearing lubricating ability at high loads of the water-glycol base fire-resistant fluid class. Cordiano et al. illustrated this weakness in 1956 in their paper (ref. 61). More recent experience has shown that the MIL–H–19457 aromatic phosphate esters also tested in reference 60 can be manufactured to give equal bearing fatigue-life performance to that of petroleum oils in the Cordiano et al. test procedure, but the water-glycol base fluid class appears not to have made similar progress. Successful research to provide improved water-glycol base fluid formulations should result in a wider use of these otherwise very attractive fluids for high-performance machinery in potentially hazardous applications.

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I have three comments to make on this paper.

First, Dr. Lansdown refers to the SI unit of viscosity (N-sec-m^{-2}) as the pascal second. This usage is strongly deprecated by the Institute of Petroleum and the British Society of Rheology, largely because of possible confusion with Redwood seconds and Saybolt seconds. At present, there is no accepted simple name for the SI unit analogous to the poise for the CGS unit. The name "pascal second" arises because the unit of pressure in the SI system (N/m^2) is in some quarters called the pascal. In the United Kingdom the rather cumbersome Newton second per square meter is preferred.

Second, in a reference to the pioneering work of Barlow and Lamb (ref. 7), Dr. Lansdown records that the relaxation times at atmospheric pressure are of the order of 10 psec for saturated hydrocarbons and 1 nsec for monoaromatics. I wish to point out that I tested this result by determining the relaxation spectra of saturates and monoaromatics fractions of oils (ref. 62). It was shown that the width and general shape of the spectrum was the same for a whole oil as for its fractions. By comparing details of the spectra, it was concluded that the spectrum of an oil cannot be interpreted solely in terms of the hydrocarbon-type analysis. To continue to put such precise figures as those quoted to the values of relaxation times is not justified.

The body of experimental data shows that with few exceptions the relaxation spectra of nonassociated, nonpolymeric liquids are closely similar and well represented by the spectrum of the Barlow, Erginsav, and Lamb (BEL) model (ref. 63). This result applies equally well to pure liquids of low molecular weight and to complex mixtures of moderate average molecular weight such as oils and oil fractions. The BEL spectrum is a unique function; all the molecular characteristics are contained in the two parameters of the model; namely, the viscosity at zero shear frequency and the shear modulus at infinite shear frequency.

Finally, in discussing viscosity-shear rate relationships, Dr. Lansdown mentions that "in a rotary viscometer with either concentric cylinder or cone-and-plate geometries, there is a known tendency for non-Newtonian fluids, including greases, to migrate to zones of lower shear rate."

Is this a reference to secondary flows? A number of secondary flows (transverse to the primary flow) have been investigated experimentally and theoretically, including those for the viscometers mentioned. They do not generally involve a migration of liquid from high to low rates of shear, nor do they occur only for non-Newtonian fluids. Inertia forces in Newtonian liquids give rise to secondary flows in rotary viscometers; for example, Taylor vortexes in concentric cylinders. If the liquid also has elastic properties, the secondary flow can be modified. Sometimes secondary flow is more pronounced, sometimes less pronounced, than for the equiviscous Newtonian liquid. Sometimes, as in the cone-and-plate geometry, the secondary flow pattern divides into more than one zone with the secondary flow rotating in opposite directions in adjacent zones. A few references to work on secondary flows are given in my own paper [5] in the section on liquid failure.

Alternatively, is it a reference to liquid failure? Liquid failure, as discussed in a section under this heading in my paper, is often associated with secondary flows but is not predictable from secondary flow theory. One

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[5] See the lecture "Theory of Rheology" by J. F. Hutton appearing later in this volume. (Editor's note.)

type of liquid failure that I have studied seems to involve a migration of liquid from the shearing zone, but in detail it is seen that the liquid separates in the shearing zone. The effect is similar for silicone fluids (ref. 64) and lubricating greases (ref. 65).

R. L. Johnson (NASA Lewis Research Center, Cleveland, Ohio)

Dr. Lansdown has provided an extensive review of lubricant technology that is an effective background for the more detailed discussions that will follow. My comments on this paper should be considered supplementary rather than critical. There are some added elements that merit more detailed consideration at this symposium.

Pressure viscosity and rheology of lubricants in general require much more detailed treatment. An important question is, What pressures are really important to EHD contacts? As mentioned, the general observations are that the entrance conditions determine film thickness; some further indications are that the Hertzian contact conditions dominate the fluid behavior with regard to traction. The shear stress and real oil film temperatures are further contributing factors. We know there are very few aerospace liquid lubricants that are Newtonian under shear conditions of thin-film lubrication. Further, early American Society of Mechanical Engineers (ASME) and more recent high-pressure viscosity measurements (e.g., Winer, Cameron, Reiner, etc.) suggest that phase transformations may provide a solid or semisolid film material at pressures in the Hertzian contacts. Is it this behavior that makes high-traction fluids behave as they do? High-traction fluids in general do have high pressure-viscosity coefficients. Is that the key?

It is suggested that the more positively stated definition for boundary lubrication in the 1969 OECD Glossary of Terms and Definitions on Friction, Wear, and Lubrication be considered by the author. There boundary lubrication is defined as "A condition of lubrication in which the friction and wear between two surfaces in relative motion are determined by the properties of the surfaces and by properties of the lubricant other than bulk viscosity." For years many workers in boundary lubrication recognized the importance of thin-film hydrodynamic effects that include empirical observations of EHD and other means for generating fluid films. With the delineation of these effects into rational models, strengthening of our basic understandings is being achieved. The important message to us should be to avoid being purists in a very complicated and obviously interdisciplinary technology such as lubrication.

The failure modes for liquid lubricants for varied mechanisms of lubrication should be explored in thermodynamic terms. Some early work along those lines by Blok and others were notable; much more detailed understanding of the properties of lubricants and surfaces now being gained should allow more satisfying efforts. The mechanisms of failures like the lubrication models need careful delineation.

Starvation of lubrication in concentrated contacts is believed more prevalent than the literature would suggest. The very high speeds of advanced aircraft turbines and the sparse lubricant supplied provided by mist lubrication further accentuate the starvation problem. This problem is one that is most effectively approached by a combined experimental and analytical study as performed by L. D. Wedeven (ref. 66) and which he is continuing at NASA Lewis Research Center. His results indicated the importance of surface energy relations in the realm of physical chemistry such as surface tension and interfacial energies as well as the more commonly considered fluid properties. Optical interferometry is a powerful tool in studying lubricant starvation, because it allows us to document the film shape, boundaries, and thickness simultaneously. Some of the strictly analytical approaches use models not confirmed by experimental determination.

Surface energy is commonly discussed with respect to liquid lubricants. Its relevance to real problems is often in question; however, in the role of the lubricant as a coolant it is anticipated that surface energy relations can be shown to be of critical importance. If the vapor phase of the lubricant in the wake of a concentrated contact (fig. 7, ref. 67) is in contact with the solid surface, the lubricant's efficiency as a coolant will be impaired. On the other hand, if the entire solid surface is wetted by the liquid phase and the vapor is completely entrained by the liquid, cooling can be more efficient. It has been suggested in reference 67 that wetting or nonwetting of surface films may be the key to achieving acceptable thermal equilibrium in lubricated mechanical components.

The paper mentions rubber lip seals as the primary sealing devices considered for liquid lubricant systems. In fact, with aerospace devices it is very rare that lip seals can be used at all because the operating conditions are most commonly beyond their capabilities; that is, surface speeds, temperatures, and pressures are greater than the limitations of lip seals. The more promising sealing devices now available for extreme conditions include the self-acting gas-film face and shaft-riding seals that have been studied extensively in NASA Lewis Research Center in-house and contractual programs (ref. 68). With appropriate windbacks to keep oil from the gas-film interface, these seals have been operated at 500 ft/sec, sealing 300 $\mathrm{lb/in^2}$ air at 1200° F; further performance gains are anticipated.

F. G. Rounds and N. A. Hunstad (General Motors Research Laboratories, Warren, Mich.)

Dr. Lansdown has presented a broad, realistic appraisal of the state of the art in liquid lubrication. In general, we agree with his assessment. However, in discussing automotive lubrication problems, he has limited himself to the European viewpoint. To supplement his paper, we would like to discuss some aspects of automotive lubrication in the United States.

In this country, the owner of a car has come to expect that it will start easily, run well, and give good performance over a long period of time under extremes of operating conditions, and that it will give such service with relatively little maintenance. Continuing improvements in lubricant quality have contributed significantly to satisfying the owner's expectations.

What are the U.S. car lubrication problems? Past and present problems include both oil- and grease-lubricated areas. Oil-lubricated problem areas are the engine, transmission, and rear axle. Engine problems involve viscosity, volatility, varnish and sludge, oil thickening, rust, and valve train wear. Transmission problems include viscosity, oxidation, friction, elastomer compatibility, foam, and corrosion, while rear axle problems are viscosity, scoring and wear, and friction. Grease-lubricated problem areas are the wheel bearings, with problems at low-temperature torque and high-temperature stability, and the suspension system, with problems of brine sensitivity and torque stability. Past lubrication problems are listed, even though they are presently under control because experience has shown that many of them recur. Changes in automotive component design or manufacture, service operating conditions, or lubricant formulation can lead to such recurrence.

Engine Oil.—In the engine, the oil must be sufficiently viscous at high operating temperatures to provide adequate lubrication of journal bearings and to prevent excessive consumption. At low temperatures and low shear rates, it must be sufficiently fluid so that it will flow readily to the pump inlet. Also, at low temperatures, viscosity must be low enough at high shear rates to permit easy cranking and starting. Volatility is another factor that must be limited to control oil consumption.

Oil oxidation resulting in the formation of varnish and sludge can lead to oil screen plugging and ring sticking. Another oil oxidation problem, thickening, recently caused trouble in some U.S. cars. In some instances, thickening was severe enough to prevent engine starting or to cause engine seizure. This thickening is caused by high-temperature operation that has become more common as high-speed expressway driving for sustained periods, trailer towing, and air conditioning become more common. Engine modifications for emission control have also contributed to higher operating temperatures.

Short-trip operation promotes rust formation, which can cause stuck or excessively worn valve lifters.

Valve train wear is generally held to acceptably low levels by incorporating suitable antiwear agents in modern oils. However, problems occasionally arise in this area; and further antiwear quality improvement is desirable.

The forthcoming removal of lead antiknock agents from gasoline will have significant effects on engine oil performance. The most dramatic effect will be the near elimination of rust. Sludge will also be greatly reduced. However, varnish may be slightly increased.

Automatic Transmission Fluid.—Viscosity is a major consideration for automatic transmission fluids. At high temperatures, the viscosity must be sufficiently high that internal leakage does not cause inadequate hydraulic pressure. At low temperatures, the fluid must flow readily to the pump inlet and throughout the hydraulic circuit. If pressures and flow rates are too low, friction elements cannot be engaged effectively and as a result will burn.

Automatic transmission fluid friction properties are carefully controlled by the incorporation of suitable friction modifiers. To obtain smooth shifts, most U.S. transmissions are designed to use a fluid that produces a static coefficient of friction lower than the dynamic. As a fluid oxidizes, the oxidation products compete with the friction modifier for the friction element surfaces, causing static friction to increase. The resulting change in the friction-speed characteristics can lead to clutch stick-slip motion and chatter. Also, kinetic friction may decrease sufficiently with use to cause excessive clutch slippage and burning.

Foam and air entrainment can be serious problems, and antifoam agents are included in fluid formulations to reduce the incidence of such problems. A related practical consideration is the quantity of fluid in the transmission. If the fluid level is high enough to reach the rotating transmission parts, a great deal of foam can be generated even with a fluid containing a normally sufficient amount of antifoam agent. Such foam generation can lead to expulsion of fluid out the filler pipe resulting in an underfilled condition that will permit induction of air by the pump. Air in the hydraulic circuit, for whatever reason, can reduce the pressure below the desired level. At the least, this causes undesirable changes in shifting action and at the worst, failure of the friction elements.

Compatibility between transmission fluids and seals is another important consideration. Shrinkage and hardening of seals lead to both internal and external leakage. Internal leakage interferes with friction element actuation; external leakage can reduce the fluid level below that necessary for satisfactory transmission operation.

Corrosion of transmission components has been a very minor problem in past years. Recently, however, corrosion of copper-lead bushings and brass suction screens was observed in efforts to develop long-life fluids. While success was achieved with respect to improved durability of other transmission parts, portions of the bushings and screens corroded away in extended dynamometer durability tests with some fluids. Apparently, the cause is exposure of these components to partially oxidized fluid for periods of time longer than previously experienced with fluids having shorter lives.

Rear Axle Lubricant.—Low-temperature viscosity of rear axle lubricant must be low enough for lubricant to flow freely to the pinion bearings. If the flow is inadequate, the outer pinion bearing can fail quickly when a car is driven at expressway speeds before the lubricant has had a chance to warm up from subzero temperatures.

High-temperature viscosity is not critical. Satisfactory rear axle operation has been achieved with lubricants having viscosities much lower than those of current products.

Rear axle lubricants must be properly formulated to prevent pinion and ring gear scoring. Also, they must protect against excessive wear of the cross shaft, tapered roller bearings, and limited-slip differential clutch plates. Good antiscore additives are not necessarily adequate antiwear additives.

Satisfactory operation of limited-slip differentials requires suitable lubricant friction characteristics. The static coefficient of friction must be lower than the kinetic to prevent chatter. Finding a friction modifier that is effective in the presence of antiscore agents is a difficult formulation problem.

Grease.—Several problems are faced in grease-lubricated components. For example, the low-temperature torque of wheel bearings is influenced principally by grease characteristics. Excessive torque resulting from too stiff a grease can cause skidding of the front wheels on the road surface or slipping of the inner race on the spindle.

Disk-brake-equipped cars subject wheel bearing grease to high operating temperatures. For this application, greases must have good thermal and oxidative stability.

Suspension joints have their own unique grease requirements. Squeaks resulting from brine contamination and changes in ride and handling caused by changes in joint rocking torque are undesirable. Greases can be formulated to prevent the development of such problems.

Another problem that can be alleviated by careful grease formulation is wheel bearing fretting. This is not a service problem, but one that develops in cars shipped long distances over land.

Performance Tests.—To deal with the foregoing problems, the automotive industry has been developing performance tests for engine oil, automatic transmission fluid, rear axle lubricant, and grease. Typical examples are—

(1) Sequence tests IIC, IIIC, and VC for engine oil
(2) Powerglide oxidation test for automatic transmission fluid
(3) Brine sensitivity and torque stability tests for chassis grease

In the case of rear axle lubricant, performance tests included in the MIL–L–2105B specification are used in defining GL–5 gear lubricant, which is recommended for servicing many rear axles.

These performance tests are continually being updated, and new ones developed, to keep pace with developments in automotive components and service operating conditions.

Future Work.—Although satisfactory answers have been found for many of these automotive problems, there are others that require further study. Some of these are bulk oil related, others are surface related. Bulk-oil-related problems include viscosity as function of temperature, pressure, and shear rate; oxidation in the engine environment; elastomer compatibility (elastomer reversion); and grease high-temperature performance. Surface-related problems include wear and antiscore activity and friction-speed characteristics (additive competition).

Engine oils and transmission fluids are non-Newtonian. As a consequence, the commonly used low shear rate viscosity measurements do not satisfactorily describe the performance of oils in some parts of the engine or transmission. Further, viscosity measurements at a temperature higher than the traditional 210° F may be needed.

Present indications are that engine oil temperatures will continue at their current high levels or possibly increase somewhat. While the problem of high-temperature thickening is under control at this time, more knowledge of oil oxidation in the engine environment is needed for understanding the phenomenon and for dealing with similar future problems.

A potential future problem is seal durability at sustained higher operating temperatures. With longer lived transmission fluids, seal reversion has been observed.

Another area in which understanding is lacking is grease performance. The effect of composition variables on high-temperature performance is of particular interest currently.

Some changes in the surface-active additive systems will also be needed. If engine oil operating temperatures increase in current piston engines or in some future alternate powerplant, the conventional zinc dialkyl dithiophosphates may no longer be adequate for either antioxidant or antiwear purposes.

A better understanding of the interrelationships among additives, base oils, and rubbing surface metallurgy is needed to make future progress in combating wear and controlling friction. In the case of the limited-slip differential, combining antiwear, antiscore, and friction-modifying properties in a single molecule may be required. Control of friction-speed characteristics for a longer period of time is needed in both the transmission and rear axle.

A possible future development in automotive transmissions is the friction drive type of device. The potential of such devices has been improved with the development of fluids providing 50 percent more traction than conventional lubricants. But, work remains to make friction drives practical.

Summary.—In this discussion, we have not attempted to provide an exhaustive review of automotive lubricant problems. Rather, we have given examples of some that are under control and some on which more information is needed. Continued efforts to better match automotive requirements and lubricant capabilities will produce improved automobile component performance and durability and greater customer satisfaction.

T. Salomon (OMER, Israel)

The author states that "there is some evidence . . . that part of the 'wear' metals can exist in true solution in the lubricant, even . . . a plain mineral oil." In normal cases this statement applies only to minute amounts of metals. According to a survey made by an International Study Committee, the copper content in filtered used light mineral oils (insulating oils) never exceeded 1 ppm; in most cases the metal content was about a few tenths of 1 ppm. There are, however, two typical cases where the metal content in filtered used oils may largely exceed this value:

(1) Highly acid-refined mineral white oils containing some chemical impurities may dissolve a much larger quantity of copper as green copper soaps.
(2) Mineral oils submitted to electrostatic discharges dissolve iron as organoferrous compounds. Some filtered used oils from steam turbines, where such electrostatic discharges had occurred, contained up to 0.3 percent dissolved iron.

The statement ". . . the overall rate of oxidation will often be controlled by the rate of replenishment of oxygen" must be more restrictive. It is a well-established fact that the rate of oxidation in a stagnant atmosphere is much greater than that in the case of replenishment with oxygen. In a stagnant atmosphere the oxidation is catalyzed by the volatile oxidation compounds formed, mostly aldehydes, which cannot escape, as it happens in the case of the replenishment of oxygen. The type of oxidation occurring in a stagnant atmosphere is different from that produced with replenishment of oxygen. This explains also why oxidation inhibitors are much less effective in a stagnant atmosphere.

There is a practical example illustrating this fact. In the 1930's, a 60 000-kW steam turbine was built with a completely tight oil circuit to avoid any entry of air during the operation and to suppress any oxidation of the oil. When this set was put into operation, the opposite effect occurred: no mineral oil of the best quality available then could withstand more than 3 months without producing heavy oxidation and corrosion problems. As soon as some holes were made in the oil circuit to let the volatile oxidation products escape and to insure a normal replenishment of oxygen, the rate of oxidation became normal and no corrosion occurred.

LECTURER'S CLOSURE

I would like first to respond to some specific points in the written discussions and then to summarize the general position as I see it.

Dr. Brown has suggested that we need order and direction in our studies. Certainly few lubrication specialists would defend the present allocation of effort and priorities. A very high proportion of the total effort is devoted to the invention and application of lubricant additives because this is the area in which the greatest financial returns to the sponsoring group can be expected. A major effort also goes into the solution of defense problems. At the other end of the scale, the sums of money spent on university research are pitiful, yet this is where many of the great advances are made.

But if we accept that more order and direction are needed, who would we trust to define the required order and direction? Most scientists will agree with C. P. Snow (ref. 69) that no single scientist should be in a position of such authority. Even a single committee allocating funds for research will not be accepted by the majority of workers in the field. It seems inevitable that decisions will be made by a great number of separate committees and individuals, each with a different special interest and bias, which is the situation we see today.

Perhaps the best we can hope for is, first, that the range of special interests should be wide enough that no worthwhile research proposal goes unsupported, and second, that all the decisions should be well informed. This is Dr. Brown's second point. The problem of information gathering and translation is particularly important and particularly difficult in an interdisciplinary technology. One of the original targets of the tribology activities in the United Kingdom was to improve liaison between specialists in different disciplines, and there has certainly been considerable progress in this respect. But there is still room for better communication, and I personally would welcome a new approach to this problem.

Mr. Glassman has rightly drawn attention to the importance and difficulties in marine lubrication. I would only question two comments in his contribution, both of which relate to fire resistance.

The first comment is that "For the effective use of fire-resistant fluids, the problem is not so much the design of new equipment but rather the cost of changing existing designs." I wish I could accept that statement, but it seems to me that we have been saying the same thing for well over 10 years, and that much of the equipment we are now trying to convert was designed and built during that 10 years. I hope fervently that I won't be saying the same thing 10 years hence; but I suspect that I will. While we concentrate on the problem of converting existing equipment and neglect the design of new equipment, we will be continuing to run hard to stay in the same place.

Second, Mr. Glassman has said that "In practice a consumer will analyze his machinery system and its use, make a definition of the likely hazard(s), build a model to simulate the sensitive areas of the system . . . and then use the model to evaluate fire-resistant fluid candidates." I have no doubt that this is, or should be, the method adopted by large, high-technology organizations such as Government departments, but the risk with simple standard tests is that they may be adopted uncritically by smaller or less knowledgeable organizations, and for this reason we should make sure that their limitations are clearly and widely understood.

Mr. Hutton has accused me of referring to the SI unit of viscosity as the pascal second. What I said in fact was that "the adoption of the SI system is bringing strong pressure for . . . pascal seconds," and this is unfortunately quite true. The difficulty is that newton-second per square meter is too cumbersome for convenient use, while the poise, although a compatible unit, is not pure enough for the SI purists. Because of the peculiarities of grammatical construction, the possibility of confusion between pascal seconds and Redwood seconds is greater in English than in other languages, so the unit of viscosity remains one of the stumbling blocks in SI.

I am grateful to Mr. Hutton for his other comments, and especially for his clarification of secondary flows.

Mr. Johnson has suggested that I might have used the OECD definition of boundary lubrication. I would counter by suggesting that the OECD definition, taken literally, certainly includes EHD lubrication, so on the whole I prefer Tabor's definition.

I accept Mr. Johnson's comment that lip seals can rarely be used in aerospace systems. The numerical dominance of lip seals for liquid lubricants comes mainly from their use in hundreds of millions of piston engines, comparatively few of which are now used in aircraft.

The sheer number of road vehicles in existence makes automotive problems very important, and the contribution by Rounds and Hunstad is a very useful review of some of the present work and problems in that field.

It may be true, as they have said, that most U.S. automatic transmissions are designed to use a fluid that produces a static coefficient lower than the dynamic, but one of the biggest manufacturers in the United States and elsewhere specifies exactly the reverse. It seems to be one of the most curious anomalies in current lubrication practice that the designers of automatic transmissions fall into two groups having diametrically opposite requirements for a major lubricant property.

I would like to correct two misapprehensions in the Rounds and Hunstad contribution. The first is that in discussing automotive lubrication problems, I limited myself to the European viewpoint. It is true that the scuffing problem is apparently not serious in North America, but the oil thickening which I also highlighted is, or has been, very much more of an American problem than a European one.

Their second misapprehension lies in their comment that in the United States "the owner of a car has come to expect that it will start easily, run well, and give good performance over a long period of time under extremes of operating conditions, and that it will give such service with relatively little maintenance." I can assure them that there is nothing peculiarly American about this hopeful expectation; but whether the American or the European car owner comes closest to realizing his expectation, I would hesitate to guess.

Professor Salomon has implied that only in special circumstances is the content of dissolved metal in used oils likely to exceed 1 ppm. Positive proof of higher concentrations is generally lacking, but I believe we will find that concentrations to 10^{-5} are not uncommon. However, even concentrations below 1 ppm raise some interesting questions of reaction mechanisms and composition of the organometallic compounds present.

My statement that "the overall rate of oxidation will often be controlled by the rate of replenishment of oxygen" does not necessarily imply that there is always a positive correlation between oxidation rate and available oxygen, because as Professor Salomon points out the reverse may sometimes be true. Nevertheless, in most bench tests for the oxidation of lubricants, the assumption is rightly made that a high rate of oxygen supply will be associated with a high rate of oxidation.

In closing, I would like to return to one of the comments made by Dr. Brown, "We should consider establishing a clearing house of ideas and problems." Why should such a clearinghouse be necessary? I think the answer to that is fundamental to this whole problem of interdisciplinary technologies.

We have all paid great attention in recent years to improving communication between the different disciplines involved in tribology, and I am sure that all the specialists are now much better aware of work in other disciplines and of its importance to their own work.

But there is another danger that can even be increased by improved communication. That is that an individual worker, having read research publications from other disciplines, and having understood at least the summary and the conclusions, may come to feel competent to apply the results of such research in his own work without getting expert advice. To some extent, of course, we all have to, and there are many who have very successfully switched from one discipline to another, but we need to take great care to make sure of our ground when we do.

I have been concerned at times recently to see a chemist misapplying EHD theory, a rheologist misunderstanding colloid chemistry, an EHD specialist making metallurgical mistakes, and another engineer trying unsuccessfully to cope with surface chemistry. These were all able men, making these mistakes in the course of their own research.

As a chemist I find it salutary to be reminded of how thin the ice is when I venture out into stress analysis or rheology.

How, then, can the designer with a problem be sure of getting good advice, especially if his problem is near the frontier of existing technology? This is where, to my mind, the clearinghouse has a role to fulfill.

No organization can afford to have available within itself the sort of spectrum of knowledge that is brought together for these NASA Interdisciplinary Symposia, so no specific engineering problem is ever exposed to the sort of searching analysis which a group like this ought to be able to bring to bear.

So I would support the idea that a group of specialists from widely differing disciplines and backgrounds should be brought together from time to time to consider real problems. The subjects might be specific design problems, the planning of a research program, or a stumbling block in an existing program. The value of such a discussion to the sponsoring organization could be very great indeed, while the specialists taking part would all benefit from the contact with new problems outside their own work and from an improved awareness of how much or how little they understand of each other's subjects.

This is still not what is implied by a clearinghouse. A clearinghouse implies a more permanent sort of organization, and the merit of the multidisciplinary problem discussion lies partly in its nonpermanence. Each specialist would come to such a meeting from a different background, and any permanent organization would tend to diminish the infinite variety of the individual contributions.

Perhaps the clearinghouse as envisaged by Brown is more like what our Tribology Centres were intended to be, but have not yet succeeded in becoming.

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Mineral Oils

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The scope of lubricants made from mineral oils is outlined, and the predominant position of these petroleum-derived products is cited. Relatively good stability, low cost, and ample availability of mineral oils have restricted the use of more expensive synthetic oils to relatively low-volume applications requiring unique properties.

Types and compositions of base stocks are reviewed, and the product demands and compositions of typical products outlined.

Refinery processes and crude oil source are related to chemical composition of the refined base stock. Thus, nonhydrocarbon components, such as sulfur, nitrogen, and oxygen compounds, may vary considerably. Superrefining removes these impurities and permits formulation for maximum stability. Hydrocracking may provide a practical commercial process for this end. Important base stock properties are discussed.

Mineral oil base products are predicted to play for many years the major role in lubricating the Earth's machinery.

SCOPE OF PRODUCTS

MINERAL OILS derived from petroleum comprise by far the most important class of base stocks used in the manufacture of liquid lubricants, as well as greases. Although synthetic base lubricants have unique qualities and are essential for some applications, the great bulk of the lubricants used in the world employ mineral oils. The free-world lube oil demand is almost 5.7 billion U.S. gallons a year (ref. 1), of which more than 97 percent is mineral oil. Additives for mineral oils and synthetics have become essential for many applications but comprise a small fraction of total lubricant composition. There are several reasons for the dominance of mineral oils as base stocks. First, lubricants made with properly refined and selected mineral oils perform very well in an extremely wide variety of applications. In some cases, such lubricants are better than any synthetics yet developed. In particular, mineral oils are relatively stable to thermal or hydrolytic stress and relatively inert chemically. Second, the cost of mineral oils is relatively low, roughly an order of magnitude less than syn-

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thetics. Third, they are readily available. Estimates for the future predict even more excess capacity (ref. 1). Finally, because mineral oils have been the principal lubricant ingredient through the Industrial Revolution and up to the present, very many lubricant applications and specifications were tailored to fit existing mineral oil types of lubricants. The reverse of tailoring synthetic lubricants to fit existing applications. The importance of this factor in perpetuating the dominance of mineral oils cannot be overemphasized. It has severely impeded the introduction and growth of synthetic lubricants.

The variety of applications of mineral oil base lubricants is almost without limit. Even where synthetics will perform better, e.g., fire-resistant phosphate esters, petroleum products often are used for reasons of lower cost, ready availability, or convenience. A list of individual applications would fill several volumes. Applications are grouped under broad categories such as automotive, industrial, and process and testing. Further breakdowns within each category are made as shown in tables 1 and 2, together with relative importance (volume used) of the applications (ref. 1).

One may wonder why there are so many different lubricant products. Although, in part, this derives from the obvious advantage of functional or application names for products that indicate the intended use, it is a fact that many different compositions are required to obtain optimum balance of performance and cost. In most cases, the goal is the lowest cost composition that will give satisfactory performance. Generally, lubricants contain additives; these are covered in a separate paper of this symposium. With regard to the base stock, choices are possible for functional as well as cost reasons. For example, nonsynthetic refrigeration oils require a base stock made from wax-free naphthenic crude. Turbine oils have longtime oxidation test requirements, and this demands a highly treated base stock (low aromatics) to achieve adequate response to antioxidants. Spray oils must not have more than specified contents of aromatic structure to minimize plant damage. On the other hand, some rubber process oils must contain at least a specified minimum amount of aromatics to provide proper plasticization of that particular synthetic rubber. In some cases, the base stock composition is not critical because of mild, once-through use (marine oil) or because its primary function is to carry potent chemical additives (metalworking oils) that are, in the main, largely responsible for product performance.

By way of illustration, table 3 summarizes these points for 10 product types, out of the scores of types in use.

Thus, lubricants made with mineral oils include a very broad range of functions. In addition to lubrication, functions of power transmission, heat transfer, insulation, solvency, and many other specialized purposes are served by these products. Although some of these functional aspects may

TABLE 1.—*1969 U.S. Lubricant Markets*

	Volume, millions of barrels
Automotive	23.9
Industrial lube oils:	
Hydraulic and circulating oils	
Gear oils	
Turbine oils	
Gas engine oils	
Railroad diesel oils	
Metalworking oils	
Base oils and miscellaneous oils	
Total	17.3
Process and testing oils:	
Process area:	
Rubber process oils	
Wood preservatives	
Petroleum additives	
Spray oils	
Leather and paper	
Plastics	
Textiles	
Newsprint ink	
Others	
Application:	
Synthetic rubber production	
Logging and lumber	
Petroleum products	
Plant food consumption	
Leather products plus paper and board production	
Total plastics production	
Textile mill products	
Newsprint consumption	
Total	7.2
Grand total	48.4

appear unrelated to lubrication, most are found to play a role. For example, the electrical properties of hydraulic fluids can have a profound effect on the wear, by an electrical mechanism, of hydraulic system spool valves (ref. 2).

Returning to relative supply and demand, the United States produces about 55 percent and consumes about 39 percent of the petroleum lube

TABLE 2.—*1969 Automotive Lubricant Market*

Area	Volume, millions of gal	Percent of automotive market
Engine oils:		
Passenger cars:		
Initial fill	18	1.8
Service station	325	32.4
Other retail	169	16.8
Fleet autos	48	4.8
Trucks and buses	170	17.0
Farm	33	3.2
Marine	19	1.9
Two-cycle	5	.4
Aviation piston engines	21	2.1
Government purchases	37	3.7
Construction equipment	9	.8
Total engine oils	854	84.9
Automatic transmission fluids	78	7.8
Gear oils and miscellaneous	46	4.6
Greases (oil equivalent)	27	2.7
Total automotive lubricants	1005	100.0

base stocks of the free world. In the United States, the largest and most important area has been the automotive lubricant market. Crankcase oils alone account for over 40 percent of the total U.S. lubricant market. However, in recent years, increase in demand has been relatively higher for industrial oils, which soon will exceed demand for automotive lubricants. A major reason for the lowered rate of increase in demand for automotive oils has been the steady drop over many years of the ratio of motor oil to gasoline sales at service stations. Referring to figure 1 (ref. 3), the ratio in 1970 is only about one-third that of 1953. This is the result of tighter engines that consume less oil and of longer drain periods. There is a suggestion in current data that the ratio may be leveling off.

WORLD PRODUCTION OF LUBES: TYPES AND COMPOSITIONS OF BASE STOCKS

Free-world lube base stock manufacturing capacity has increased in recent years at an average rate of about 4 percent (ref. 1). During the past 5 years, there have been a considerable number of lube plants built outside the United States, while only a very few have been added to the U.S. total in the last 20 years. Table 4 lists capacities by regions around the world (ref. 3). Table 5 lists refineries producing lube oils in the United

TABLE 3.—*Examples of Product Types and Requirements*

Product type	Application	Base stock type	Additives
Crankcase oils	Automobiles	Paraffinic, moderate treatment	Antioxidants, detergents, dispersants, viscosity index (V.I.) improvers, pour depressants, rust preventives, antiwear additives.
Turbine oils and hydraulic and circulating oils	Steam turbines, gas turbines	Paraffinic, high treatment	Antioxidants, rust preventives, antiwear additives.
Insulating oils	Transformers, switch gear	Naphthenic, low pour point	Antioxidants.
Refrigeration oils	Freon compressors	Naphthenic, low pour point	Antioxidants, corrosion inhibitors.
Spray oils	Agricultural plant spray	Not critical except for aromatic content.	Emulsifiers.
Textile oils	Lubricating textile mill machinery	Paraffinic and naphthenic	Antioxidants, rust preventives.
Marine oils	Marine steam engines, air tools	Not critical	Emulsifiers.
Gear oils	Gears, transmissions	Paraffinic	Antioxidants, extreme-pressure (EP) additives.
Metalworking oils	Cutting, grinding, drilling, milling, reaming, tapping, lathe work.	Not critical	Variety of EP additives.
Rubber process oils	Plasticizing synthetic rubbers	Paraffinic, naphthenic, and aromatic.	Antioxidants in a few.

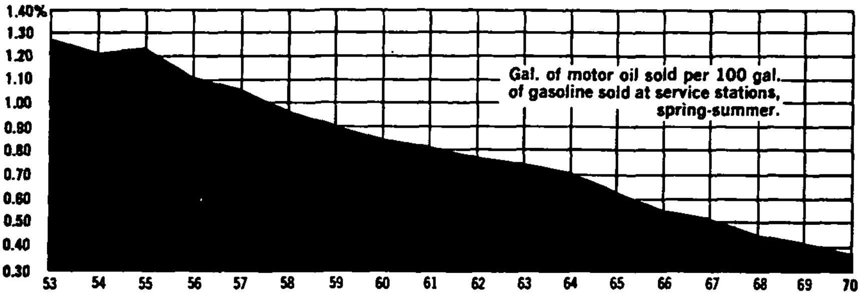


FIGURE 1.—Motor oil/gasoline ratio, U.S. service station sales.

TABLE 4.—*Worldwide Lube Manufacturing Facilities*

Region	Capacity, bbl/day[a]
Asia Pacific	40 430
Western Europe	81 275
Middle East and Africa	10 600
Latin America	25 260
United States	214 480
Canada	9 570
Total	381 615

[a] Figures for United States and Canada as of Jan. 1, 1970; for others as of Jan. 1, 1971.

States (ref. 4). Also shown are refining methods, about which more will be said later.

Consideration of the crude oil sources of lube base stocks is important because the final composition of the refined oil is related to its crude oil source. For example, a considerable amount of lube stock is made from Middle East crudes that typically are high in sulfur content relative to most other crudes. And the lube base stocks derived from them are also relatively high in sulfur content, unless made by a severe treatment with hydrogen or sulfuric acid.

Crude oils also vary widely by content of constituents such as asphalt, wax, and nitrogen compounds. Table 6 (ref. 5) compares several residua (containing the lube fractions) by content of some of these constituents. Also shown is the nature of the raw (unrefined) lube stock and yield of 100 V.I. oil. The wide range in compositions is apparent. Thus, normal refinement of these lube stocks would yield refined oils that would differ considerably in chemical nature. An example is shown in table 7, comparing the

TABLE 5.—*U.S. Refineries Producing Lube Oils*

[Nat. Petrol. Refiners Ass. Capacities as of Jan. 1, 1970, released Apr. 7, 1970]

Company	Refinery location	Crude capacity	Solvent extraction, barrels per day	Solvent dewaxing, barrels per day	Propane deasphalting	Hydrogenation	Finished lube capacity
U.S. locations:							
Allied Materials Corp	Stroud, Okla.	5 000	—	1 000	—	—	900
American Oil Co	Casper, Wyo.	34 400	1 730	1 490	970	—	1 030
	Whiting, Ind.	295 000	11 700	10 500	—	3 400	8 900
Atlantic Richfield Co	Philadelphia, Pa.	160 000	8 500	4 500	4 500	3 500	4 700
	Houston, Tex.	210 000	5 000	4 000	4 000	7 500	6 100
	East Chicago, Ind.	135 000	5 500	5 200	5 500	3 500	3 400
Bayou State Oil Corp	Hosston, La.	2 400	—	—	—	—	800
Berry Petroleum Co	Waterloo, Ark.	1 500	—	—	—	—	500
CRA, Inc	Coffeyville, Kans.	30 200	2 500	1 800	—	—	1 500
Calumet Refining Co	Burnham, Ill.	—	—	—	—	—	750
	Princeton, La.	2 400	—	—	—	—	2 400
Cit-Con Oil Corp	Lake Charles, La.	—	28 000	12 500	—	—	10 000
Champlin Petroleum Co	Enid, Okla.	37 000	3 000	—	—	—	1 500
Continental Oil Co	Ponca City, Okla.	79 000	4 500	4 000	—	—	2 300
Cross Oil & Refining Co	Smackover, Ark.	4 000	—	—	—	2 000	1 280
Elk Refining Co., Div. Pennzoil United, Inc	Falling Rock, W. Va.	4 000	—	—	—	—	1 200
Flint Chemical Co	San Antonio, Tex.	1 250	—	—	—	—	700
Golden Bear Div., Witco Chemical Corp	Bakersfield, Calif.	9 500	3 000	—	—	1 000	3 000

TABLE 5.—*U.S. Refineries Producing Lube Oils*—Continued

[Nat. Petrol. Refiners Ass. Capacities as of Jan. 1, 1970, released Apr. 7, 1970.]

Company	Refinery location	Crude capacity	Solvent extraction, barrels per day	Solvent dewaxing, barrels per day	Propane deasphalting	Hydrogenation	Finished lube capacity
U.S. locations—Continued:							
Gulf Oil Co.—U.S.	Port Arthur, Tex.	329 300	14 400	10 400	4 900	13 700	13 000
Humble Oil & Refining Co.	Bayonne, N.J.	33 000	—	[a] 8 000	—	—	200
	Baytown, Tex.	345 000	40 000	18 200	19 000	35 000	23 500
	Baton Rouge, La.	434 000	22 000	16 000	8 500	14 000	12 200
Kendall Refining Co., Div. of Witco Chemical Corp.	Bradford, Pa.	6 000	1 300	3 300	1 400	—	2 600
Kerr-McGee Corp.	Cushing, Okla.	14 000	1 900	—	1 100	—	1 200
Lion Oil Co., Hydrocarbons & Polymers Div., Monsanto Co.	El Dorado, Ark.	37 000	—	—	—	800	800
Lubrication Co. of America	Saugus, Calif.	800	—	—	—	—	—
Macmillan Ring-Free Oil Co., Inc.	Norphlet, Ark.	4 500	—	—	—	—	2 000
Mobil Oil Corp.	Beaumont, Tex.	315 000	15 300	12 100	—	—	8 000
	Paulsboro, N.J.	87 300	12 800	[b] 7 500	9 100	—	[c] 7 300
Pennsylvania Refining Co.	Karns City, Pa.	1 500	—	—	—	—	300
Pennzoil United, Inc.	Rouseville, Pa.	10 000	—	2 250	1 267	—	2 250

Phillips Petroleum Co.	Kansas City, Kans.	85 000	3 000	2 500	2 000	—	2 500
	Martinez, Calif.	110 000	1 670	—	—	—	1 670
Quaker State Oil Refining Corp.	Emlenton, Pa.	3 350	1 680	2 000	—	—	1 700
	Farmers Valley, Pa.	6 000	1 680	3 000	1 000	—	2 300
	St. Marys, W. Va.	4 600	1 200	—	800	—	1 200
Shell Oil Co.	Martinez, Calif.	97 400	6 500	—	—	5 800	4 200
	Wood River, Ill.	245 000	8 100	6 600	4 500	6 700	5 500
	Houston, Tex.	162 000	8 500	6 500	4 000	6 500	6 400
Sonneborn Div., Witco Chemical Corp.	Franklin, Pa.	2 000	—	—	—	—	700
Standard Oil Co. of California	Richmond, Calif.	190 000	24 000	9 000	—	2 000	10 000
Standard Oil Co. (Ohio)	Cleveland, Ohio	—	—	—	—	—	1 900
	Lima, Ohio	54 000	6 200	3 100	—	—	2 200
Sun Oil Co.	Marcus Hook, Pa.	158 000	8 000	6 500	—	12 900	14 000
	Tulsa, Okla.	85 000	10 000	8 000	9 000	8 500	7 000
Texaco Inc.	Port Arthur, Tex.	310 000	23 000	17 000	—	—	20 000
Three Rivers Refinery	Three Rivers, Tex.	1 500	—	—	—	—	750
Union Oil Co. of California	Nederland, Tex.	105 000	—	—	—	—	2 800
	Rodeo, Calif.	60 000	10 500	5 000	—	—	3 600
Valvoline Oil Co., Div. of Ashland Oil, Inc.	Freedom, Pa.	5 500	—	—	—	—	1 000
Wolf's Head Oil Refining Co., Inc.	Reno, Pa.	2 500	—	—	—	—	750
Total		4 314 900	295 160	191 940	81 537	126 800	214 480

TABLE 5.—*U.S. Refineries Producing Lube Oils*—Concluded

[Nat. Petrol. Refiners Ass. Capacities as of Jan. 1, 1970, released Apr. 7, 1970]

Company	Refinery location	Crude capacity	Solvent extraction, barrels per day	Solvent dewaxing, barrels per day	Propane deasphalting	Hydrogenation	Finished lube capacity
Canadian locations:							
Gulf Oil Canada Ltd	Montreal, Que.	67 500	—	—	—	—	560
	Clarkson, Ont.	55 400	1 920	1 250	720	—	1 150
Imperial Oil Ltd	Edmonton, Alta.	39 900	4 200	2 900	—	2 000	2 000
	Sarnia, Ont.	122 600	6 800	3 000	—	3 500	3 500
Shell Canada Ltd	Montreal, Que.	100 000	5 500	3 100	2 650	—	2 360
Total		385 400	18 420	10 250	3 370	5 500	9 570

[a] Wax manufacturing only.
[b] 8,200 B/CD as of July 1970.
[c] 7,920 B/CD as of July 1970.

Except for Allied Materials Corp. and Cross Oil & Refining Co., all companies have packaging and/or canning facilities at the plants listed.

NOTE: For a directory of U.S. refineries, see p. 224 of ref. 4.

NOTE: For more information on Canada, see pp. 116–120 of ref. 4.

TABLE 6.—*460° F Flashpoint Residua Showing Different Combinations of Constituents*

Crude	Sulfur, wt %	Asphalt, wt %	Wax, wt %	Dewaxed oil		100 V.I. oil yield from residuum, wt %
				wt %	V.I.[a]	
Texas crude B	0.24	17.6	4.3	78.1	103	78
Arabian crude B	3.1	26.0	9.0	65.0	72	50
Sumatra crude A	.15	21.6	41.8	36.6	68	20
Venezuela crude A	5.6	53.9	3.3	43.1	39	8
Borneo crude A	.20	10.6	30.0	59.4	−142	13
Texas crude D	.51	19.5	3.2	77.3	−171	8

[a] Viscosity Index.

TABLE 7.—*Comparison of Properties of a Naphthenic and a Paraffinic Spray Oil of Same Viscosity and Unsulfonated Residue*

Petroleum type	Naphthenic	Paraffinic
Viscosity at 100° F, SUS	88	88
Density at 68° F	0.8710	0.8519
Flashpoint, COC, °F	320	370
V.I.	60	110
Pour point, °F	−45	30
Unsulfonated residue, %	96	96
Aniline point, °F	195	219
Molecular weight	320	335
Refractive index	1.4760	1.4686
Percent carbon atoms in—		
Aromatic rings	2	2
Naphthenic rings	45	33
Paraffin chains	53	65

properties of spray oils made from naphthenic and paraffinic crudes, both of the same viscosity and refined to the same aromatic content. Note the differences in density, flashpoint, viscosity index, pour point, aniline point, molecular weight, refractive index, and naphthenic-paraffinic balance.

Examples of familiar typical hydrocarbon structures in lube oil are depicted in figure 2. Of course, there is an almost endless number of individual molecular species within each broad class. In addition, there are nitrogen, sulfur, and oxygen compounds and small amounts of organo-

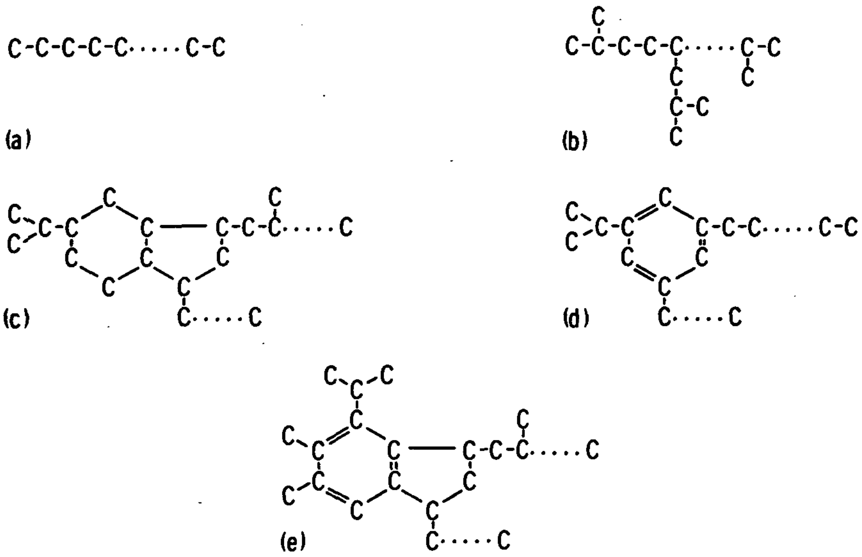


FIGURE 2.—Typical structures in lube oil. (*a*) *n*-Paraffin. (*b*) Isoparaffin. (*c*) Naphthene. (*d*) Aromatic hydrocarbon. (*e*) Mixed aliphatic and aromatic ring.

metallic compounds, especially in unrefined residual (undistilled) fractions. Relationships of components to properties of most interest are linked in table 8. There are a number of methods for characterizing the structure of a lube stock. Most used is the so-called *n-d-M* method of Van Nes and Van Westen (ref. 6). Based on empirically derived property relationships involving refractive index, density, and molecular weight, it produces a division into percent carbon atoms in the three structural types: aromatic rings, naphthenic rings, and paraffinic structure. Relatively low in cost and quite accurate, this method has proven very useful in correlation studies. A more detailed analysis is obtained by mass spectrometer. Examples of *n-d-M* and mass spectrometer analyses are compared in table 9. The California and Midcontinent (MC) neutrals were both refined by solvent extraction, and the hydrotreated 500 neutral by severe hydrotreatment. Although the hydrotreated neutral contains a somewhat higher proportion of paraffinic structure and lower naphthenic structure, it is of interest to note that it contains all but one of the type groups listed and roughly in like proportion. Further development of mass spectrometer analysis will help in elucidating structure in greater detail. This is sorely needed to understand better the functional role of molecular types. Knowing this, more selective refining methods could be devised to produce better lube stocks. American Petroleum Institute (API) research project 6 has for many years been engaged in separation and identification of the compounds in petroleum. A brief summary of the results relating to

TABLE 8.—*Base Oil Composition and Dependent Properties*

Component	Properties affected by presence in oil
Hydrocarbons:	
Paraffins Naphthenes Aromatics	Bulk properties such as— Viscosity, V.I. Gravity Pour point Aniline point Unsulfonated residue Solvency Oxidation: Stability and response to antioxidants Volatility Response to V.I. improvers
Nonhydrocarbon:	
Nitrogen compounds Sulfur compounds Oxygen compounds Organometallic compounds	Oxidation: Stability and response to antioxidants Demulsibility Lubricity Solvency EP properties Foaming Rusting

the composition of viscous petroleum oils is given in a paper by Mair (ref. 7).

After carbon and hydrogen, sulfur is the next most prominent element present in base oils. Some refined base stocks contain more than 2 percent sulfur. For well-refined oils, the sulfur compounds are relatively stable; they do not easily release sulfur. A wide variety of lubricants made with such stocks show no adverse effects of the sulfur. However, it seemed likely that in EP (gear) conditions, the sulfur might be released and assist in preventing seizure or reducing wear. Figure 3 shows an apparent correlation of sulfur content with seizure load in a four-ball test. In figure 4, there is an apparent effect on wear in a high-load, short-duration, four-ball test. When a conventional automotive gear oil additive (such as used for automotive differentials) is added to these base oils, wear characteristics (fig. 5) are all essentially the same over a range of loads. The high concentration of relatively reactive sulfur and phosphorus compounds in the additive overwhelms the sulfur activity of the base oil.

REFINING PROCESSES: EFFECT ON COMPOSITION AND PROPERTIES

Lube refining processes can be divided into separation and conversion methods. These are summarized in table 10. The separation processes at-

TABLE 9.—*Composition Analysis*

Type of compound	California paraffinic 480 neutral 90 V.I.	Hydrotreated 500 neutral 101 V.I.	MC paraffinic 350 neutral 97 V.I.
n-d-M analysis:			
Percent carbon atoms in aromatic rings	5.5	3.5	2
Percent carbon atoms in naphthene rings	32	26.5	33
Percent carbon atoms in paraffin chains	62.5	70	65
Mass spectrometer analysis (volume percent):			
Paraffins	11.5	14.8	13.9
Cycloparaffins:			
1 ring	19.4	19.6	15.9
2 rings	11.3	19.7	18.0
3 rings	15.6	11.9	14.6
4 rings	15.3	6.7	10.5
5 rings	10.6	8.2	11.6
6 rings	0	0	0
Alkylbenzenes	4.8	7.5	5.7
Indanes-tetralins	2.6	2.8	1.7
Benzodicycloparaffins	2.7	2.3	2.4
Naphthalenes	.7	.6	.5
Acenaphthenes	.6	.5	.2
Fluorenes	0	0	0
Phenanthrenes	1.1	1.8	.9
Pyrenes	1.1	1.3	.7
Chrysenes	2.3	1.8	2.7
Benzothiophenes	.3	0	.2
Dibenzothiophenes	.1	.5	.5
Naphthobenzothiophenes	0	0	0
Summary:			
Paraffins	11.5	14.8	13.9
Cycloparaffins	72.2	66.1	70.6
(3 rings and larger)	(41.5)	(26.8)	(36.7)
Aromatics	15.9	18.6	14.8
(3 aromatic rings and larger)	(5.1)	(5.4)	(4.5)
Thiophenes	.4	.5	.7
Total saturates	83.7	80.9	84.5

tempt to isolate selectively from the crude charge stock that part of material that has the most desirable properties. By chemical (H_2SO_4 or $AlCl_3$) or physical (distillation, solvent extraction, or clay treating) means, the undesirable aromatic compounds, sulfur, nitrogen, and oxygen compounds, are partially removed, leaving the most desirable portion to be

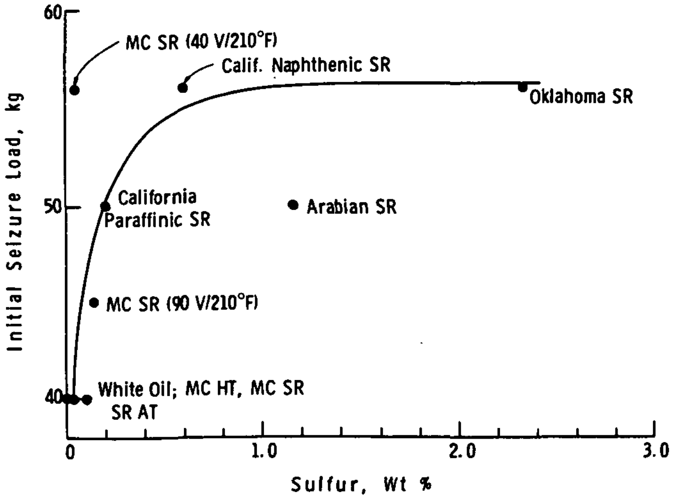


FIGURE 3.—Effect of sulfur content on initial seizure load. Four-ball mean Hertz screen test: 60-sec runs, ambient temperature. Base oils of 60 SUS/210° F.

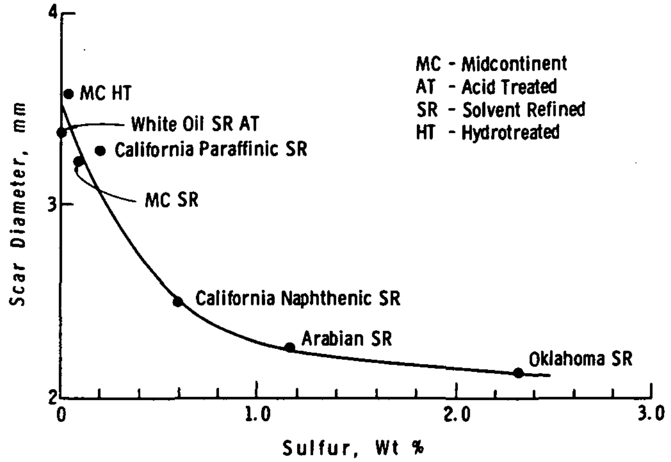


FIGURE 4.—Effect of sulfur content on wear. Four-ball mean Hertz screen test: 63 kg, 60-sec runs, ambient temperature. Base oils of 60 SUS/210° F.

recovered as final product. The only conversion process used is hydrogen treating, carried out at high pressure in the presence of a catalyst. The conditions can vary from very mild, in which the only significant changes are removal of color bodies and some sulfur and nitrogen compounds to very severe conditions, producing hydrocracking, in which extensive molecular changes occur and synthetic stock is produced (fig. 6). In severe

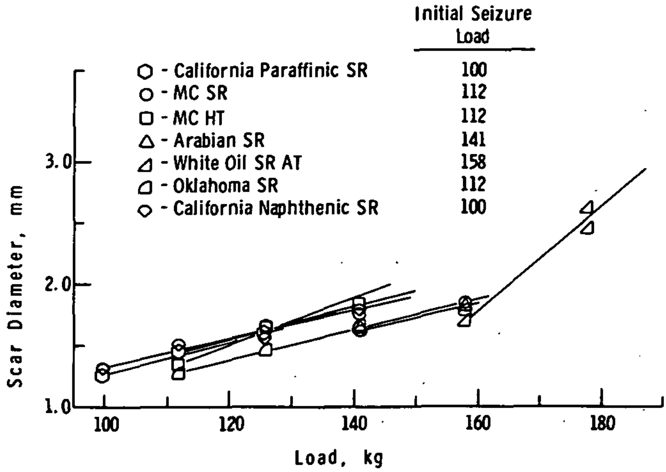


FIGURE 5.—Response of base oils to EP (gear oil) additive. Four-ball mean Hertz screen test: 60-sec runs, ambient temperature. Base oil (~60 SUS/210° F) + 7 percent API-GL-5 additive.

hydrocracking, the boiling range is lowered and nearly all aromatic compounds, sulfur, nitrogen, and oxygen are removed.

Hydrogen treating has become the most popular refining process. It appears that most future lube plants will use this method. Development of lube hydrotreating has been greatly accelerated by the rapid growth in recent years of catalytic technology for fuel production. Reasons for the popularity of lube hydrotreating include the advantages that it—

(1) Reduces or eliminates solvent, acid, and clay treatment
(2) Reduces or eliminates byproduct disposal problem (solvent extracts, acid sludge)
(3) Increases yields as much as 50 percent
(4) Lowers lube oil unit cost
(5) Permits use of wider range of crudes for lube production
(6) Is the most effective means of color improvement.
(7) Permits production of higher V.I.'s at tolerable cost

The major disadvantage is the decreased solvency for additives or oxidation products (severe hydrotreating). The decreased solvent power (higher aniline points) of hydrotreated stocks is shown by the comparative aniline points of figure 7.

The problem of devising or selecting an optimum refinement is complex. Table 11 presents a qualitative summary of key base oil properties against a degree of refinement as measured by V.I. An attempt is made to estimate the effect on each property of increased refinement. Thus, increasing the severity of refinement may be beneficial, harmful, without effect, or unknown.

TABLE 10.—*Lube Refining Processes*

Process	Charge stock	Yield range, vol %
I. Separation		
A. Chemical		
H_2SO_4, $AlCl_3$	Distillates	20 to 95
B. Physical		
1. Distillation	Crudes, treated stocks	100
2. Solvent extraction		40 to 80
Single solvent: SO_2, phenol, cresol, propane	Distillates	
Double solvent (Duosol)	Residua (distillates)	
3. Clay treating	Treated stocks	95 to 100
4. Dewaxing	Raffinates	75 to 95
II. Conversion-hydrogen treating		
A. Mild: Hydrofining-hydrogen replacement of S and N	Treated stocks	100+
B. Moderate to severe: Hydrogenation, hydrogenolysis	Distillates Extracts, treated stocks	80 to 100

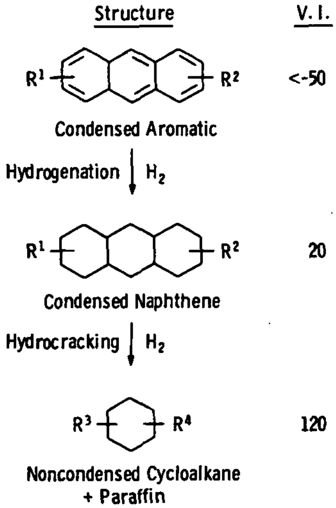


FIGURE 6.—Structural changes resulting from severe hydrotreating.

Properties improved are response to antioxidants, thermal stability, volatility at given viscosity, low-temperature viscosity, and sunlight stability. Properties degraded are solvent power for additives and oxidation products, response to V.I. improvers, and oiliness or EP, neat (no additives). The one property best at an optimum refinement is oxidation stability, neat (no additives). Properties not correlating with severity of

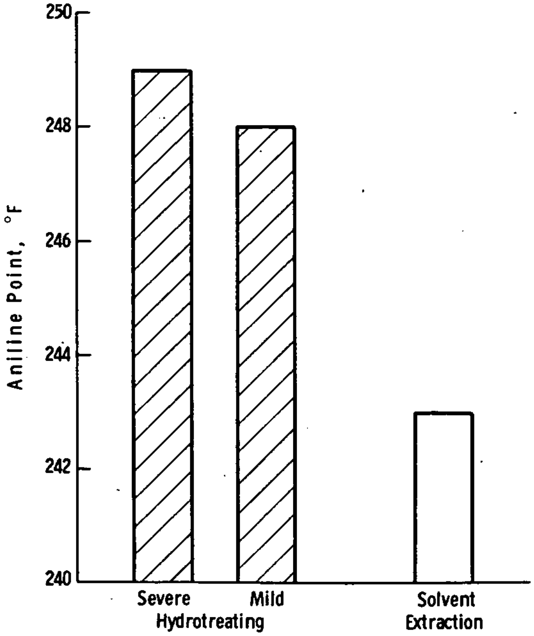


FIGURE 7.—Effect of refinement method on aniline point. Typical 95 to 100 V.I. SAE 30 oils.

refinement are response to oiliness or EP additives, response to pour depressants, response to rust inhibitors, and response to dispersants.

EVALUATION OF BASE STOCKS

Certain properties are commonly used to assess the quality of lube stocks. Routine tests are appearance, gravity, flashpoint, pour point, acid number, V.I., unsulfonated residue, oxidator A, oxidator B (reference compounding), and neutralization number. More detailed tests include type analysis (*n-d-M*), nitrogen, oxygen, sulfur, aniline point, copper strip, Conradson carbon, emulsion, distillation, and mass spectrometric group type of analysis.

A Freon floc test is used for refrigeration oils. These may vary, depending upon the application. The function of many of the listed properties is self-evident. Flashpoint is a measure of front-end volatility as well as one measure of flammability. V.I. refers to the viscosity-temperature relationship. Unsulfonated residue is the percent of the oil not reacting with an excess of sulfuric acid; thus, it is a measure of aromatic content as well as a rough measure of reactivity (chemical stability). Oxidator A and B is the Chevron Research Co. designation for resistance to oxidation, as measured in a Dornte-type (ref. 8) oxygen absorption apparatus. Normally, the

TABLE 11.—*Base Oil Performance and Degree of Refinement*

Property	Effect of increased refinement	V.I. of possible trouble
Solvent power (for oxidation products and additives)	Poorer	110 or greater
Oxidation stability, neat	Better, then poorer	100 or greater [a]
Response to antioxidants	Better	20 or less
Thermal stability	Better	
Volatility	Better	
Low-temperature viscosity	Better	
Sunlight stability	Better, with adequate finish treatment	
Response to V.I. improvers	Poorer	115 or greater
Response to dispersants	Correlation not established	135 or greater
Response to pour depressants (present)	Functions of crude source and processing	130 or greater
Bearing corrosion	Correlation not established	
Silver bearing lubrication	Correlation not established	
Oiliness or EP, neat	Poorer	
Response to oiliness or EP additives	No correlation	
Rusting	Correlation not established	135 or greater
Foaming	Poorer	95 or greater

[a] V.I. =90 is optimum refinement.

conditions are 1 atm of pure oxygen at 340° F, and the hours to absorption of 1000 ml O_2 by 25 g of oil is reported. In the A version, no catalyst is used and the oil is tested neat (without additives). The B version uses a catalyst, and a reference additive package is added to the oil. The catalyst is a mixture of soluble metal naphthenates simulating the average metal analysis of used crankcase oils. Thus, the A and B methods measure, respectively, the oxidation stability of the base oil as manufactured and the response to conventional inhibitors in a simulated application. Returning to other tests, the aniline point is a measure of the aromatic-paraffinic balance or paraffinicity, as it is normally called. This is an important property relating to solvent power and will be discussed later. The Freon floc test is another measure of solvent power for Freon refrigerant and is specific to refrigeration oils.

The resistance to oxidation of a base oil is one of its most important properties. The change that occurs as refinement severity changes is shown in figure 8. A naphthenic 100 neutral and a paraffinic 480 neutral refined to normal severity, on further refinement, become less resistant to oxidation. This results from removal of natural oxidation inhibitors, probably sulfur and aromatic compounds (refs. 9 and 10). At the same time, response to

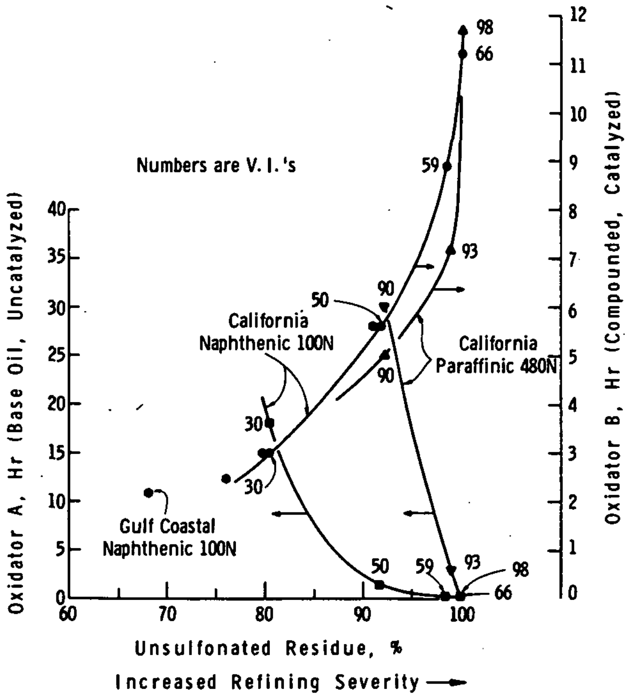


FIGURE 8.—Effect of refining severity on oxidation.

added inhibitors increases. Finally, at the stage of complete removal of aromatics, e.g., medicinal white mineral oil, the base stock neat has virtually no resistance to oxidation, while the inhibited oils have maximum resistance. At the white oil level of refinement, these oils inhibited have about twice the resistance of average compounded motor oils. It is impractical to make motor oil base stocks to this level of refinement because of the high cost. At the white oil level, both stocks of figure 8 have about the same inhibitor response, although they differ in naphthenic ring content.

Returning to the property of solvent power, this quality is important in at least two respects. First, it may limit the kind and amount of additive that may be used in compounded oils. This has become more important as additive technology has advanced and additives have been used in greater variety and dosage. Many otherwise useful additives are limited by inadequate solubility. Second, the solvent power affects the ability of an oil to dissolve oxidation products formed during use. Such products could precipitate as lacquers or sludge. The aniline point of base stocks (temperature of solution of equal parts of base stock and aniline) correlates well with solvent power for conventional lubricant additives. Figure 9 pictures the relationship between viscosity (molecular weight) and aniline point for six different base stocks. These show a considerable range in aniline point for a given viscosity. Aniline point increases (solvent power decreases) with increase in viscosity. For example, base oil R has the lowest range of aniline points (highest solvent power), and base oil D (a hydrotreated oil)

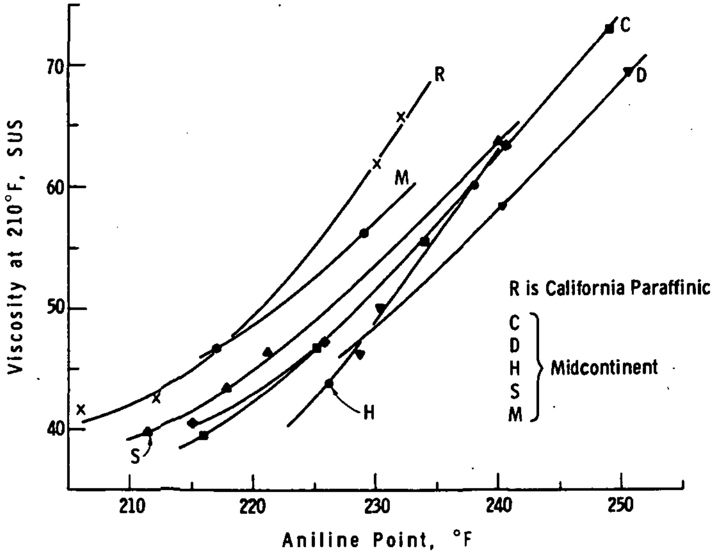


FIGURE 9.—Aniline point versus viscosity at 210° F, California and midcontinent neutrals.

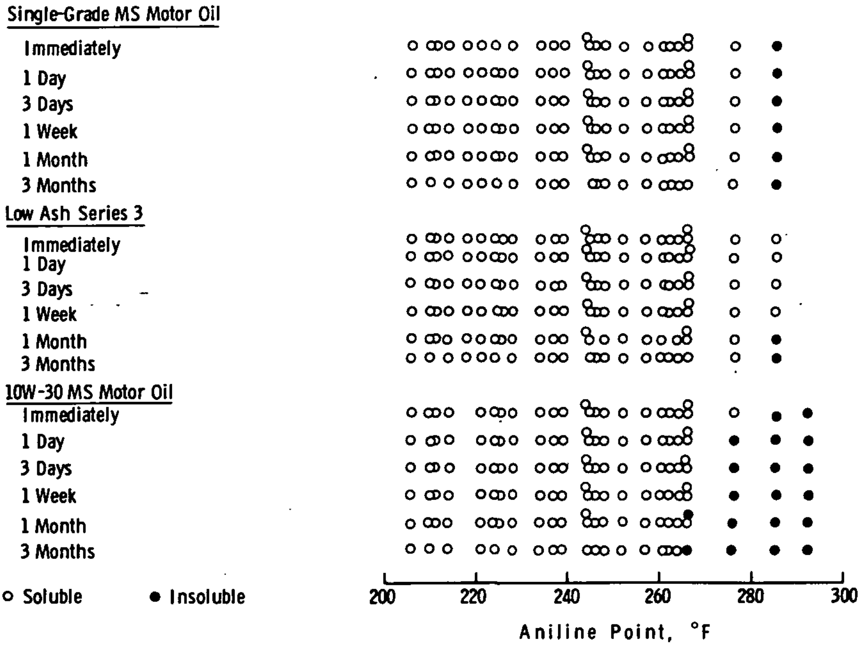


FIGURE 10.—Solvency of base oils.

has the highest range (lowest solvent power). In fact, some conventional additives have borderline solubility in base oil D. Figure 10 depicts the way in which the solubility of three engine oil packages was explored as related to solvent power (aniline point) of base oil. Oils representing a nearly continuous range of aniline points were blended with the additive package and observed over a period of time. Each open circle represents an observation of no insolubles, and each solid dot indicates that an insoluble floc or precipitate was observed. Note that storage over several months may be required to determine whether insolubles separate. The limiting aniline point shown here is 267° F. However, other additives may have limiting aniline points much lower. Based on data obtained in this way, figure 11 allows one to predict whether a given base oil will have adequate solvent power for a given additive component or package. For example, a Society of Automotive Engineers (SAE) 20 Ultra VI base stock made by severe hydrocracking ($V.I._E = 140$) will have adequate solvent power for a particular 10W-30 MS motor oil package, while the corresponding SAE 30 Ultra VI base stock will not dissolve the package.

SUPERREFINED MINERAL OILS

As outlined above, normal commercial lubricant base stocks contain a range of nonhydrocarbons (nitrogen, sulfur, and oxygen compounds). The

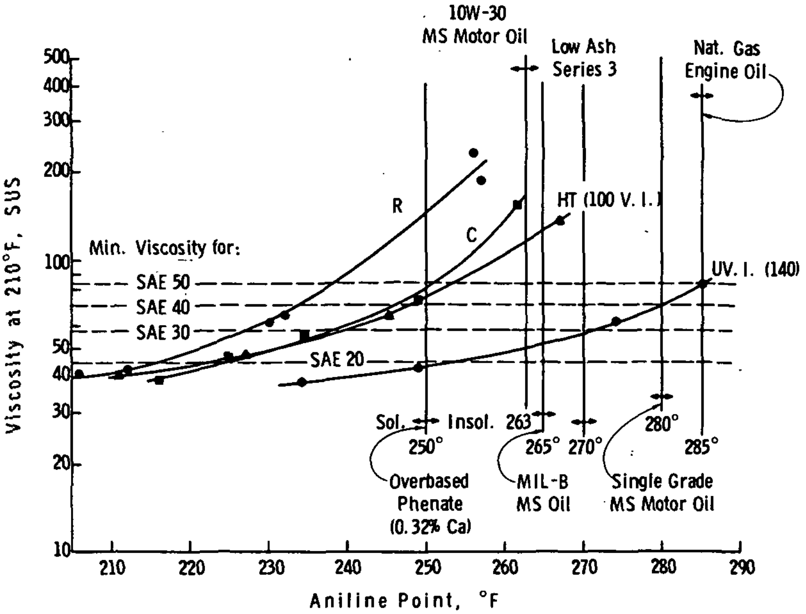


FIGURE 11.—Solubility limit aniline points of selected additive packages.

concentrations of these and of aromatic hydrocarbons vary widely depending upon the crude source and method of refinement. About the only exception is white oils used in a very few products to lubricate food-processing machinery. White oils are essentially free of aromatics and nonhydrocarbons.

The presence of the aromatic hydrocarbons and the nonhydrocarbon impurities reduces thermal stability and response to antioxidants. Superrefining removes these materials and produces base stocks of maximum stability when properly compounded.

Klaus and associates (ref. 11), in very extensive work over a period of years, have explored the manufacture, properties, performance, and applications of superrefined oils. Processes used include exhaustive hydrogenation (or hydrocracking), severe treatment with sulfuric acid, adsorption treatment, or a combination of these processes. Products made from superrefined base stocks outperformed products using available synthetic base stocks, especially in a combination of high-temperature tests involving thermal and oxidative stability, corrosivity to metals, and general cleanliness after oxidation. A number of severe product applications resulted, including a high-temperature hydraulic fluid (superrefined, deep dewaxed) for an important military (USAF) application (ref. 12).

The extension of superrefined base stocks into many commercial lubricants would produce superior products. Cost is the main deterrent. Products using relatively low viscosity base stocks are of most interest as high-viscosity, superrefined stocks are difficult to make and have limited solvent power. It is possible that superrefined base stocks made by hydrocracking may become commercially available at reasonable cost.

THE FUTURE FOR MINERAL OILS

A 1962 quotation from W. A. Zisman (ref. 13) appears valid today. "Beyond doubt, the great bulk of lubricants used in the next several decades will be manufactured from petroleum oils because of their greater availability and low cost and, also, because they usually satisfy the more common needs for lubrication." Dr. Zisman also predicted increasing use of synthetic lubricants. Synthetic lubricants, per se, are covered in a separate paper of this symposium. It is true that there are many synthetic types with unique combinations of properties (ref. 13). Occasionally, the performance requirements of an application will require one of these. An example is the current military specification MIL–H–83282 (USAF) covering a fire-resistant hydraulic fluid for aircraft (ref. 14). The prototype fluid is a synthetic hydrocarbon whose flammability properties are better than can be achieved with a refined petroleum fraction. The type of synthetic hydrocarbon employed was similar to that described by Duling et al. (ref. 15) and in several patents assigned to Socony Mobil Oil Co. (ref. 16). However, such applications are relatively few in number and low in volume of lubricant required. Synthetics have not been able to gain a significant portion of the high-volume markets, such as for crankcase oils. It does appear that mineral oils will yield further to synthetics in specialized high-performance areas such as space and military applications.

Performance requirements in many areas are continually becoming more severe. The increasing severity of operating conditions for automotive engine oils is well recognized (refs. 17 and 18). Factors of engine design, low-profile bodies, and emission control devices raise oil operating temperatures. Laboratory work, using a severe engine test, showed a significant difference for different base oils, while additives were found to play a minor role (ref. 17). Thus, mineral oil base stocks must meet more severe requirements through more rigorous selection or through improved refinement. As stated above, base stocks made by severe treatments to produce oils approaching superrefined base stocks will perform better than average current products. Again, hydrocracking appears to be the most likely refining process for future oils of this quality level. Synthetics are not expected to take over a significant fraction of this market for many years, although some authors are more sanguine (ref. 18).

DISCUSSIONS

E. E. Klaus (Pennsylvania State University, University Park, Pa.)

The excellent review on the developments in mineral oil lubricants could be extended to consider the areas of competition with some of the materials covered in the excellent review on synthetic lubricants. Considering both classes of lubricants, one of the most important developments in the last decade was the resolution of the relative roles of the base stock and the additive package in the complete lubricant formulation. Important properties contributed by the base stocks include thermal stability and such physical properties as volatility, liquid range, and basic viscosity characteristics. Important properties contributed by the additive package include enhanced lubricity, oxidation stability, and controlled corrosion properties. Much of the research and development work on hydrocarbon and mineral oils in recent years has been directed toward optimization of the physical properties and additive response to meet the challenge of the synthetics.

The thermal stability of the carbon-carbon single bond becomes the limiting value for the optimum stability of the mineral oil base stock. Most of the synthetic lubricants contain carbon-carbon single bonds but also may contain functional groupings such as an ester linkage, which is less thermally stable. To take full advantage of the excellent thermal stability of the hydrocarbon in the finished lubricant, additional refining steps are required to narrow the boiling range, widen the liquid range (dewaxing), and improve additive response by the removal or conversion of nonhydrocarbons and unsaturated hydrocarbons.

To provide volatility characteristics dependent only on viscosity-temperature properties and comparable to specific esters for example, it is necessary to produce fractions with a boiling range of the order of 50° F. Under these conditions viscosity-volatility relationships for the hydrocarbons, mineral oils, and many synthetics can be correlated as shown in figure 12.

When treated with the additional refining techniques described previously, hydrocarbons from several synthetic and conversion processes as well as from physical separation can be considered as lubricant base stocks. Table 12 shows five classes of hydrocarbons studied as base stocks along with values for thermal stability and viscosity-temperature properties. In the case of the viscosity-temperature properties, these values represent measured values in the study. In almost all classes of compounds, values of the order of 140 V.I. or higher have been suggested in the literature. The technology exists for the production of all of these materials on a commercial scale. In general, the saturated oligomer of alpha olefins and the saturated alkyl naphthene are the only two materials that have been prepared to have good low-temperature properties without a dewaxing step. The

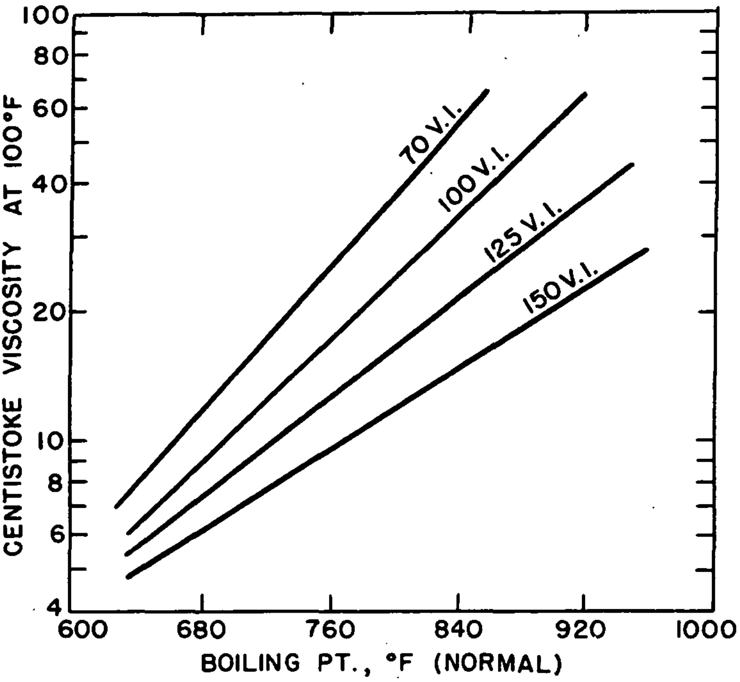


FIGURE 12.—Viscosity-volatility relationship.

TABLE 12.—*Hydrocarbon Fluids*

	Thermal stability, °F	V.I.
Superrefined mineral oil	650 to 700	110
Oligomer of alpha olefin	600 to 650	130
Saturated alkylate	600 to 650	110
Isomerized wax	650 to 700	135
Hydrocracked naphthene	650 to 700	115

other materials, to achieve a viscous pour point, require a dewaxing step. There is considerable evidence to show that the low-temperature dewaxing is the most difficult and costly processing step in the preparation of these wide liquid range hydrocarbons.

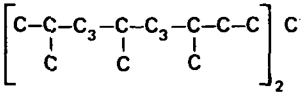
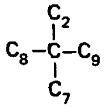
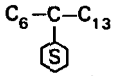
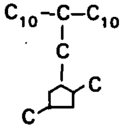
The hydrocarbons that exhibit good low-temperature fluidity also show unusual low-temperature viscosity characteristics. Low cold-test mineral oil stocks with good natural pour points give a straight-line relationship on the American Society for Testing and Materials (ASTM) viscosity-temperature chart. Waxy stocks show a tendency to give a higher viscosity than predicted at low temperatures starting 10° to 20° F above the ASTM cloud point. Similarly, polymer solutions tend to give higher than predicted values for viscosity at low temperatures. Deep dewaxed oils of high V.I. tend to give viscosities considerably lower than predicted on the ASTM chart. Typical examples of this behavior are shown in table 13. In all cases these values were obtained for fractions that conform fully to the definition of superrefined mineral oils (SRMO). Some synthetic materials that can be defined as dense-centered molecules, such as pentaerythritol esters, phthalate esters, phosphate esters, etc., also tend to show this same advantage in measured low-temperature viscosity over predicted low-temperature viscosity. A number of pure hydrocarbons from the API research project 42 hydrocarbon bank have been evaluated for low-temperature viscosities. These data are shown in table 14. The structures indicate that these materials are in general conformity to the idea of a dense-centered molecular configuration. In all cases they show a major reduction in measured low-temperature viscosity over that predicted from the ASTM chart. In fact, the branched chain C_{27} paraffin shown as the second material in table 14 shows a measured viscosity that is only 27 percent of the predicted value. The low-temperature viscosities of all of the high V.I. hydrocarbons evaluated show that conventional viscosity-temperature characterizations do not adequately show the competitive position of the hydrocarbons exhibiting the wide liquid range.

Additive response is probably the most important property of the base stock when the future demands on lubricants are considered. In order to provide optimum additive response, it is necessary to remove essentially all the nonhydrocarbons and unsaturated hydrocarbons. The complete removal of these impurities can be accomplished by acid extraction with the loss of the impurities and unsaturated materials in the extract phase. Hydrogenation, on the other hand, is an effective way of converting the hydrocarbon portion of the molecules containing sulfur, nitrogen, and

TABLE 13.—*Dewaxed Oil Properties*

Centistoke viscosity at 100° F	Pour point, °F	Centistoke viscosity at −65° F		V.I.	
		Calculated	Measured	210° to 100° F	210° to −65° F
14.6	−70	44 500	21 000	98	121
20.9	−70	131 000	57 000	102	127
35.1	−70	660 000	287 000	104	120

TABLE 14.—*Some Viscosity Properties of Pure Hydrocarbons*

Formula	V.I.	Centistoke viscosity at—			
		100° F	−65° F		
			Predicted	Measured	Percent developed
 $\left[\mathrm{C{-}\underset{C}{C}{-}C_3{-}\underset{C}{C}{-}C_3{-}\underset{C}{C}{-}C{-}C}\right]_2\mathrm{C}$	122	20.9	80 000	44 000	−45
 $\mathrm{C_8{-}\overset{C_2}{\underset{C_7}{C}}{-}C_9}$	102	15.9	55 000	15 000	−73
	110	17.0	55 500	18 400	−67
	90	25.1	330 000	114 000	−65

oxygen as well as the unsaturated hydrocarbons to saturated hydrocarbons. The saturated hydrocarbons from either process and from all classes of crude oil show essentially the same optimum additive response. The comparison of additive response from conventionally refined oils and the optimized SRMO's are shown in figure 13. A typical ester formulation designed to meet MIL–L–7808 specification is shown as a reference point. The large difference between conventional oils and optimum superrefined oils should be emphasized. In many cases such as the present problem with automotive crankcase oils, an incremental improvement may be adequate rather than complete optimization. In a series of hydrogenation studies, stable life or additive response was studied as a function of sulfur concentration. In this case it can be shown that substantial improvement can be made by additional refining that falls short of optimization. The results of partial refining by hydrogenation as measured by response to an oxidation

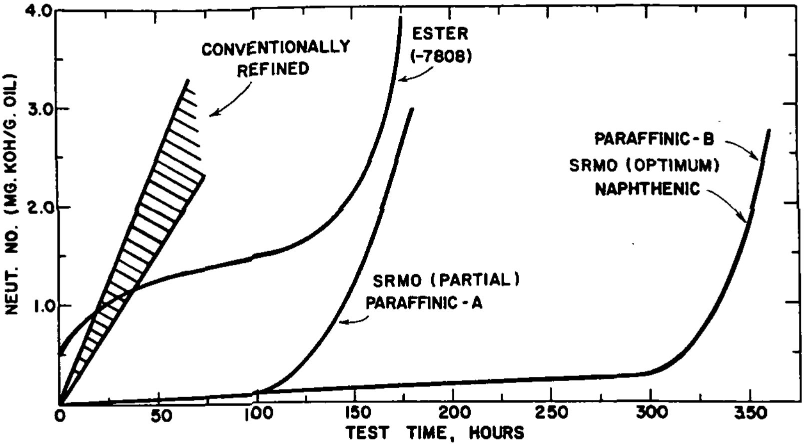


FIGURE 13.—Oxidation stability. 347° F; 5 liters/hr; 100 ml; Cu, Fe, Al, and Mg; all fluids contain antioxidants.

inhibitor is shown in figure 14. These data show clearly the advantage of partial as well as complete removal of sulfur. It should be noted that the concentration of nitrogen as well as olefinic and aromatic unsaturates was decreased by the same hydrogenation process using a reduced nickel catalyst at about 550° F and 2000-psig hydrogen pressure. The sulfur was taken as a good measure of the degree of total refining.

The same general trends can be shown for these SRMO's with regard to response to anticorrosion and lubricity additives. At the moment, response to oxidation inhibitors appears to be the most sensitive area in the competition between mineral oils and synthetics.

In conclusion, it should be emphasized that all of the processing required to accomplish the optimization of the mineral oil and hydrocarbon properties described here has a demonstrated technical feasibility. Fluids with these properties have in many cases been prepared on commercial and/or pilot-plant scale. It is particularly interesting to note that Mr. Furby suggests that over half of the current mineral oil lubricants may receive some hydrogen treatment. The most difficult and least developed process involved in this refining sequence is low-temperature dewaxing. Development studies show some new techniques that should provide low-temperature dewaxing on a large scale for a reasonable price. In general, what is required for the improvement of mineral oil lubricants to approach the optimum already demonstrated is a large-scale market with appropriate requirements beyond those now provided by conventional refining.

T. Salomon (OMER, Israel)

There are many ways to oxidize a mineral oil; however, the selection of the oil has to be based on the type of oxidation that occurs in actual serv-

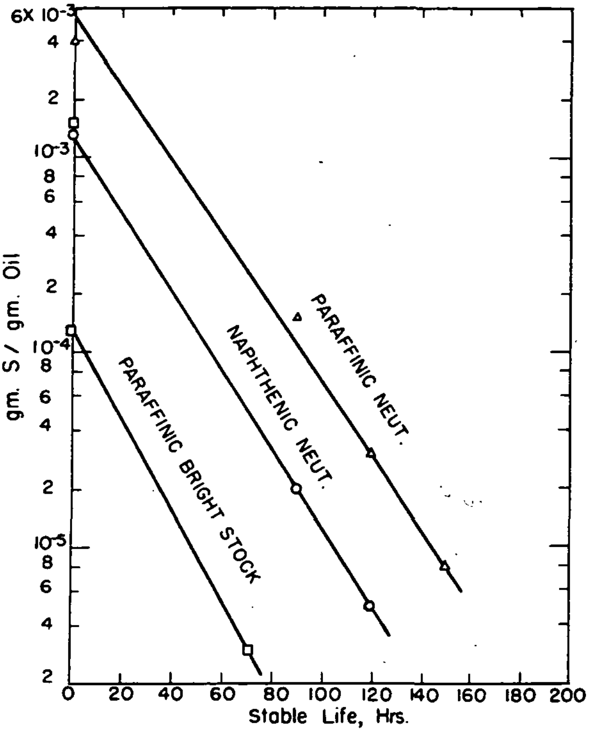


FIGURE 14.—Sulfur content versus oxidation stability. Fluids contain 1 percent PAN.

ice. Therefore the question to ask is not how to oxidize the oil, but why the oil is oxidized and why harmful oxidation products are formed.

Starting with this point of view, it may be misleading to express the resistance to oxidation by the volume of oxygen absorbed under test conditions that are quite different from those prevailing in actual service. Some oils may absorb a very great volume of oxygen without producing harmful oxidation products, whereas some other oils may absorb a small volume of oxygen and nevertheless give rise to harmful oxidation products. The latter type of oil may thus become more harmful to the machine. It may also be misleading to use soluble metal naphthenates as catalysts, as its mechanism of oxidation is quite different from that produced in actual service.

The statement that the resistance to oxidation decreases with increasing severity of the refining is not a general truth. Such an effect may be observed with highly acid refined oils, containing chemical refining impurities. It is not due to the removal of the so-called natural oxidation inhibitors. This can be stated when a physical refining treatment with solid adsorbents is applied, which is not an economical process. In this way we may prepare highly refined white oils with a much better oxidation stability than medium-refined oils. This refining technique will also remove the so-called natural oxidation inhibitors, without introducing chemical refining impurities into the oil.

Mr. Furby states that "it is impracticable to make motor oil base stocks to this level of refinement [white oils] because of the high cost." The main reason why white oils are not used as base stocks for motor oils is the fact that the dispersant agents are much less active than in a medium-refined oil. This fact was shown 20 years ago by R. G. Larsen and other American colleagues.

To prepare mineral oils with better oxidation and thermal stability, which are needed in coming engines, we must pay more attention to the content in and the nature of the minor constituents of the oil. The knowledge about the content in and the composition of these minor constituents of the base oil is as important as, or even more important than, the knowledge of the composition of the pure hydrocarbon material.

W. J. Huth (Sun Oil Co., Marcus Hook, Pa.)

Mr. Furby's excellent paper brings us up to the present and provides a glimpse into the future of mineral oil. Undoubtedly, synthetics will find increased use, but until there is a major change in the automotive power train and other high-volume uses, I agree with Mr. Furby that they will not displace the bulk of mineral oil. Assuming such a change, however, which puts the major consumers beyond the capability of current mineral oil, the work done on superrefining by Klaus et al. may well point the way to super mineral oils of the future.

My comment on this paper is neither a criticism nor a question. Rather, it is an attempt to extend it into the future through extrapolation of what has been and is happening to mineral oils. From the synthetic viewpoint, mineral oil is still a rather crude, unrefined material. Until very recently, oil refining techniques were aimed only at removing the problem molecules. The inherent limitations of the remaining molecules were not changed by such separation techniques. About 1912, acid treatment began to supplement distillation as a refining technique. It does selectively remove bad molecules. I use "bad" here in the sense of undesirable in engine oils, hydraulic oils, and other lubricants that require a high degree of oxidation stability. Not all the materials removed by acid are undesirable for all purposes, however.

Acid reacts with unsaturated molecules, primarily aromatic structures, and in doing so destroys them. The resulting acid sludge is practically useless and poses a difficult disposal problem. Fortunately, about 1930, solvent extraction was applied in place of acid. Instead of bothersome sludge, solvent extraction produces an aromatic material that found valuable use in rubber compounding and other applications requiring good solvency. Acid treatment continues, on a limited basis, to make specialty oils, such as electrical and refrigeration, but most lubricant stock results from solvent extraction.

Up to this point, refining had either destroyed (acid treating) the extracted molecule or removed it for another use (solvent) without really improving the characteristics of the remaining mineral oil. Then, 1955 introduced hydrogen treating to mineral oil refining. It left the bad molecule in the oil, but altered it to make it a good one. The most recent aspect of hydrogen treatment is hydrocracking, which is really a major step forward by itself. It not only makes good molecules from the bad ones, but it also manipulates the good ones to make them better.

Let us now consider the quality of hydrocracked oils and other synthetic hydrocarbons relative to the solvent-refined mineral oil. They exhibit improved V.I. and sensitivity to oxidation inhibitor. On the other hand, they have less solubility for additives, which, however, is not important to oxidation stability because of their high sensitivity to oxidation inhibitor. In other words, these new hydrocarbon oils incorporate an additive function (V.I.) into the base oil and decrease drastically the amount of another additive (oxidation inhibitor) required. These steps to eliminate mineral oil deficiencies normally remedied by additive additions represent only the first commercial attempts to manipulate the hydrocarbon molecule chemically. Extrapolation of these developments predicts that future manipulations will remove further deficiencies and decrease other additive requirements. In other words, the mineral oil of the future should have inherently better properties, not require additives, and be more sensitive to additional additive treatments.

A potent motivating force behind the above extrapolation is the increasing pressure to renew the ecology. Many additives are under attack; lead is on the way out in lubricants as well as fuel, and zinc may not be far behind. There is agitation now for completely ashless lubricants. In view of these pressures, oils with inherent additive capabilities present an attractive possibility.

Pollution problems are also bringing great pressure against the piston engine, and some alternates are emerging. A certainty for trucks, and a good possibility for automobiles, is the turbine engine. Because it is critical of the thermal stability of current mineral oil, we can expect the resources of the lubricant suppliers to be put behind necessary petroleum lubricant improvements if the turbine engine becomes a viable replacement.

The development of superlubricants and mechanisms requiring them catalyze each other, but the catalyst poison is cost. At the present time, petroleum-based synthetics that may be available are considerably more costly than the broad-base normal oil. However, much of the cost difference reflects capital cost and low potential volume, not raw material and processing. When a new engine, or new transmission, or other high-volume application that the broad-base oil cannot handle, comes along, synthetic petroleum-based oil will get the impetus it needs to take the next big step. I believe that petroleum lubricants of the future will be converted to specific end uses by chemical refining techniques that will find ways to incorporate additive functions now provided separately.

G. Salomon (Central Laboratory, TNO, Delft, The Netherlands)

The author reviewed the highly successful development of lubricants, based almost entirely on empirical testing. For reasons stated by Beerbower,[1] this period is entering into its final phase. To insure steady progress in the design and production of mechanical goods, additional information on lubricants is needed. Concentrated efforts are being made in several European countries, most noticeably in France, to select optimum surface treatments by systematic analysis of available technologies. As a corollary, lubricants have to be screened to fit such optimum surfaces.

At present, designers and production engineers depend entirely on the technical service information of suppliers, unless they are backed by a large testing laboratory. For example, the author states that the disturbing lack of correlation between sulfur content and four-ball reactivity (figs. 3 and 4 of the paper) is taken care of simply by compounding with a conventional gear oil additive. However, Smalheer [2] concludes that matching base stock and additives has to be done in trial-and-error fashion.

Therefore additional information is needed; such future data will belong to one of the two following categories, material properties and tribological properties.

Material Properties.—Analytical data such as that summarized in tables 8 and 9, in particular, data on the nonhydrocarbons listed in table 8, are not yet readily available from the technical service of suppliers. Additives, either natural or intentionally added, will react differently if present as fine-particle suspensions or emulsions. An interesting question in this area is the role of nonhydrocarbons as emulsifiers.

A plausible explanation of the term "oiliness" is found in the paper in this volume by Beerbower; it would seem that the term used in table 11 is synonymous with "lubricity" listed in table 8. The author could well explain how the merit rating of "lubricity" and "oiliness" is achieved and how the user is instructed as to the significance of this important lubricant property.

Tribological Properties.—Oil specifications are based on tests with certain standard steels. The user who wishes to lubricate hard chromium

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[1] See the lecture "Environmental Capability of Liquid Lubricants" by A. Beerbower in this volume. (Editor's note.)

[2] See the lecture "Additives" by C. V. Smalheer in this volume. (Editor's note.)

steels or nonferrous metals faces great uncertainties. These could be reduced by a different design of conventional friction and wear tests.

In the thermodynamic approach proposed by Beerbower, a distinction can be made between adiabatic and isothermal conditions of testing. The interface is heated almost adiabatically in the conventional four-ball test. If now the same combination of materials is tested under isothermal conditions, namely, at moderate speeds of sliding and by stepwise heating of the oil, the EP contributions will be less pronounced or even absent. At the previous conference, Kelley (ref. 19) has described this situation as "viscosity protected surfaces" (ref. 19, fig. 9). As Kelley pointed out, at a certain critical temperature level the base oil fails, while the EP additive is not yet reacting fast enough. It is this no-man's land of badly protected surfaces encountered in lubrication with straight or moderately compounded oils that needs closer specifications.

Under such isothermal conditions, plasticity and metallurgy of metals will have a pronounced influence on the merit rating of base oils. Extrapolating from our own experience with white oils and with solid lubricants, the following factors should be kept in mind:

(1) The "wear scar" in the softer metal is frequently a "plastic deformation scar," formed during running-in and independent of the duration of the test (ref. 20).

(2) Flattening of surface asperities depends on the ratio of the hardness of the pair of metals. In a pin-and-ring arrangement, asperities on the ring will be flattened only if the hardness ratio is about unity. On a hard ring, in contact with a soft pin, asperities react elastically (ref. 21).

(3) "Cold seizure" can take place under these conditions (ref. 22, fig. 5), and this phenomenon, in turn, will depend on metallurgical factors (see also the discussion following ref. 19) and on the environment (ref. 23).

(4) With nonferrous metals, lubricated by white oils, a critical temperature of transition from mild to severe wear and simultaneously from isothermal to adiabatic heating is readily observed (ref. 24).

In summary, isothermal testing requires a different philosophy of merit rating and corresponds to a condition that is frequently encountered in engineering practice.

J. K. Appledoorn (Esso Standard Italiana, Rome, Italy)

Mr. Furby has taken an interesting approach, describing mineral oils by their comparison with synthetics. This reverses the usual procedure of describing synthetics in terms of mineral oils, but it is more revealing because mineral oils are far more difficult to characterize than synthetics.

In making his comparison, Mr. Furby emphasizes that the most striking difference between synthetics and mineral oils is that 97 percent of the lubricants currently sold are mineral oils. One might be tempted to dismiss this overwhelming preference by suggesting that most applications are not very demanding on lubricant quality, but Mr. Furby shows that this is not the case. The facts are that mineral oils are excellent lubricants, far better than one would expect from Nature's unskilled hand. This, coupled with their low price, makes them an exceptional best buy.

What makes mineral oils so good? The fact is that we do not know. In spite of 100 years of use, we still know less about mineral oils than we do about most synthetics. A synthetic is much simpler: it consists of a single molecular type, polyolefin, silicone, ester, etc., and frequently of a single molecular weight. Because of this homogeneity, the physical and chemical properties are relatively easy to define. Mineral oils, on the other hand, are a complex mixture of paraffinic, naphthenic, and aromatic hydrocarbons, along with some heterocompounds containing sulfur, nitrogen, and oxygen. This mixture does not behave in a simple additive fashion, and fortunately its properties are usually better than would be predicted.

Because of space limitations, Mr. Furby has given only an overview of the situation. There are three important properties that deserve to be treated more fully: viscosity-temperature characteristics, lubricating ability, and oxidation resistance.

Viscosity-Temperature Properties.—Good V.I. is obtained by having molecules so flexible that they can move past each other with minimum interference. In many synthetics, this flexibility is obtained by an ether linkage; i.e., by an oxygen atom repeated periodically along the chain. Rotation around an oxygen atom is so free that exceptional flexibility is obtained. Silicones, polyalkylene glycols, polyphenyl ethers, and perfluoropolyglycols all owe their V.I. to their oxygen atoms. Silicones are exceptional in this regard, and although neither the polyphenyl ethers nor the perfluoropolyglycols have outstanding V.I., they would be solids or negative V.I. liquids without their oxygen atoms.

Mineral oils have no such convenient ether linkages. They depend for their V.I. on having molecules that do not have excessive branching or bulky condensed-ring structures. In this regard, they are like the synthetic esters, which likewise depend mostly on molecular shape. If one were to manufacture a hydrocarbon with the same molecular structure as, say, 2-ethylhexyl adipate, but with carbon atoms substituting the oxygen of the esters, they would have about the same V.I. as the esters. (See table 15.) The work of API research project 42 (ref. 25), carried out at Pennsylvania State University, gives many such examples of pure hydrocarbons of high V.I.

Unfortunately, mineral oils are a mixture of many hydrocarbons, most of which have some branching or some bulky ring structures. The bulky ring structures are normally removed by any of a variety of refining

TABLE 15.—*Viscosity Characteristics of Sample Hydrocarbons*

Compound	Viscosity, cP	
	100° F	210° F
2-Ethylhexyl adipate (ester)	7.7	2.2
11-*n*-Amylheneicosane	7.9	2.0
2-Methyltricosane	7.4	2.1

methods, as already discussed by Mr. Furby. These methods give a marked boost in V.I., and they are mostly specific for removing aromatic rings. Aromatic rings have therefore often received the entire blame for the poor V.I. of untreated mineral oils.

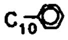
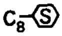
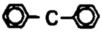
This is an oversimplification on two counts. In the first place, ring structures, per se, do not give low V.I. values. Compare, for example, the viscosity properties of the compounds, synthesized by API research project 42, listed in table 16.

All have very nearly the same viscosity and V.I., although the first is a straight-chain paraffin and the last is predominately a condensed-ring aromatic. The ring structure does not give low V.I. here, because the molecules are all fairly simple, and they can move past each other easily. As the molecules get more complex, the importance of branching and fused rings becomes more important. Particularly bad are combinations of aromatic and naphthenic rings fused together. Such molecules tend to be as rigid as the condensed-ring aromatics but do not have the attendant advantage of being planar.

In the second place, it is wrong to suppose that naphthenic rings have better V.I. than aromatic rings. Mr. Furby gives an example that is true for a particular molecular species. However, for mineral oils, which are a mixture of many molecular species, naphthenic rings are no better than aromatic rings. Waterman and his associates hydrogenated 357 different mineral oils very carefully to avoid any ring breakage. Aromatic rings were converted into naphthenic rings, but the fraction of carbon atoms in rings (C_R) remained the same. Roelands (ref. 26), in analyzing the data, noted that this fraction C_R completely and uniquely determines the viscosity-temperature properties. It makes no difference whether the rings are aromatic or naphthenic.

The increase in V.I. obtained by hydrogenation is therefore exclusively the result of ring breakage; i.e., because the complex fused-ring structures are changed into aliphatic chains. Simple conversion of aromatics to

TABLE 16.—*Viscosity of Selected Compounds*

Name	Structure	Viscosity (cP) at—	
		100° F	210° F
n-Hexadecane	$n\text{-}C_{16}$	2.33	0.90
1-Phenyldecane		2.54	.99
1-Cyclohexyloctane		2.35	.91
Diphenylmethane		2.20	.91
cis-Decalin		2.31	.92
Methylnaphthalene		2.23	.88

naphthenics gives a decrease in density and viscosity; it does not affect viscosity-temperature properties significantly.

Lubricating Ability.—Mineral oils are generally better lubricants than most of the synthetics, but this is not because of a superiority of hydrocarbons over other compounds. Pure hydrocarbons themselves are rather poor lubricants, regardless of whether they are aliphatic or aromatic. This shows up when a mineral oil is overrefined, the ultimate in overrefining being medicinal white oils. These oils have been so exhaustively refined that all the lubricity has been removed. They are capable of lubricating the human interior but cannot carry the heavy loads of industrial machinery.

Such an oil can have its lubricity restored by adding certain chemical compounds, of which sulfur compounds are the most widely used. Inasmuch as sulfur compounds also occur in normal mineral oils, they have been widely credited with imparting the good lubricity to these oils. This classical explanation has been adopted by Mr. Furby.

However, there is a growing body of evidence that the classical explanation is wrong, that it is not the trace elements that give mineral oils their good lubricity. Instead, the hydrocarbons themselves, or rather the mixture of hydrocarbons, are responsible.

The unexpected synergistic behavior between aliphatics and condensed-ring aromatics was first pointed out by Appeldoorn and Tao (ref. 27) when working with pure hydrocarbons. Small amounts of methylnaphthalene (an aromatic) greatly improved the wear and load-carrying properties of cetane (a straight-chain paraffin), and vice versa. This behavior was found to be typical of all such mixtures: a heavy aromatic naphtha added to a heavy white oil in 10-percent concentration gave a fourfold reduction in wear, even though the viscosity was decreased by 50 percent. This improvement was common to all metallurgies. The mechanism of this synergism is still not entirely clear, but Goldblatt (ref. 28) has proposed an interesting hypothesis involving radical anions.

The true synergistic character of hydrocarbon mixtures was further shown by Groszek (ref. 29). He separated a mineral oil into several fractions and noted that none of the fractions, not even the one containing most of the trace elements, was as good a lubricant as the original whole oil. It is the combination of components that is important and not the presence of highly active materials.

Still more evidence is given by Appeldoorn and Dukek (ref. 30) who added several sulfur, oxygen, and nitrogen compounds to a jet fuel having poor lubricity. Surprisingly, almost none of these compounds gave an improvement, and many of them, particularly sulfur compounds, were actually prowear agents. Rudston and Whitby[3] have confirmed these findings independently.

Lastly, it has been found that mixtures of aliphatics and aromatics are much less responsive to antiwear and EP additives than are aliphatics alone (ref. 31). The aromatics improve the lubricity of aliphatics but in so doing they make it more difficult for other additives to act. This exactly parallels the behavior of SRMO's. In the refining process their lubricity is decreased, but they are then much more responsive to small concentrations of EP additives.

A great deal still needs to be learned about the synergism and antagonism of hydrocarbons with other hydrocarbons, hydrocarbons with EP additives, and EP additives with other EP additives.

Oxidation Resistance.—The oxidation stability of mineral oils is probably the most interesting phenomenon of all. There are several reasons for this. First, oxidation is an exceedingly complex reaction even with pure hydrocarbons and is greatly altered, both in degree and kind, by temperature, oxygen availability, and the presence of catalysts, both homogeneous and heterogeneous. For hydrocarbon mixtures and for oils containing inhibitors, the reaction occurring can be hopelessly complex for any true understanding. Second, poor oxidation resistance is a natural characteristic of crude mineral oils and is the major reason for refining these oils in the first place. Third, most synthetics enjoy their advantage over mineral oils, even refined oils, because of better oxidation resistance, particularly at

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[3] Rudston, S. G.; and Whitby, R. D.: Effect of Model Lubricating Oil Constituents on the Wear of Steel. J. Inst. Petrol., to be published.

elevated temperature when properly inhibited. Finally, refined mineral oils have considerably better oxidation stability than would be predicted from the stability of their components.

Mr. Furby has not tried to give an extensive treatment of oxidation, for to do so would require an entire book. However, two points should be discussed at greater length.

First, the criterion used to measure oxidation has a major effect on the conclusions. Mr. Furby uses as his criterion oxygen absorption; that is, the amount of oxygen reacting. This is reasonable enough from a chemistry point of view but it does not tell what is happening to the oil. Much of the oxygen that reacts may end up as water and CO_2 (ref. 32), and a good deal of the remainder forms oil-soluble reaction products (esters, ketones, etc.) that are not particularly harmful.

A more meaningful criterion is the condition of the oil itself after oxidation. Oxidation causes oils to increase in acidity, viscosity, and the amount of insoluble matter (sludge). Each of these is bad, and usually one of them is the limiting factor on oil life. Insolubles are particularly harmful for they plug oil passages or form resinous films that interfere with heat transfer and cause sticking of valves, injectors, piston rings, etc.

If, for the criterion for oxidation, a combination of acidity and sludge is used, an entirely different rating of oils is obtained than when oxygen absorption is used. Highly extracted oils are the best, and unextracted, the worst. The villains are the aromatics, which easily form insoluble oxidation products (ref. 33). Removal of these aromatics is therefore the prime purpose of all refining methods, whether by acid treating, solvent extraction, or hydrogenation.

Superrefining carries this to the ultimate by removing essentially all aromatics. Parenthetically, it should be noted that most of the sulfur and nitrogen compounds end up in the sludge, which casts some doubts as to whether they are the actual natural inhibitors present.

Second, there is still great confusion on the role of metal catalysts. In most applications, the oil is in contact with a large surface of metal and, frequently, several different metals. These metals are attacked by the oxidizing oil and, concurrently, act as catalysts to accelerate the oxidation process. There is argument about the mechanism of this catalysis. Statements are found in the literature that metals are catalysts only when they are dissolved in the oil; i.e., as homogeneous catalysts (ref. 34). And there is no doubt that oil-soluble metal salts can be powerful prooxidants. Hence, it is a common test procedure to add metal salts (lead naphthenate or copper oleate, for example) to an oil at the start of the oxidation test to simulate the presence of metal surfaces. Mr. Furby uses this method.

Another school of thought believes that solid metals behave much differently than their oil-soluble salts do, not only in degree but in kind. Some oxidation tests therefore call for the metals themselves to be present (e.g., corrosion/oxidation-stability test, FTMS 5308). To pass this test, the oil must not only withstand oxidation but also prevent corrosion of any of the metals. Tacit in this requirement is the acknowledgment that metal corrosion (i.e., the formation of oil-soluble salts) does not automatically cause oil oxidation: it is possible to have metal corrosion without serious oil degradation.

Moreover, in many test methods, the simple presence of metal surfaces is not considered sufficient. Metal surfaces can be rapidly passivated and will no longer serve as catalysts. To prevent this, these test methods require that the surfaces be rubbing together during the test. Examples of such tests are the Navy work factor test (FTMS 3451), Rolls-Royce conical pump rig (ref. 34), and the standard CRC L–4, CRC L–38, and Petter W–1 engine tests. In all cases it has been found that the oxidation proceeds differently (again both in degree and kind) when the surfaces are activated by rubbing. The very fact the L–38 engine test is still required to measure oil oxidation is proof that oxidation under these conditions proceeds differently; 30 years of trying for a simple screening test to replace the L–4 have been totally unsuccessful.

In our laboratory in Rome we have been studying oxidation in the presence of the cavitation that continuously gives a fresh metal surface. We have found that lead and copper, which have always been considered among the most active of metal catalysts, are not as active as iron or aluminum (table 17). In fact, lead appears to act as a kind of oxidation inhibitor in a number of instances. These results merely emphasize the depths of our ignorance about this very complicated phenomenon we call oxidation.

In summary, our understanding of mineral oils still has many gaps. We have a good grasp of the physical properties and how they can be measured or predicted. About chemical properties, our knowledge is limited by the very complexity of the mineral oil mixture itself.

TABLE 17.—*Oxidation of Mineral Oil During Cavitation*

Metal	Amount of oxidation (IR absorption 1720 cm^{-1})	
	Fe tip[a]	Al tip[a]
Al	1.48	1.80
Fe	1.48	1.37
Cu	1.07	1.00
Pb	.70	.65

[a] Tip of 20-kc cavitation horn.

A. J. Groszek (BP Research Center, Sunbury-on-Thames, England)

It is quite clear that superrefined oils may have important applications in the near future, but the severe handicap in the wider use of the oils is their high cost.

A potential new method of dewaxing has been found at the BP Research Center. The method depends on selective adsorption of waxes on graphite adsorbents (ref. 35).

Graphite has a strong tendency to selectively adsorb compounds containing long *n*-paraffin chains, the strength of adsorption increasing with the chain length. Percolation of waxy distillates, waxy raffinates, or ordinary grades of mineral oils through columns of graphite adsorbents yields fractions containing gradually increasing pour point ranging from $<-70°$ F to the melting point of the wax contained in the feedstock. This may be illustrated by the results given in table 18 of pour points and carbon-type analyses of fractions separated from the N+P component obtained of a Middle East 500 pale oil.

The percolation was carried out at 20° C using isooctane as solvent and the ratio of oil percolated to adsorbent was 1:5 by weight.

The method has been applied to a wide range of mineral oils, and in every case deeply dewaxed oils could be easily separated by collecting the first fractions eluted with isooctane or *n*-pentane.

LECTURER'S CLOSURE

Prof. E. E. Klaus has pointed out several interesting facts. The desirable deviation (downward hook) from the ASTM charted viscosities at low temperature for deep dewaxed oils and some synthetics is very important. He pointed out this goes along with dense-centered molecules. I agree with

TABLE 18.—*Analysis of Middle East 500 Pale Oil*

Cumulative percent oil eluted	Viscosity, cs		V.I.	Pour point, °F	Cloud point, °F	Carbon-type analysis		
	100° F	210° F				C_p	C_N	C_A
14	52.86	7.04	99	[a]−45	<−60	56	44	-----
32	65.83	8.03	96	[a]−45	<−60	59	41	-----
55	67.59	8.43	103	−30	−35	68	32	-----
80	69.14	8.63	105	10	5	71	29	-----
92	44.46	6.88	119	45	45	86	14	-----
Feed	62.06	8.02	104	10	---------	65	35	0

[a] Viscous pour point.

him that incremental improvement of conventional oils, to a degree less than full superrefined, would solve the current performance problems of some lubricants, It is expected that future commercial practice will include such changes. Professor Klaus referred to development studies yielding economical low-temperature dewaxing techniques. This will be of great significance if commercially feasible.

Dr. T. Salomon questioned the use of oxygen absorption tests and the use of soluble metal naphthenates as catalysts. Results from such tests may not correlate precisely with performance in a given lubricant application, but they do have good overall correlation with resistance to oxidation in product use. Obviously a variety of oxidation tests is required to cover all aspects of oxidizability. I cannot agree with Dr. Salomon that white oils prepared in different ways have significantly different oxidation stabilities. Whether refined by sulfuric acid treatment, by hydrogenation, or by adsorption separation, oils at the white oil stage of refinement (i.e., having essentially no aromatic compounds, or oxygen, sulfur, or nitrogen) are all very susceptible to oxidation. Also, I believe white oils are not used in motor oils primarily because of high cost and limited availability, rather than low activity of dispersant agents in them. It is true that the lower solvent power of some white oils precludes the use of some additives. I agree that the content and nature of minor constituents is important and merits further study. Professor Klaus has long pointed this out.

Mr. Huth commendably praised the value of hydrogen treatment in lieu of older refining methods. However, I do not believe that it will be possible by future refining techniques "to incorporate additive functions now provided separately." Improved refining techniques may reduce the amount of an additive required; for example, by making a base stock more responsive to an antioxidant. At the same time, in one sense the base stock is usually less stable without antioxidant because natural inhibitors have been refined out. Thus, superrefining makes additives more effective and even more necessary.

Dr. G. Salomon asked about the role of nonhydrocarbons as emulsifiers. Indeed, these play the major role in determining the so-called demulsibility of a base oil. White oils and highly hydrogen-treated oils have essentially no nonhydrocarbons and separate rapidly from an oil-water mixture. A measure of this property is the interfacial tension (against water), which will be 45 to 50 dyne/cm in the case of these oils as compared to 35 to 40 for a normal solvent-refined oil. Regarding the terms "lubricity" or "oiliness" as used in my paper, both refer to the ability to lubricate (prevent metal adhesion) under conditions of boundary lubrication where viscosity (hydrodynamic lubrication) plays no part.

Mr. Appeldoorn's lengthy comments added interesting details and modifications, most of which require no reply. I would agree that the chemical properties of mineral oils contain more mysteries than do the physical properties. The effects cited of chemical constitution of base oil on lubricity are indeed very important. Further data in a variety of EP and wear tests will be of great interest. Mr. Appeldoorn referred to the complexity of oxidation phenomena and to the criteria of the extent of oxidation. For this very reason of great complexity, if one must choose a single test for initial judgment of oxidization resistance of base oils, the Dornte-type test described in my paper appears to be a good choice. See my reply to Dr. G. Salomon on the same subject. Mr. Appeldoorn states parenthetically that sulfur and nitrogen compounds end up in the sludge, and this casts doubt on their being natural inhibitors. This seems not so since inhibitors are themselves oxidized in performing their inhibitory function and thus would be expected to end up as sludge or acids. The use of fresh metal catalysts produced by in situ cavitation is an intriguing concept. The data shown do not include the concentration (surface area) of freshly produced metal that might be correlated with extent of oxidation.

Mr. Groszek presents an interesting process for dewaxing by percolation of an isooctane solution of oil through graphite. In view of the high adsorbent-to-oil ratio, one wonders whether commercialization of this process is practical.

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Synthetic Oils

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Many chemical classes have found application as synthetic lubricants. These materials have made possible the design and practical operation of many items of machinery that would not function as well or at all if only petroleum lubricants were available.

Synthetic lubricants are discussed by chemical class and their general strengths and weaknesses in terms of properties important in lubrication are pointed out. Comparative ratings are given for 14 chemical classes and can serve as a guide to lubricant selection. The effects of chemical structure on properties are described with special emphasis on one property, thermal stability.

Synthetic lubricants have the potential of satisfying a wide range of requirements since they can be made available with nearly any desired range of a specific property. However, certain other properties fixed by the chemical structure must be accepted. Equipment design must therefore take all properties into account.

A recent paper stated:

> in many applications conventional lubricants have been weak sisters that limit the performance pace. This is the reason for the interest in synthetic lubricants that can be tailored to meet specific and demanding requirements. But, choosing the right synthetic for an application can be tricky because to get the special characteristics you want, you usually have to trade off some other performance feature (ref. 1).

This quotation reflects both the promise and the problem of synthetic lubricants: the promise to provide outstanding performance and the problem of designing the equipment to accommodate all the properties of the lubricant. This paper will discuss some of the many synthetic liquids proposed as lubricants and will attempt to make some generalizations that can aid in the selection of the best lubricant for a given application.

WHY SYNTHETIC LUBRICANTS?

Looking back, we find that the earliest lubricants were oils and fats derived from animals and from plants. The use of petroleum hydrocarbons as lubricants is relatively recent. Their advantages and wide uses are well recognized and have been ably described by the author of the previous paper. The constant improvement of these products through refining techniques and by the application of highly developed additive technology will certainly continue, and petroleum-derived liquid lubricants will be our most important commercial source for a great number of years to come.

If these materials are so good, the next question is why anyone should be interested in replacing them with synthetically produced products. This is particularly true because synthetic materials are generally of higher cost because of the complex chemical reactions required. There are several reasons. The major reason for the development of synthetic lubricants has been the necessity to provide lubrication under conditions that could not be adequately satisfied by petroleum hydrocarbons or, to state in other terms, to prevent wear and reduce friction under extreme conditions. Such conditions easily occur in military and space uses but also exist in many everyday applications. From a research standpoint, one reason has been to provide insight into lubricating theory by the use of pure compounds as compared to the wide range of materials that are found in even a highly refined petroleum hydrocarbon fraction. At particular times in past history, it became important to extend a limited supply of petroleum by the use of lubricants derived from other sources by synthetic techniques.

CLASSIFICATION OF SYNTHETIC LUBRICANTS

In discussing synthetic oils, two basic classification systems can be followed. The first one involves grouping them together in terms of specific properties, such as viscosity-temperature range, volatility, density, etc. This method offers certain advantages in terms of selection and application of the synthetic lubricants, but suffers from considerable complexity in describing the products in a logical fashion.

The second approach involves classification in terms of their basic chemistry. The oils can then be discussed as single chemical classes, which allows for considerable generalization as to variation between classes and within each class. Both systems will be used in this paper, with emphasis on the second method.

A brief review of the technical literature reveals that the number of organic compounds or semiorganic compounds that have been investigated as liquid lubricants is sufficiently large to defy complete classification other than in terms of a full-sized organic textbook. Perusal of the patent literature extends the numbers even further. It is undoubtedly true that almost all known classes of organic materials have been examined and, if liquid, claimed as synthetic lubricant base stocks. The materials of most interest can be described in the following way: compounds consisting of carbon and hydrogen, e.g., synthetic hydrocarbons; compounds containing carbon, hydrogen, and oxygen, e.g., polyglycols, organic esters, and ethers; compounds containing carbon, hydrogen, phosphorus, and usually oxygen or sulfur, e.g., phosphate esters; and compounds containing carbon, hydrogen, oxygen, and silicon, e.g., silicones and silicate esters. The halogens, particularly chlorine, fluorine, and, to some extent, bromine, have been found to be quite useful substituents for hydrogen in many of these classes in preparing synthetic fluids. Nitrogen and sulfur are often incorporated to modify the characteristics of the compounds listed above. This classification is summarized as—

(1) Carbon and hydrogen: superrefined petroleum oils and synthetic hydrocarbons
(2) Carbon, hydrogen, and oxygen: organic esters, polyglycols, and polyphenyl ethers,
(3) Carbon, hydrogen, and phosphorus (usually oxygen and sulfur): phosphate esters
(4) Carbon, hydrogen, and silicon (usually oxygen): silicate esters, silicones, and silanes
(5) Carbon and halogen (usually hydrogen and often oxygen): halogenated polyaryls, fluorocarbons, and perfluoropolyglycols
(6) Carbon, hydrogen, and nitrogen (often oxygen)
(7) Carbon, hydrogen, and sulfur (often oxygen)

MARKETS FOR SYNTHETIC LUBRICANTS

The market for synthetic lubricants ranges from high volumes for industrial uses at moderate prices to very small volumes for special applications at relatively high prices. In a recent summary presented to the Chemical Marketing Research Association, T. G. Smith presented some numbers that appear to be quite valid (ref. 2).

The market was analyzed in terms of present and potential volumes. The automotive market represents a lubricant use of approximately 300 million gallons, of which about 250 million gallons are petroleum crankcase lubricants that are not likely to be replaced by synthetics. The most apparent opportunity for synthetics in the automotive use appears to be the replacement of petroleum oil in the automatic transmission. This potential is thought to be somewhere in the neighborhood of 40 million gallons.

The second largest potential use for synthetic oils is probably in the hydraulic fluid area. Although these products are not primarily lubricants, their lubricating ability is important to their end use. The total market is thought to be in the neighborhood of 250 million gallons, with a possibility of the synthetics capturing 15 million gallons of this market by 1975.

Industrial lubricants represent a total market of somewhere near 150 million gallons, and it is estimated that no more than 10 percent of this total is filled by synthetic fluids. These have found application as rolling oils, cutting fluids, heat transfer fluids, transformer oils, textile and rubber lubricants, etc.

The greatest success of the synthetic lubricants has been as gas turbine lubricants. The total market, including both military and commercial aircraft, is probably in the range of 2.25 to 3.25 million gallons per year. The market for industrial turbine lubricants is not well defined but is considerably larger and is rapidly growing.

In summary, Mr. Smith states that the above markets together with some other smaller uses involve about 750 million gallons of product annually. Of this, approximately 35 to 40 million gallons per year are synthetic oils. These data are summarized in table 1. This represents a considerable amount of material and includes a wide range of chemical classes. Prices range from $1 to $10 per gallon.

In addition to the large-volume uses described above, synthetic lubricants are used in a number of more specialized applications. These range from watch and instrument oils to nuclear power generation system lubricants. Prices range up to several thousands of dollars per gallon.

PROPERTIES OF SYNTHETIC LUBRICANTS

In discussing the various classes of synthetic lubricants, one must first review the properties that may be of some concern in their total performance. A great number of properties can be considered, and some of the important ones include—

(1) Viscosity-temperature properties
(2) Viscosity-pressure properties
(3) Viscosity-shear properties
(4) Boundary lubrication characteristics
(5) Heat transfer properties
(6) Thermal, oxidative, and hydrolytic stability
(7) Noncorrosiveness to and compatibility with other system materials

TABLE 1.—*Lubricant Markets*

Type	Total volume, in millions of gallons	Synthetic volume, in millions of gallons
Automotive	300	—
Industrial hydraulics	250	15
Industrial lubricants	150	15
Other	50	5 to 10
Total	750	35 to 40

(8) Contamination-generation tendencies
(9) Density
(10) Coefficient of expansion
(11) Volatility
(12) Foaming tendencies and gas release rates
(13) Bulk modulus
(14) Fire resistance
(15) Electrical properties such as conductivity, dielectric constant, etc.
(16) Radiation resistance
(17) Toxicity
(18) Service life
(19) Cost-to-performance ratio

It should be emphasized again that the reason for the existence of and the great diversity in types of synthetic lubricants is that many applications demand special properties that can best be provided by synthesizing and/or formulating a specific liquid to fulfill the requirements. It is possible to scientifically design molecules that have certain outstanding properties. However, it should always be kept in mind that these advantages are not always obtained without certain disadvantages or, at the least, differences in some properties from the normally used petroleum hydrocarbons. The most common problems and errors experienced in the application of synthetic lubricants arise from expecting these materials to provide the outstanding property for which they were selected and still maintain all the other properties of the replaced material. Experience over the years has shown that the application of sound engineering practices and the realization that the synthetic lubricant is an essential part of the overall system will enable the satisfactory solution of problems and will result in improved total performance.

Generalized Ratings

Thousands of liquids have been suggested in the literature and in the research laboratories for use as synthetic lubricants. A majority of these have been discarded because of obvious or serious deficiencies. A number have survived vigorous screening and are candidates for or have found use in commercial applications. It is not the purpose of this paper to catalog specific fluids. However, an attempt is made to give general ratings to a number of properties for several classes of fluids (ref. 3). Table 2 summarizes the comparative ratings.

A few comments should be noted concerning table 2. Two rating systems are used in table 2. The first grades the viscosity-temperature, liquid range, low-temperature, thermal stability, oxidative stability, hydrolytic stability, lubricating ability, and handling and storage properties on a scale from excellent (E) to poor (P). The second system grades the fluids

TABLE 2.—*Comparative Ratings of Synthetic Lubricants*

Class	Property												
	Viscosity-temperature	Liquid range	Low-temperature properties	Thermal stability	Oxidative stability	Hydrolytic stability	Fire resistance	Lubricating ability	Bulk modulus	Volatility	Radiation resistance	Density	Handling and storage
Petroleum oils	G	G	G	F	F	E	L	G	A	A	H	L	G
Superrefined petroleum oils	E	G	G	G	F	E	L	G	A	L	H	L	G
Synthetic hydrocarbons	G	G	G	G	F	E	L	G	A	L	H	L	G
Organic esters	G	E	G	F	F	F	L	G	A	A	A	A	G
Polyglycols	G	G	G	F	F	G	L	G	A	L	A	A	G
Polyphenyl ethers	P	G	P	E	G	E	L	G	H	A	H	H	G
Phosphate esters, alkyl	G	G	G	F	G	F	H	G	H	A	L	H	G
Phosphate esters, aryl	F	P	P	G	G	F	H	G	H	L	L	H	G
Silicate esters and polysiloxanes	E	E	E	G	F	P	L	F	A	A	L	A	F
Silicones	E	E	E	G	G	G	L	P	L	L	L	A	G
Silanes	G	G	G	G	F	E	L	F	A	H	L	L	G
Halogenated polyaryls	G	G	F	G	G	E	H	G	H	H	L	H	G
Fluorocarbons	F	G	F	G	G	F	H	P	L	A	L	H	F
Perfluoropolyglycols	F	G	G	G	G	G	H	G	L	A	L	H	G

Ratings: E = excellent, G = good, F = fair, P = poor; H = high, L = low, A = average.

in terms of fire resistance, bulk modulus, volatility, radiation resistance, and density in terms of high (H), low (L), and average (A).

The ratings should be considered as representative of the class as a whole. Individual members of the class may be better or worse than the rating given. Further, it should be emphasized that proper formulation can improve many of the properties. The use of additives to improve a specific property may result in some degradation of other properties. A proper balance between properties must be determined. Further, additive concentration or activity may decrease with use and thus can influence service life. The subject of additives is adequately covered by a number of papers in this symposium. However, in terms of synthetic lubricants, additives that have proven effective in one base stock cannot automatically be assumed to be of equivalent value in a second base stock.

The ratings used in table 2 are general and relative terms. Numerical limits are impossible because of the wide variation in properties in a given class, the lack of standard test methods for certain of the properties, the imperfect correlation of small-scale test results with full-scale operation, and the uncertainties of defining system and operation parameters in exact mathematical terms.

Certain important properties are not included in the rating chart of table 2. These properties do not lend themselves to comparative rating because very great variation can occur between members of a given class or because their performance depends so greatly upon system materials selections. Compatibility and corrosion ratings are particularly difficult. The wide range of available materials will nearly always allow correct matches to be made.

Properties Versus Structure

The literature contains many studies that show how physical and chemical properties vary with chemical structure within a given class of materials. This is also true for other characteristics such as lubricating ability. From such work a number of general trends are apparent, but knowledge has not reached the point that one can sit down with a paper and pencil and design the ideal lubricant for a given application. Synthesis of candidate fluids, based upon a consideration of their known properties, must be carried out followed by evaluation in terms of the expected performance in the real or simulated system.

A few generalizations can be made. For example, straight-chain linear alkyl groups give better viscosity-temperature characteristics than isomeric branched-chain groups. Low-temperature fluidity is usually in the reverse order. Incorporation of major amounts of halogen or phosphorus in the molecule gives improved fire resistance. Aromatic compounds are generally more stable than aliphatic compounds. In a given class, properties such as viscosity, volatility, and density are related to molecular weight. Bulk modulus is generally much higher for products that contain appreciable amounts of aromaticity.

A Specific Property: Stability Versus Chemical Classes

A reason often cited for the use of synthetic lubricants is their improved stability under conditions of use; for example, lubricants. Petroleum oils were replaced by the synthetic diester lubricants, which are now being replaced by the polyol or hindered ester lubricants. Even better products are foreseen for the future.

The term "stability" includes many aspects that have varying importance in various applications. Stability includes thermal, oxidative, hydrolytic, and mechanical effects. The nature of the decomposition or reaction products formed during use are also of great importance. It is therefore quite difficult to determine the best method for measuring stability. In the area of thermal stability, one of the most useful tests for pure compounds is the isoteniscope measurement of decomposition temperature. Decomposition temperature T_D is the temperature at which dp/dt is 0.014 mm Hg/sec determined under carefully controlled and standardized conditions. A comparison of the decomposition temperatures of a number of chemical classes is given in table 3 (ref. 4). It should be noted that the values shown do not necessarily indicate the maximum usable temperature. The maximum temperature a particular lubricant can tolerate in a given application will depend upon the environment, the products of decomposition, and possible catalytic effects, in addition to the actual decomposition temperature. Also, some degree of degradation may be tolerated using

TABLE 3.—*Decomposition Temperatures of Various Chemical Classes*

Type	Maximum T_D, °F
Polyphenyls	850
Polyphenyl ethers	850
Silicate esters, aryl	840
Phosphate esters, aryl	790
Silicones	730
Methyl-substituted polyphenyl ethers	730
Chlorinated polyphenyls	680
Silicate esters, alkyl	650
Hydrocarbons—aliphatic, naphthenic	640
Polyol esters	600
Fluorinated esters	600
Dibasic acid esters	540
Phosphate esters, alkyl	380

temperatures higher than the decomposition temperature if the application can accept a limited life or can tolerate frequent fluid changes.

With some synthetic lubricants, metals catalyze or otherwise accelerate degradation. The rate of decomposition for such a fluid is not a constant with time. Several examples are shown in table 4.

Thermal stability is greatly influenced by molecular structure. Differences are found between members of the same class as well as between classes. The mechanism of the decomposition reaction is of utmost importance. Reference to the literature is suggested for more complete information.

Recognizing all the problems involved, an attempt has been made to list classes of synthetic lubricants in terms of approximate operating temperature ranges. These are summarized in table 5. Two ranges are given, one representing long-term operation (several hundred hours or more) and one giving short-term or hot-spot operation. These limits are the author's best estimates, and some variation among members of each class must be expected. The ranges are based primarily on thermal and oxidative stability data. It is assumed that conventional oxidation inhibitors are used where the fluids of that class are normally formulated to include them. It should be noted again that the operational temperature ranges can be affected by the presence of metals and other system materials and by the environment. The ranges given should be used as a guide to selection of classes of fluids for further examination at required system temperatures.

Just as important as the upper temperature limits are the low-temperature requirements for synthetic lubricants. The liquid range is often used to designate this parameter. The liquid range is defined at the lower end of the temperature scale by the solidification of the fluid and/or the maximum viscosity allowable in the system. The low-temperature and crystallinity properties of materials in a given class vary widely. Formulation

TABLE 4.—*Effect of Metals on Decomposition Temperatures*

Fluid	T_D, °F	
	No metal	With metal
Dibasic acid ester	540	440
Polyol ester	600	500
Superrefined mineral oil	640	640
Modified polyphenyl ether	720	720
Silicone	730	720
Polyphenyl ether	850	830

TABLE 5.—*Operational Temperature Ranges*

Class	Long term, °F	Short term, °F
Petroleum oils	200 to 250	275 to 300
Superrefined petroleum oils	350 to 450	600 to 650
Synthetic hydrocarbons	350 to 450	600 to 650
Organic esters	350 to 375	425 to 450
Polyglycols	325 to 350	400 to 425
Polyphenyl ethers	600 to 700	800 to 900
Phosphate esters, alkyl	200 to 250	275 to 300
Phosphate esters, aryl	300 to 350	400 to 450
Silicate esters and polysiloxanes	375 to 425	500 to 550
Silicones	425 to 525	600 to 650
Silanes	350 to 450	600 to 650
Halogenated polyaryls	400 to 500	550 to 600
Fluorocarbons	550 to 650	750 to 850
Perfluoropolyglycols	450 to 500	550 to 650

of mixtures of materials of related structure often improves the low-temperature capabilities.

This specific examination of a property and how it varies from class to class of fluid illustrates the first method of classifying synthetic lubricants. The second method involves general descriptions of each class in terms of its outstanding characteristics and deficiencies together with some indication of the variance of properties within the class.

CHEMICAL CLASSIFICATION OF SYNTHETIC LUBRICANTS

Each chemical class of synthetic lubricants has properties that make it different or useful. The following review summarizes some of these. Reference should be made to the general chemical literature for specific properties and also to numerous reviews previously published (refs. 5 to 11). Reference 5 reviews the literature before 1962 and should be used as a beginning to facilitate literature searching. Additional sources of data are manufacturers' technical bulletins and Government agencies. In a very practical sense, most synthetic lubricant applications are developed using presently available products. If a deficiency develops during the design and test phases, research is then undertaken to improve or change the lubricant. Knowledge developed in such studies is then applied to develop new products.

Synthetic Hydrocarbons

When various refining processes such as those used to produce conventional petroleum lubricants are carried out in proper sequence and under very rigorous conditions, the products are referred to as superrefined oils.

These oils show somewhat different and often improved properties compared to the conventional petroleum oils. Both types are used in the previous tables to serve as baselines for comparison.

Synthetic hydrocarbons are defined as compounds containing only carbon and hydrogen that are prepared by chemical reactions starting with low-molecular-weight materials (fig. 1). A wide range of synthetic hydrocarbon lubricants has been described in the literature. The most useful types include polymers of straight-chain terminal alpha olefins, polybutenes of a wide range of molecular weights, alkylated aromatics, cyclic alkanes, and polyaromatic compounds.

The synthetic hydrocarbons differ in many important aspects from conventional petroleum lubricants. For example, they normally possess narrower boiling ranges for a given viscosity as a result of their more easily controlled molecular weight. In many properties such as compatibility, corrosivity, etc., they are generally similar to the conventional hydrocarbon lubricants derived from petroleum.

The primary reasons for preparing synthetic hydrocarbons for use as lubricants is that chemical synthesis provides specific structures and characteristics and molecular weight can be controlled to very narrow ranges. This latter factor enables one to control nearly all the properties that depend on molecular weight. These properties include vapor pressure, boiling point, viscosity, and low-temperature characteristics. As an example of control of property by change of structure, thermal stability has already been discussed and is shown in table 3 for aliphatic compared to aromatic compounds. The ability to vary structure and then study properties has made the synthetic route very valuable in lubricant research.

The polybutenes have found some commercial use, but primarily in uses other than as lubricants. Products made by polymerizing cracked waxes and other olefin-containing materials have been made and used, but offer little if any advantage over the conventional products.

The literature contains many examples of recent work in synthetic hydrocarbon lubricants. One of the most promising classes is the polymerized alpha olefins. These are being examined for use as military aircraft hydraulic fluids that are more fire resistant than the currently used petroleum hydraulic fluid (MIL–H–83282). They are also proposed for a number of industrial applications.

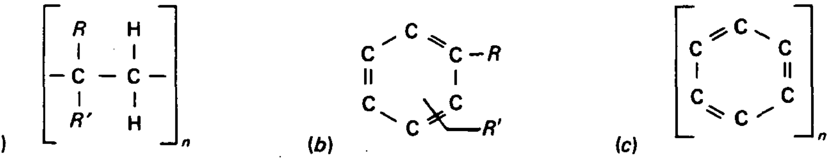


FIGURE 1.—Synthetic hydrocarbons. (a) Olefin polymers. (b) Alkylated aromatics. (c) Polyaromatics.

The alkylated benzenes have been suggested for use in supersonic transport hydraulic applications because they have good thermal stability and viscosity-temperature-volatility characteristics.

Recently there has been interest in certain aliphatic cyclic materials because of their superior tractive properties.

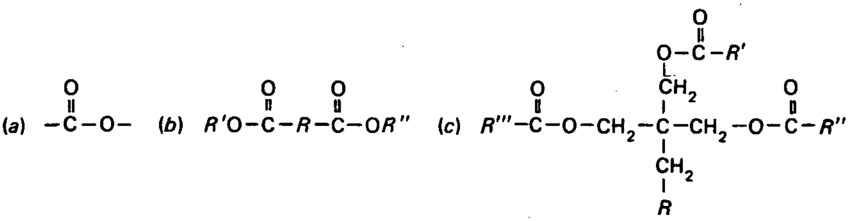
One very useful property of the synthetic hydrocarbons is the excellent resistance to radiation of the aromatic structure. This led to the development of biphenyl, terphenyl, and quatraphenyl mixtures as reactor coolants, which were used in design and operation of organic-cooled nuclear reactors. This class is also one of the most thermally stable of known organic compounds.

Organic Esters

The term "organic esters" is applied to those materials that consist of carbon, hydrogen, and oxygen and contain an ester or carboxyl linkage (—COO—) in the molecule (fig. 2). A large number of compounds are included in this class and are categorized by the acids and alcohols used in their preparation. The most widely used as lubricants are those that contain two ester groups and are made from dibasic acids. They are commonly called diesters. These first found wide use as synthetic lubricants for jet engines because of their good temperature-viscosity characteristics and thermal stability. They remain the most widely used synthetic lubricants. The products primarily used are the dialkyl sebacates, adipates, and azelates.

The esters have a good overall balance of properties, particularly in liquid range and in viscosity-volatility characteristics. They possess desirable lubricating ability with good response to additives. These aliphatic diesters are thermally stable to about 500° F but are exceedingly vulnerable to oxidation above 300° F, which results in increased viscosity, oil insolubles, and large amounts of acid or corrosive material.

The major difficulty in extending the operating range of diester lubricants has been their inability to function at higher temperatures. This thermal instability results from the relatively low energy mode of decomposition that involves the beta hydrogen on the alkyl group. In an effort to overcome this deficiency, a number of compounds were prepared



(a) $-\overset{O}{\overset{\|}{C}}-O-$ (b) $R'O-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OR''$ (c) $R'''-\overset{O}{\overset{\|}{C}}-O-CH_2-\overset{\overset{\overset{O}{\overset{\|}{O-C-R'}}}{|}}{\underset{\underset{R}{\overset{|}{CH_2}}}{\overset{CH_2}{\overset{|}{\underset{|}{C}}}}}-CH_2-O-\overset{O}{\overset{\|}{C}}-R''$

FIGURE 2.—Organic esters. (a) Ester group. (b) Dibasic acid ester. (c) Polyol ester.

and tested that do not have this structure. The most successful class has been the polyol esters. They are made from a polyglycol and low-molecular-weight aliphatic monobasic acids. The present commercial fluids are usually derived from pentaerythritol or trimethoylpropane and monocarboxylic acid mixtures. One disadvantage of these products compared to the diesters is their poorer low-temperature performance. However, by carefully selecting the molecular weights and the proper mixtures, it is possible to prepare reasonably low pour point products. These are now being used as jet engine lubricants by commercial air transport fleets and by the military and will continue to see service in this and other applications. These lubricants are quite similar in overall performance properties to the diesters except for their higher thermal stability. Additives are also quite important in this class in preparing optimum performance products.

The monoesters have not been widely used, but they do offer the advantages of extreme low-temperature operating capabilities and low viscosity. However, they are somewhat limited in high-temperature applications by volatility.

There has been some interest in esters derived from phenols. In general, these products have poor temperature-viscosity properties. They are also somewhat volatile and do not respond well to inhibitors.

The replacement of hydrogen in the ester molecule by fluorine or other halogens has been accomplished and a number of compounds have been made. However, none of these materials have been found to be particularly useful from a price-to-performance standpoint, and they have found little commercial acceptance. The halogen increases fire resistance and density. Thermal stability has been difficult to achieve with these materials.

Polyglycols

The polyalkylene glycols are the most widely used of this class (fig. 3). They are high-molecular-weight polymers of ethylene or propylene oxide, or both, and are available in a wide range of viscosities. One type is completely soluble in water. It can be diluted with water and used as fire-resistant hydraulic fluids and lubricants. Another type of polyalkylene glycol is water insoluble. These materials find wide use as lubricant-formulating base stocks. Characteristics are easily varied in the poly-

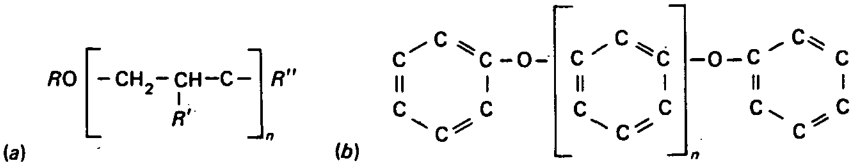


FIGURE 3.—(*a*) Polyglycols. (*b*) Polyphenyl ethers.

alkylene glycol materials by changes in molecular weight, in the groups used to modify the terminal hydroxyl (esters and ethers), and in the specific alkylene oxide or mixture used.

The polyglycols are excellent lubricants and respond well to additives. They have high flashpoints, good viscosity-temperature properties, low wax-free pour points, and shear stability. They have little or no adverse effect on many of the common seal materials but do have a strong solvent action on nonresistant paints. One interesting characteristic is that thermal and oxidative breakdown tends to form products that are volatile rather than insoluble sediments. However, volatility can be a problem, particularly under severe thermal and oxidative conditions. Stability characteristics even when improved with appropriate additives are not outstanding among the synthetics. Rust-preventing characteristics are poor.

The polyglycols have found use as industrial lubricants such as in rubber-processing applications, machining lubricants, lubricants for rubber seals, and in heat transfer applications. They have found their widest application in the formulation of automotive brake fluids.

Polyphenyl Ethers

The ether class of compounds, i.e., those containing carbon-oxygen-carbon bonds, have been studied as synthetic lubricants. The aliphatic materials have shown little advantage over similar molecular-weight hydrocarbons.

Analogous to the hydrocarbons, one way to improve the thermal stability of the ethers is to incorporate aromatic structures (fig. 3). The aromatic ethers have been recognized for a long time as having excellent thermal stability, and diphenyl ether has been used as a component of high-temperature heat transfer fluids.

Higher molecular-weight aromatic ethers are difficult to prepare in liquid form. A considerable amount of work was undertaken in the middle 1950's, and it was shown that metalinkages result in the best fluid properties and that unsubstituted ethers in the 4, 5, and 6 phenyl range were most useful. These compounds are stable for reasonable periods at temperatures in the 800° F range and can be used for short periods of time up to 1000° F. They are essentially nontoxic and inactive chemically. Although they will burn they are not readily flammable because they have high autogenous ignition temperatures. High-temperature lubricating studies with the polyphenyl ethers have shown that they are reasonable lubricants, particularly in the presence of air. Some of the difficulties experienced by some experimenters are thought to be due to the inertness of the polyphenyl ethers and their inability to wet metal surfaces. However, under oxidative conditions these compounds show lubricating ability at temperatures above that expected for their viscosity ranges.

A major deficiency of polyphenyl ethers is their low-temperature properties. Although their useful liquid range is extremely wide, they do have high pour points. A number of studies have attempted to improve this property. The use of aliphatic substituents on the benzene rings gave improved physical properties but generally resulted in lessened thermal stability. The substitution of atoms for oxygen between the rings has resulted in improved products, and work is continuing in this area.

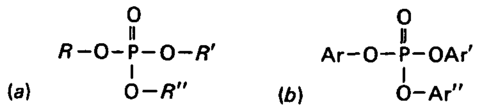
The polyphenyl ethers as a class represent one of the most promising classes of high-temperature lubricants. They are quite resistant to nuclear radiation. They have high bulk modulus and good heat transfer properties. Volatility at higher operating temperatures is relatively high (compared to polymeric materials), and viscosity-temperature characteristics are only fair. Oxidation resistance is good and can be further improved with additives.

Phosphate Esters

The incorporation of phosphorus into organic molecules has been studied extensively by organic chemists. From the standpoint of products useful in the lubricating area, the phosphate esters have been most advantageous. The phosphate esters are a diverse group of chemical compounds varying widely in physical and chemical characteristics depending upon the organic groups attached to the phosphate moiety. Both alkyl and aryl groups may be present (fig. 4). Thus there are trialkyl, triaryl, and mixed alkyl-aryl phosphate esters. In general, the phosphate esters are relatively easy to prepare and low in cost, and the starting materials are readily available.

The viscosity of the phosphate esters varies over a wide range. Viscosity-temperature characteristics can be classified as medium for the triaryl phosphate esters to good for the trialkyl phosphate esters. The trialkyl phosphates have excellent low-temperature properties and specific gravities near unity. The triaryl phosphates, in general, have poorer low-temperature properties and higher specific gravities. The mixed alkyl-aryl compounds are intermediate between the two other groups, as would be expected. Volatility of the phosphate esters is quite low.

The oxidative stability of most phosphate esters is quite good and the thermal stability is excellent at medium temperatures but poorer at higher temperatures. The triaryl phosphates are much better than the trialkyl derivatives in this characteristic. Hydrolytic stability ranges from poor to good. In severe applications, extensive thermal, oxidative, or hydrolytic



(a) $$R{-}O{-}\underset{\displaystyle O{-}R''}{\underset{|}{\overset{\overset{\displaystyle O}{\|}}{P}}}{-}O{-}R'$$

(b) $$Ar{-}O{-}\underset{\displaystyle O{-}Ar''}{\underset{|}{\overset{\overset{\displaystyle O}{\|}}{P}}}{-}OAr'$$

FIGURE 4.—Phosphate esters. (*a*) Trialkyl phosphate. (*b*) Triaryl phosphate.

breakdown of the phosphate esters can form quantities of acidic substances that may corrode metals.

Phosphate esters have excellent chemical solvency properties resulting in ready mixtures with other materials. For this same reason they are also good solvents for certain resins, paints, and elastomers. However, a number of rubber and plastic materials have been found that are compatible with phosphate esters, and practical systems can be easily designed and used.

The two outstanding properties of the phosphate esters are their ability to lubricate moving surfaces and their fire resistance. These two properties have led to widespread use of phosphate esters. They have been used as the sole component or as the major component of synthetic lubricants and hydraulic fluids. They are also widely used in additive amounts in both synthetic lubricants and petroleum oils.

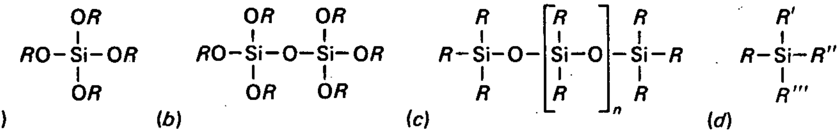
In addition to the phosphate esters, nearly all other possible classes of organophosphorous compounds have been examined for their lubricant and fluid characteristics. Many of these products have found particular application as extreme-pressure (EP) additives and in other places where extremely active lubricating properties are needed. They are most useful because of their ability to react with and form films on metal surfaces.

Silicon-Containing Compounds

One of the more fruitful areas of research in modifying the carbon, hydrogen, and oxygen compounds has been the inclusion of silicon in the molecule. Many types of materials have been made, and three classes will be discussed as lubricants. These are the silicate esters, the silicones, and the silanes (fig. 5).

Silicate Esters and Polysiloxanes

The silicate esters of particular interest are low-molecular-weight orthoesters; i.e., those with four hydrocarbonyl groups attached to the silicate moiety. They have found use as base stocks for wide temperature range fluids and lubricants. They have excellent viscosity-temperature characteristics and good lubricating properties. Silicate esters vary greatly in hydrolytic stability and are generally considered poor in this characteristic. Nevertheless, they have found application because of their unusual combination of viscosity-temperature-volatility characteristics. These


(a)

$$\begin{array}{c} OR \\ | \\ RO-Si-OR \\ | \\ OR \end{array}$$

(b)

$$\begin{array}{c} OR \quad\;\; OR \\ | \qquad\quad | \\ RO-Si-O-Si-OR \\ | \qquad\quad | \\ OR \quad\;\; OR \end{array}$$

(c)

$$\begin{array}{c} R \\ | \\ R-Si-O- \\ | \\ R \end{array}\left[\begin{array}{c} R \\ | \\ Si-O \\ | \\ R \end{array}\right]_n\begin{array}{c} R \\ | \\ -Si-R \\ | \\ R \end{array}$$

(d)

$$\begin{array}{c} R' \\ | \\ R-Si-R'' \\ | \\ R''' \end{array}$$

FIGURE 5.—Silicon-containing compounds. (*a*) Orthosilicate (silicate ester). (*b*) Disiloxane (silicate ester). (*c*) Silicones. (*d*) Silanes.

products have extremely good dielectric properties. They are quite thermally stable, although they are somewhat easily oxidized. Response to antioxidant additives is good.

Closely related to the orthosilicates are the disiloxanes or polysiloxanes. In these compounds a series of silicon atoms alternate with oxygen atoms to form the backbone of the molecule. The hydrocarbonyl groups are attached to the silicon through oxygen. These products have improved viscosity-temperature characteristics compared to the orthosilicate esters. They are similar to the orthosilicate esters in thermal, oxidative, and hydrolytic stability characteristics. These two classes have found use as heat transfer fluids and as high-temperature hydraulic fluids, but have not found much application in uses requiring extensive boundary lubricating ability.

Silicones

The silicone group imparts unique properties to this class of synthetic lubricants. The silicones, properly called siloxane polymers, are made up of repeated silicon-oxygen linkages with substituent hydrocarbonyl groups attached directly to the silicon atoms. The nature of the substituents determine the characteristics of the silicones.

The dimethyl silicones are characterized by low freezing points and probably the best viscosity-temperature properties of any synthetic lubricant. Dimethyl silicones have better thermal and oxidative properties than corresponding hydrocarbons, polyglycols, or aliphatic diesters, but can form gels when permitted to degrade excessively, particularly above 400° F. Stabilization is possible, permitting properly inhibited fluids to be used at temperatures as high as 600° F. The dimethyl silicones are inert to most common plastics, elastomers, and paints, are noncorrosive, and are chemically inert. They have low surface tension and are shear stable.

Their major shortcoming is the lack of steel-on-steel lubricating ability. The fact that silicones are not effective film formers on metal surfaces, especially steel, appears related to their low surface tension, which permits extensive spreading rather than formation of an adherent film. The silicones show relatively weak response to the usual lubricating additives.

Thermal stability of silicone oils can be improved significantly by altering the structure to include aromatic constituents. However, the phenylmethyl silicones have poorer viscosity-temperature properties. Lubricating ability of silicones as well as their receptivity to additives can be improved by the introduction of longer chain alkyl groups (compared to methyl).

Another method of improving the properties of silicones is to incorporate chlorine or fluorine into the molecule. Lubricating ability, particularly in boundary conditions, has been improved using chlorophenyl groups with some decrease in stability and metal compatibility.

The fluorosilicones have been recently made commercially available.

The fluorine is present in the alkyl portion of the molecule. Improved lubricating ability together with a high level of thermal stability, resistance to chemical attack, and fire resistance make them an extremely interesting class of fluids.

Overall, the silicones have found many applications as fluids and lubricants where their desirable and unique characteristics give excellent cost-to-performance ratios.

Silanes

The silanes are compounds that contain only carbon-silicon bonds. Tetraalkyl, tetraaryl, and mixed alkyl-aryl figurations have been prepared. These products possess wide liquid ranges and thermal stabilities up to 700° F but are poor lubricants for sliding surfaces. Thus far they have not shown enough promise over other classes to receive continuing attention.

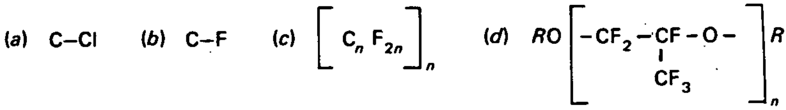
Halogen-Containing Compounds

The incorporation of halogen atoms into organic molecules has been widely studied as a way of modifying properties. The two most commonly used halogens have been chlorine and fluorine in studies on potential lubricants (fig. 6). Some bromine compounds have been made, particularly in efforts to obtain very-high-density products.

In general, the inclusion of the halogens results in higher densities and reduced flammability compared to the parent compound. Chlorine tends to increase pour point and viscosity. Fluorine has little influence on the pour point or viscosity. However, it greatly decreases surface tension.

Chlorine-aliphatic carbon bonds are generally weak, and therefore chlorinated aliphatic compounds have found little use as synthetic lubricants, per se. They have found use in lubricants as additives to provide a source of chlorine that can be reacted with the surface to improve boundary lubrication.

Fluorine-containing aromatic and aliphatic materials are difficult to prepare, and fluorine has found most application in fluorocarbons and halocarbons, which will be discussed later. Stable fluoroaliphatic and fluoroaromatic compounds can be obtained with proper selection of structure. These materials have not found particular application as lubricants because on a price-to-performance basis, the desired properties can better be obtained by other methods. However, the usefulness of certain fluorine-containing compounds has already been recognized, and fluorine substitu-



(a) $C{-}Cl$ (b) $C{-}F$ (c) $\left[C_nF_{2n}\right]_n$ (d) $RO\left[-CF_2-\underset{\displaystyle CF_3}{\underset{|}{C}F}-O-\right]_n R''$

FIGURE 6.—Halogen-containing compounds. (a) Chlorine-containing compound. (b) Fluorine-containing compound. (c) Fluorocarbons. (d) Perfluoropolyglycols.

tion for hydrogen should be remembered as a useful tool for future research.

Halogenated Polyaryls

The chlorine-containing biphenyls and polyphenyls have found some use as lubricants. These products range from mobile liquids to tacky solids. They exhibit marked change of viscosity with temperature, and uses are somewhat limited because of the poor viscosity-temperature characteristics. Because of their aromatic structure, resistance to thermal breakdown and oxidation is good to temperatures approaching 600° F. They have found use as lubricant base stocks, heat transfer agents, industrial lubricants, and additives. However, some of these uses may be prohibited because of potential environmental problems.

Fluorocarbons

Fluorocarbons are compounds containing only fluorine and carbon. Such compounds have been made and proposed as synthetic lubricant base stocks. In general, they are thermally and oxidatively stable and have physical properties quite similar to those of the corresponding hydrocarbons, except for higher density and lower surface tension. They have a tendency to creep over surfaces but do not appear to wet them in terms of boundary lubrication. Such compounds are particularly useful because of their extreme chemical inertness. These compounds are resistant to ignition by any source and represent some of the most fire-resistant organic compounds known.

Recent studies have been concentrated on the tetrafluoroethylene polymers. These have been used as liquid oxygen-resistant fluids, lubricants, and greases.

Although not strictly fluorocarbons, the chlorotrifluoroethylene polymers are listed here. They have found some applications and are better lubricants because the reactivity of chlorine toward metals is greater than that of fluorine. These materials generally have similar properties to the fluorocarbons but are significantly less stable.

Perfluoropolyglycols

The perfluoropolyglycols are polyalkyleneglycols in which all of the hydrogens have been substituted by fluorines. These types of products derived from propylene oxide have recently become available and are under consideration for a number of applications. Their primary advantages are high thermal stability, extreme fire resistance, relatively good liquid range, and moderate lubricating characteristics. However, they lack stability in the presence of certain commonly used high-temperature metals, have high specific gravities, and do not respond to common additives. Studies are underway to improve performance in these areas.

Miscellaneous Compounds

The chemical classes mentioned above include those that provide the majority of the synthetic lubricant base stocks in use today. However, it does not include all the promising classes nor those that have been previously studied.

For example, one of the most desired properties in lubricants is thermal stability. Based upon the work done thus far, polyaromatic structures are the most stable to heat. Therefore other cyclic structures are being studied. These include pyrazines, triazines, triphosphonitrilates, and others.

It is impossible in a review of this magnitude to give complete references to the literature. It is therefore suggested that those interested in synthetic lubricants read the general reviews and spend some time discussing his particular problems with those experienced in the field. It is amazing how often a chance remark during a recital of previous experiences has led to the solution of a particular problem.

CONCLUSIONS

This brief review has discussed a number of chemical classes that have found application as synthetic lubricants and has attempted to qualitatively rate the materials on properties that are important in performance. These general ratings can serve as a guide to selection of a chemical class for further study. The importance of the availability of a wide range of chemical structures and properties to research cannot be overemphasized.

The synthetic oils have very practical aspects. Many items of machinery now operate satisfactorily that would be unable to function if their only source of lubricant was petroleum oil. Further, synthetic oils have improved performance of equipment, making them more economical and productive. Synthetic oils in general cost more per unit volume than the petroleum oils they replace. However, the real value of the lubricant must be calculated on a price-to-performance basis.

These types of consideration have made the synthetic oils an integral part of modern lubrication practices.

DISCUSSIONS

P. M. Blanchard (British Petroleum Co., Sunbury-on-Thames, England)

The comprehensive yet succinct nature of Dr. Hatton's paper leaves little to be discussed, but there are some points worth reinforcing and others that may be further illustrated by examples.

Dr. Hatton has rightly pointed out that the most common error made by prospective users of synthetic fluids is to expect that when attaining improvements in performance in one direction, other properties remain unchanged. As an example, in obtaining maximum thermal stability from a synthetic fluid, the viscosity-temperature properties may be impaired.

For instance, polyol esters have improved thermal stability but poorer viscosity-temperature characteristics, particularly at low temperatures. than the dibasic acid esters of monohydric alcohols. On the other hand, attempts have been made to improve the low-temperature fluidity of polyphenyl ethers by introducing alkyl substituents in the parent molecule resulting in a reduction in thermal stability. The effects of substitution of chlorine into polyphenyls upon thermal stability are similar, although the intention in this case is to obtain a degree of fire resistance. Table 3 in the paper under discussion illustrates these points.

There are, of course, applications for which a specific mode of decomposition of a fluid may be a desirable feature. One such instance is that alluded to in the paper in the section concerning polyglycols where the tendency of these fluids to decompose thermally or oxidatively into volatile products is mentioned. This is an attractive feature for air compressors where the accumulation of carbonaceous deposits are undesirable or even dangerous, but consideration must be given to the end use of the compressed air containing the volatile products in case the latter constitute a hazard. It should be noted that under appropriate conditions, polybutenes can also decompose leaving no residue.

The essential objective in choosing a fluid is to insure that it gives adequate performance and is compatible with the physical and chemical environment in the equipment concerned. This is well illustrated in the survey presented here. Improvements in performance in different directions can, as indicated, be obtained by suitable additive treatments, but care has to be exercised in the choice of additive lest benefits in one area are counterbalanced by increased difficulties elsewhere. A case in point concerns the improvement of the rust-inhibiting properties of phosphate ester hydraulic fluids. A variety of rust- or corrosion-inhibiting compounds are available for this purpose, but while many are effective, the acidic materials can also have the effect of apparently catalyzing hydrolytic decomposition. Similar effects are observed with esters and while the access of water, a necessary ingredient for hydrolysis, can be minimized or prevented in service, even small amounts can cause deterioration in storage and shorten the shelf life of the blended products. Likewise, care must be taken in the choice of antioxidants for fluids that do not produce deposits or insolubles by oxidation when uninhibited, since the rate of filter and oilway blocking in a recirculating system can be the factor that determines oil drain periods or time between overhauls.

The quality of a synthetic lubricant can be substantially modified either for better or worse by the processing route adopted for production of the fluid. The wrong choice of catalyst during esterification can lead to increased deposition tendencies from esters in service. It has been suspected that traces of catalyst have assisted in raising the load-carrying ability of some ester base oils that in other respects appeared identical with esters of inferior load-carrying ability. It is also well known that careful attention to finishing treatments can markedly improve the hydrolytic and storage stability of triaryl phosphates, for example.

One further aspect of synthetic fluids deserves consideration. By appropriate choice of starting materials or reaction conditions, it is possible to produce fluids that show high resistance to degradation whether by burning, hydrolysis, or thermal cracking. However, no fluid has an infinite life, and sooner or later the lubricant must either be reclaimed or sent away for disposal. Obviously it may be economic to reclaim very expensive fluids, but from the beginning of the development of a fluid it would be wise to consider the ultimate fate of the oil lest an unwanted, indestructible compound remains.

The final point, which is implicit in all that Dr. Hatton has said, is that the lubricant is an engineering material and should be considered as an integral part of the equipment. It is therefore advisable for the designers, engineers, and lubricant specialists to work together from as early a period as possible in the history of a project. This insures that the full potential of the selected fluid can be realized and possible problems identified at an early stage of development.

H. Ravner (Naval Research Laboratory, Washington, D.C.)

To prepare a meaningful report on synthetic lubricants is at best a difficult assignment. To accomplish this in less than a booklength review would appear to be almost impossible. Within the constraints of space limitations, however, Dr. Hatton has written a most useful discussion of the subject. Because by necessity the chemistry of synthetic lubricants is not dealt with in depth, the paper is primarily directed to nonchemists associated with programs or problems in which lubricant performance has high priority. The paper aims to strike a reasonable balance between presenting applications for diverse classes of synthetic lubricants and indicating some of their limitations. In this context, it is important to understand that modern engineering technology is now sufficiently far advanced that it can in some instances place limits on the performance of even these carefully designed lubricants. One may consider the case of aircraft engine lubricants as an example.

Zisman and his coworkers (refs. 12 and 13) during and after World War II pioneered in studies leading to the first large-scale use of synthetic aliphatic diester lubricants as instrument and aircraft gas turbine oils. They concluded that such lubricants, essentially pure compounds, could be tailor made to provide specific properties, e.g., good viscosity-temperature properties, low volatility, etc., and that other desired properties such as oxidation stability, lubricity, corrosion inhibition, etc., could be imparted by additives. This early judgment is still generally valid, as Dr. Hatton points out. However, while diesters in the 1950's adequately lubricated engines with bulk oil temperatures of about 275° F, they are now generally replaced with neopentyl polyol esters stable to 325° or 350° F, with intermittent exposure to hot spots of 600° to 700° F. Candidate fluids (polyphenyl ethers, perfluorinated compounds, triazines, etc.) for possible future high-Mach-number engines where bulk oil temperatures may be of the order of 700° F, and with hot spots several hundred degrees higher, represent about the ultimate we can expect from liquid lubricants. Even in these systems, operating with these very stable lubricants, secondary reactions among the additives, base stocks, degradation products, and materials of construction will undoubtedly create problems of major magnitude. If operating temperatures are further increased, we approach the point where ordinary chemical bonds are thermally ruptured. Thus, barring engineering breakthroughs or major design compromises, there is in sight an effective limit to the power output of very-high-performance turbine engines, that limit being the stability of the lubricant.

The above example is, of course, not intended to minimize the versatility and effectiveness of synthetic lubricants; their superior performances in countless applications as outlined by Dr. Hatton speak for themselves. It is rather intended to point out to design engineers that close cooperation with knowledgeable chemists should be the rule when mechanisms for operation under stringent conditions are being planned.

T. Salomon (OMER, Israel)

Correlation Between Structure and Properties.—Dr. Hatton's paper does not sufficiently underline the correlation between structure and properties of synthetic lubricants, as this aspect is limited mostly to thermal stability. It is quite possible to establish a correlation between the structure of a synthetic lubricant and its physical and physicochemical properties, such as resistance to oxidation and corrosion, as long as these properties are not governed by the additive blended with the base oil.

It is impossible to treat in this discussion the whole aspect of the problem; however, it may be sufficient to state that the general properties of even a complex molecule may be deduced from the properties of its links and functional groups.

In a homologous series, a higher degree of symmetry results in higher melting points and lower liquid ranges, as well as higher thermal and oxidative stabilities. This is illustrated in figure 7 for the most simple case of homologous series starting with methane and ending with neopentane. Whereas the boiling point increases rather regularly with the molecular weight, the variations in the melting point are quite irregular; a big increase is noted when going from isobutane to neopentane. Methane and neopentane have the smallest liquid range, whereas the intermediate members of the series have a much larger one; the largest liquid range is

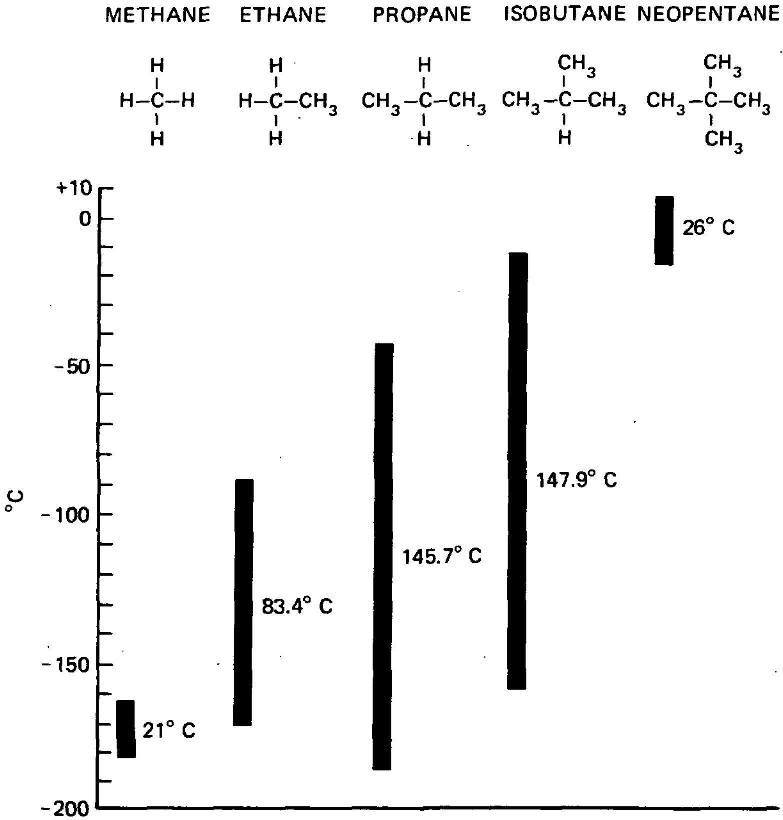


FIGURE 7.—Liquid range of symmetrical and asymmetrical molecules.

found for isobutane. The liquid range considered here is the theoretical one; i.e., the gap between melting point and boiling point.

When comparing the structures of the members of the series, we note that the smallest liquid range corresponds to a quite symmetrical molecule, like methane and neopentane, and the largest liquid range corresponds to the most asymmetrical molecule of isobutane. We can therefore introduce the following criteria for the selection of a type of synthetic lubricant. First, for a very high chemical stability, a quite symmetrical structure is needed. We have, however, to consider as limiting factors the high melting point and the narrow liquid range. Or, for a low melting point and a large liquid range, we need a compound with a quite asymmetrical structure, where the limiting factors will be the much lower thermal and oxidative stabilities. Between these two extreme cases, many compromises are possible according to the main properties involved.

The properties of a synthetic lubricant are governed by the nature of the individual groups of the molecule and by their position inside the molecule. Generally speaking, these individual groups maintain their specific properties inside the large molecular edifice, and it becomes possible to conceive a molecule with well-defined properties, built up with appropriate groups in the same way as we build a machine, to foresee the general properties of a lubricating oil when the morphology of their constituents is known.

Each lubricant has its advantages and drawbacks. It is therefore impossible to conceive of an ideal lubricant without any drawbacks. We have to do research in each case to obtain a molecular structure with the optimal balance between the required good properties and the limitations imposed by the drawbacks. Such an optimal balance of the properties has to be based on the requirements of the machine, which should be classified according to their importance for the application considered. This is called the hierarchy of the properties of a lubricant required by a machine. On the top of the list we have the essential requirements that have to be completely fulfilled. At the end of it we have the complementary requirements whose fulfillment may be an asset for the lubricant.

The discussion between the machine designer and the lubricant supplier should hence be limited to a confrontation between the hierarchy of the properties asked by the machine and those which are provided by the lubricant available. In the most general cases the essential property is the rheology of the lubricant, especially the correlation between viscosity and volatility, coupled with its compatibility with the metals involved. In other cases, we may require an essential property such as chemical stability for applications at high temperatures, special requirements for the viscosity at the lowest operating temperature for applications at low temperatures, sufficient resistance to combustion for applications including the hazard of fire, and sufficient resistance to hydrolysis for applications in the presence of water. This is the method followed by the engineer for all other materials used to build up his machine. If he applies such a hierarchy of properties for the metals used, why not apply it for the lubricant, which is also a construction material for the machine?

Problems Raised With Synthetic Base Oils.—The performance characteristics of synthetic oils are determined by the quality of the base oil used and by the properties of the additives incorporated into the oil. The performance tests, however, apply always to the finished oil. All the specifications established deal only with the finished oil, whereas no specification deals with the base oil used. It is left entirely to the oil supplier to prepare the blend of additives and base oil that will meet the requirements of the specification. However, it is well known that the oxidation stability and the corrosive activity of the finished oil depends also on the presence of minute amounts of chemical impurities in the base oil. The deleterious effect of these trace impurities cannot be always offset by the additives used.

An example is the presence of a trace of aldehyde compounds in the base oil. The lack of adequate specification governing this aspect may explain some drawbacks observed in actual operation in the United States with commercial products that were qualified to the specification. It is a well-known fact that many commercial synthetic base oils are not prepared for use as a lubricant. It is a commercial product having many other and much more important industrial applications in other fields, where the requirements in chemical stability are much less important. For instance, diesters are mainly used as plasticizers. Since the consumption of the product as synthetic lubricant is very small in comparison to its intended use as a plasticizer, the chemical industry is not interested in preparing a special grade of this product for lubrication purposes. The purity of the base oils received from the supplier may vary in some categories. This situation does not exist in some other countries, as in France. There, the producer of synthetic lubricants for aviation use re-treats the base oil received from the chemical industry to eliminate the impurities present (according to its own specifications, which are not official ones) before blending the oil with the additives.

The chemical impurities in the base oil are usually eliminated by chemical treatment. We have found that trace compounds, especially aldehydes, which impair the resistance to oxidation and corrosion of the base oil, are completely eliminated by a single passage over ion exchangers. As the nature of the impurities may vary from case to case, a complete treatment is applied with anionic and cationic ion exchangers, followed by a passage through a mixed bed of the two reagents.

The lack of a quality specification for synthetic base oils is restraining the development and the use of synthetic oils as much as their high price. The quality control of the base oil does not involve the same high-level performance tests as that of the finished oil. The performance characteristics pertaining to the finished oil require the presence of additives. However, the quality control of the base oil can be performed by an appropriate oxidation-corrosion stability test at low temperature, e.g., 115° C, as the main scope of this test is to insure the absence of trace impurities, which may impair the resistance to oxidation and corrosion, as well as its thermal stability. A thermal stability test may also be useful, as this property depends only on the structure of the base oil when trace impurities are absent. This property cannot be improved by additives.

It is well known that the resistance to oxidation corrosion at high temperatures depends on two main parameters: the thermal stability of the base oil, and the oxidation-corrosion stability of the finished oil. Blending with appropriate additives may enhance this property, but will not suppress the increased chemical instability when trace amounts of chemical impurities are present. This fact is well known to the refiners of mineral base oils, but has not yet been considered in the case of synthetic base oils.

Semisynthetic Oils.—A new application of synthetic base oils as a component of mineral oils for engines has been studied in Europe, especially in West Germany, for the last 10 years. It has already found a limited application as engine oils in overloaded diesel engines. This mixture of synthetic and mineral oils is called semisynthetic oils. As most of the work related to this subject is done and published only in German, it may be of interest to present a more detailed survey of the present status of this field. This survey is limited to one fundamental aspect of the problem, i.e., the effect produced when adding a synthetic oil to a mineral one, and to the properties of the synthetic base oils used. The composition of the finished oil and the test results obtained in the engines are not treated here in detail. However, the papers dealing with these subjects are given in references 14 to 18.

The development of engines running at higher speeds under high loads, i.e., at much higher temperatures, requires improving the quality of the mineral base oil stocks available with respect to their resistance at higher temperatures without impairing the good rheological properties at low temperatures. This applies more to oils used in diesel engines. The solution adopted to improve the low-temperature properties, when using multigrade oils, is no more convenient, as the low-viscosity base oil used lacks stability at high temperatures (characterized by high evaporation losses). The use of higher viscosity base oils with improved thermal stability is not the right economic solution; it is difficult to realize a mineral oil with sufficiently high stability at these higher temperatures, i.e., sufficiently low evaporation losses as well as sufficiently low viscosity at the lowest operating temperatures admitted.

German scientists, such as Pauer, Zorn, and their collaborators, came to another and better solution when investigating the addition of synthetic base oils to the mineral base oil (refs. 15, 16, and 19). They started from a high-viscosity mineral base oil like SAE 30 and added a limited amount (15 to 30 percent) of a low-viscosity synthetic oil to reduce the viscosity of the mixture especially at low temperatures. A limited amount of a shear-stable viscosity index (V.I.) improver is added to restore the viscosity level at high temperatures without impairing the low-temperature properties. The light mineral oil used as solvent for the polymeric V.I. improver is replaced here by the synthetic oil used as the component of the semisynthetic oil mixture (ref. 18).

Two main parameters have to be considered when choosing the constituents of the semisynthetic oils: the rheological properties at high and low temperatures and high shear stability. In this manner, the oil attains a sufficiently high viscosity at high temperature, a sufficiently low evaporation loss at this temperature, a sufficiently good resistance to heat (thermal stability), a sufficiently low viscosity at low temperature to insure easy starting of the engine, and no significant changes in the oil properties after shearing at high shear rates or stresses.

The synthetic oil that should be used must be completely miscible in the mineral oil; have low viscosity, but high V.I.; have evaporation losses that are lower than those of the mineral oil; have stability that is higher than that of the present SAE 20 or 30 grade mineral oils; and be sufficiently low priced. The aliphatic diesters, as a class, best fulfill all these conditions. However, some types of diesters like the classical products, adipates or sebacates, have to be excluded because of their higher volatility.

In West Germany the tendency of an oil to evaporate at high temperatures is controlled by the so-called Noack test, according to DIN 51581, January 1958. The oil is heated at 250° C for 1 hour. The oil vapors are eliminated by an airstream produced by a constant depression of 20-mm waterhead. The weight loss in oil is the evaporation loss of the oil or the Noack number expressed in percent w/w. There is no direct correlation between the results of this test and American Society for Testing and Materials (ASTM) tests, like D 972, operating at much lower temperature (100° to 150° C). Some examples are given in table 6. As a matter of fact, according to German practice, low volatile oils have a Noack number of less than 15 percent.

At present, three types of oils are commercially available at a sufficiently low price: trimethyl adipic ester, decane dicarboxylic ester, and heptadecane dicarboxylic ester. The last one with a branched ester group is more expensive and not yet used on a similar scale. These oils have also the

TABLE 6.—*Some Characteristics of Various Types of Lubricating Oils*

[Ref. 14]

Property	Solvent refined, dewaxed	Hydrocrack, dewaxed	Polyolefins	Diester
Viscosity/210° F, centistokes	5.4	7.3	4.25	3.25
V.I. extended	~100	≤130	125	~150
Evaporation losses, ASTM D 972, percent w/w	2.8	.7	2.5	3.5
Pour point, °C	~−15	~−15	<−60	<−70
Hydrolysis (7 hr, 150° C, 20 percent water) ΔT.A.N. (mg KOH/g)	<.05	<.05	<.05	.26
Swelling of perbunane (100 hr, 130° C):				
Change in volume, percent	−.5	−2.5	−1	16.8
Change in hardness (° Sh.)	3	3	3	−14

advantage of a much higher load-carrying capacity than a mineral oil of similar viscosity (ref. 18).

Trimethyl 2,2,4-Adipic Acid.—This ester is produced by VEBA according to the isophorone process Hibernia-Scholven. The starting material is acetone. The manufacturing steps are as follows.

(1) Cyclic condensation of acetone into isophorone at 205° C under a pressure of 16 bars in an alkaline medium.
(2) Hydrogenation of isophorone into 2,2,4-trimethyl cyclohexanol at 180° C under a pressure of 101 bars with nickel as catalyst.
(3) Oxidation of 2,2,4-trimethyl cyclohexanol into 2,2,4-trimethyl adipic acid with HNO_3 (65 percent) under ambient pressure at 60° to 70° C.

The final product is purified by recrystallization. The commercial product is a mixture of the 2,2,4 and 2,4,4 isomers. The esterification occurs in the usual way.

Decane Dicarboxylic Acid.—This ester is produced by Chemische Werke Huels. The starting material is butadiene. The manufacturing steps are as follows.

(1) Polymerization of butadiene into 1,5,9-cyclododecatriene (Ziegler-Natta catalyst).
(2) Hydrogenation into cyclododecane.
(3) Oxidation by air to obtain a mixture of a cycloalcohol (cyclododecanol) and a cyclic aldehyde (cyclododecanal).
(4) Oxidation with nitric acid to decane dicarboxylic acid.

The esterification occurs in the usual way.

Heptadecane Dicarboxylic Acid.—This ester is produced by BASF. The starting material is oleic acid. Two processes may be applied.

(1) The OXO synthesis to fix $CO+H_2$ on the double bond with formation of an aldehyde acid, which is then oxidized into a diacid.
(2) The modified Koch synthesis (refs. 20 and 21) fixing $CO+H_2O$ on on the double bond in the presence of an acid catalyst, like sulfuric acid or hydrated BF_3, at low temperature and relatively low pressure.

The esterification occurs in the usual way.

Some Properties of the Commercially Available Esters.—The main properties of four commercially available esters are grouped in table 7. Table 8 gives some more detailed characteristics of the 2,2,4(2,4,4) trimethyl adipic octyldecyl ester, dealing also with the mechanical properties, the resistance to lead corrosion, the hydrolysis stability at high temperatures, and the oxidation-corrosion characteristics according to MIL–L–7808. Table 9

TABLE 7.—*Some Characteristics of Diesters Used for the Manufacture of Semisynthetic Engine Oils*

Diester composition	Viscosity at 210° F, cs	V.I. extended	Evaporation losses, percent (Noack number)	Pour point, °C
VEBA TMA-OD ester: 2,2,4-trimethyl adipic n-C_8 and n-C_{10} ester	3.38	148	12	−71
VEBA TMA-DD ester: 2,2,4-trimethyl adipic n-C_{10} and n-C_{12} ester	3.94	154	5.2	−45
Huels Vestinol: Decane dicarboxylic di(2-ethylhexyl)ester	3.8	158	12	−50
BASF Glissovis: Heptadecane dicarboxylic di(n-butyl) ester	3.64	150	11	−50

TABLE 8.—*Some More Detailed Characteristics of VEBA Ester (2,2,4(2,4,4)-Trimethyl Adipic* n-*octyl,* n-*decyl Ester)*

Typical composition:	
TMA OD ester (percent)	96.4
Ester of acids with shorter chains (percent)	3.6

Initial boiling point (°C) at—	
0.1 mm Hg	134
1 mm Hg	191
Vapor tension (mm Hg) at—	
150° C	0.19
180° C	.65
200° C	1.5
Density at 20° C	0.906
Viscosity (DIN 53 015, falling ball) (cP) at—	
−40° C	1.376
−20° C	220
20° C	22.6
50° C	8.49
Viscosity (DIN 51 562) (cs) at—	
−17.8° C	209
37.8° C	13.14
98.9° C	3.38

TABLE 8.—*Some More Detailed Characteristics of VEBA Ester (2,2,4(2,4,4)-Trimethyl Adipic* n-*octyl,* n-*decyl Ester)*—Continued

V.I. extended (ASTM D 2270 B)	149
ASTM color (ASTM D 1550)	1
Acidity (ASTM D 664), mg KOH/g	0.05
Congealing point (DIN 51 583) (°C)	−71
Flashpoint (DIN 51 584) (°C)	223
Evaporation losses (Noack number, DIN 51 581) (percent w/w)	12
Refractive index, n_D^{25}	1.4469
Surface tension at 20° C (dyne/cm)	32.1
Solubility at 20° C:	
Water in ester (percent)	.14
Ester in water (percent)	<.01
Mechanical properties of the pure ester (without additives):	
Almen-Wieland test:	
Load-carrying capacity (pure mineral oil)	$1200K_p = 12.000N$ $(\sim 300K_p) = (3.000N)$
Friction force	$235K_p = 2.350N$
Coefficient of friction	0.196
Oil temperature (°C)	75
Bearing temperature (°C)	140
Wear (mm)	-3.8×10^{-2}
Chemical tests:	

Lead corrosion (FTM 5321.1.) (mg/m²): Ester+0.5 percent phenothiazine

Limiting value MIL–L–7808G	After 1 hr	
	163° C	204° C
<6	−0.1	−0.1

Resistance to hydrolysis (mg KOH/g), 20 hr, at 180° C, autoclave with agitation: Mixture of 60 percent w/w ester, without additive, and 40 percent w/w water

Acidity		Percent ester destroyed
Before	After	
<0.05	2.5	0.97

Oxidation-corrosion test MIL–L–7808G (72 hr; 175° C; air, 5 liters/hr): Ester+0.5 percent phenothiazine

TABLE 8.—*Some More Detailed Characteristics of VEBA Ester (2,2,4(2,4,4)-Trimethyl Adipic* n-*octyl,* n-*decyl Ester)*—Concluded

Measurement	Limiting value according to specification	Experimental result
Metal:		
Copper	±0.4	−0.0639
Aluminum	±.2	−.0220
Magnesium	±.2	−.0425
Steel	±.2	−.0075
Steel, cadmium plated	±.2	−.0073
Change in viscosity at 37.8° C (percent)	−5 to +15	1.75
Change in V.I.		−2.1
Increase of T.A.N.	2	.67
Change in flashpoint (°C)		20
Material loss (percent)		.16

TABLE 9.—*Characteristics of BASF Glissovis Ester (Heptadecane Dicarboxylic Di-*n-*Butyl Ester)*

Viscosity (cs) at—	
98.9° C	3.45
37.8° C	13.42
−17.8° C	183
−40° C	1.700
V.I.	155
Congealing point (°C)	−53
Flashpoint (°C)	~250
Evaporation losses (Noack number) (percent)	11
Density at 20° C (g/cm^3)	.907
Neutralization number (mg KOH/g)	<.1
Refractive index, n_D^{20}	1.4490
Boiling point (°C) at 0.7 mm Hg	~208 to 210

reproduces the mean characteristics of the BASF Glissovis, a di-*n*-butyl ester of the heptadecane dicarboxylic acid.

Military Specification for Semisynthetic Engine Oils.—The West German Army has issued a specification for semisynthetic oils: VTL 9150.063, edition 2, May 1969, dealing with two types of products: 0235 (an SAE 5W–20 oil) and 0236 (an SAE 10W–30 oil). Whereas this specification asks more for excellent low-temperature properties than for high-temperature properties, MIL–L–46152, which is the first U.S. military specification admitting semisynthetic oils, asks also for better high-temperature properties.

The Present Situation.—To define the present situation in this field, we reproduce a statement of A. Schilling, the well-known French specialist in the field of engine oils and engine lubrication, published in 1970 (ref. 22):

> If the cost of synthetic oils becomes competitive, the new operating conditions of the gasoline engines using gasoline without lead may facilitate the use of these oils. As a matter of fact, the lower detergency and the lower protection against corrosion needed, the better behavior at high temperatures, the higher viscosity index of the base oil, the limitation of deposits, the operation at very low or very high ambient temperatures, are all factors which favor not only the use of synthetic oils, but also that of hydro-refined oils of better quality. Finally, it is quite possible that synthetic oils or hydro-refined oils with a better restructured molecule may produce less reactive compounds in the exhaust gases than the present mineral oils, especially if the future controls will include the unburned lubricating oil.

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The isoteniscopic method for evaluating decomposition temperature must be confined to study of pure compounds. With very few exceptions, lubricants, natural or synthetic, do not fit this definition. The maximum temperature for thermal decomposition listed in tables 3 and 4 are too high by about 150° F, at least for those fluids within my sphere of knowledge, unless Dr. Hatton does not include thermal molecular rearrangement in his decomposition definition.

LECTURER'S CLOSURE

The author wishes to thank each of the discussers for their kind comments on his paper. Many of the points raised emphasize and illustrate the complexities of synthetic lubricants and the need to consider each chemical class in detail after the basic selection is made. The necessity of cooperation between machine designers and lubricant specialists early in a project is certainly the key to successful total performance.

The importance of the quality of base stock to performance of the synthetic lubricant was covered in several of the discussions, and I agree with their conclusions. Many application problems have been traced back to minor composition variations in base stocks or additives. These variations can involve method of manufacture, quality of raw materials, efficiency of purification techniques, lack of specifications and sufficiently sensitive analytical techniques, and other problems.

Mr. Blanchard raises the questions of reclaiming and disposal of synthetic fluids. This very important area has been largely neglected until recently. Certainly everyone concerned must make special efforts to assess the problems and provide suitable means of handling them. Environmental and economic factors are both involved. The suppliers and users of synthetic fluids have done an excellent job of providing toxicological and handling information. This must now be extended to include disposal and potential pollution data. Reclamation has been successfully practiced with some synthetic lubricants and has ranged from simple filtration to complete cleanup and restoration of additives. I believe that reclamation will increase and that techniques will develop that can restore the lubricant to as-new or better condition.

Mr. Ravner and Professor Salomon discuss the importance of organic esters as our most broadly used synthetic lubricant class. Their examples are valuable in demonstrating some of the technology that is required to make good lubricants after a chemical class is selected as base stock.

Dr. Brown indicates that the isoteniscope is best suited to the study of pure compounds and I agree. It is true that the maximum temperature for use of the lubricant will be lower than the value obtained by isoteniscope measurements. The amount of decrease will depend on product purity, formulation, use conditions, environment, and other factors.

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Greases

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Current state of the art, areas for further study, and future trends in the industry are reviewed. Aspects covered are definition of grease, why and when greases are used, components, types, applications, and methods of evaluation.

DEFINITION AND COMPONENTS

WHAT IS A LUBRICATING GREASE? It can be described in several ways: Webster's Third New International Dictionary defines a grease as a thick lubricant (as a petroleum oil thickened with a metallic soap) <axle> (silicone).

A patent attorney may describe a grease as—

> a composition of matter composed essentially of a fluid having lubricating ability such as (*a*) a mineral or petroleum oil of natural origin refined by procedures required to impart the desired properties, (*b*) synthetic fluids such as an ester formed by the reaction of an alcohol and acid, both of suitable types and chain lengths, (*c*) a polyorganosiloxane obtained by hydrolysis and polymerization of a suitable chlorosilane, or (*d*) a fluorinated hydrocarbon combined with a material such as a metallic soap of a triglyceride or a fatty acid having between about 12 and 22 C atoms, said metal being selected from the group consisting of alkali metals and alkaline earth metals and said soap being present in an amount sufficient to impart the desired thickening action. In lieu of metal soaps, materials such as a silica, a carbon black or an organophilic bentonite, may be used.

Other material—ad infinitum.

The definition generally accepted is as follows: "A solid to semifluid product of a dispersion of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may be included" (ref. 1).

Lubricating grease structure, as defined by the National Lubricating Grease Institute (NLGI), is the physical arrangement of the component particles of a lubricating grease thickener, additives, and liquid lubricant. It is the nature and stability of this arrangement that determine the appearance, texture, and physical properties. Grease structure may also be thought of as an oil-bearing sand or shale that releases the fluid component

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only under certain conditions of temperature, pressure, or other mechanical or chemical forces.

The relatively few people who have given any thought as to the possible composition of a grease may decide that a grease is an oil thickened with wax, asphalt, graphite, asbestos, or some similar material. In rather rare cases, they may be entirely correct. The majority of greases, however, consist essentially of petroleum oils or synthetic oils thickened with metallic salts or soaps formed by the reaction of basic metallic oxides or hydroxides with various fatty materials such as tallow or the fatty acids, inorganic thickeners such as silica, carbon black, or clay complexes such as the bentones, or any one or combination of a wide variety of materials. The sodium salt of 5,5-diphenylhydantoin, or dilantin, an antiepileptic drug, is one exotic material that was used as a thickener for a high-temperature grease.

The theories advanced as to the explanation of grease structures are numerous, varied, and complex. In general, it may be stated that the ordinary greases consist of two phases, the fluid phase having adequate lubricating properties and a thickener, both very complex in nature. A picture of a combination of the two phases can be visualized by comparing the thickener phase to a sponge having microscopic pores in which the oil is absorbed. The comparison is probably not too inaccurate because similar structures are referred to as micelle structures or space lattices.

BASIC COMPONENTS OF GREASES

Fluid Phase

Fluids used currently in descending order of volume are petroleum oils, synthetic esters, silicones, polyphenyl ethers, and fluorosilicones. In all probability, over 99 percent of the fluids used are of the petroleum type. Synthetic esters probably comprise the major slice of the remaining 1 percent.

Selection of both the fluid and thickener components depends on the applications in which the grease is to be used; the temperatures, pressures, and speeds to which they are exposed; and the service life required in any specific end use.

Petroleum Oils

When one realizes that petroleum oils are considered as being mixtures of naphthenic, aliphatic, and aromatic hydrocarbons; that they also usually contain relatively small quantities of nitrogen or sulfur components; and that the number of carbon atoms in the chain, depending on constituents, may range from about 5 to 70, it is quite evident that the oil phase itself can be quite complicated.

Properties of petroleum oils used in grease production depend on the crudes from which they are derived and the type or types of refining processes to which they are subjected. Greases have been and are made from oils derived from many crudes and refined by many different processes. The less highly refined oils and the more naphthenic type are the most widely used and are more adaptable to grease compounding. In general, those in the viscosity range of about 300 to 800 SUS at 100° F are easier to compound with than the higher viscosity oils. Greases containing oils of both lower and higher viscosities, however, are quite common.

A common classification system for lube oils is based on viscosity index (V.I.). Characteristics of some of the petroleum oils used for greases are given in table 1.

Either individual oil of the types shown or blends of any two or more of the various types or viscosities are commonly used to obtain the desired grease characteristics. It is obvious that the petroleum oil phase of a grease can be complex.

Synthetic Oils

World War II, because of its global nature, emphasized dramatically the need for lubricants operable at temperature ranges beyond those possible with petroleum base lubricants. Primary requirements for one of the first military greases of the new breed were a bearing performance life of 1000-hr minimum at 250° F, low evaporation, low torque, and low apparent viscosity at −67° F. Petroleum oils that would meet both ends of the temperature scale were not available.

Dibasic acid esters such as di-2-ethylhexyl sebacate, di-2-ethylhexyl azelate, and diisooctyl azelate were developed by several chemical companies to fulfill this need. Greases compounded from these esters exhibited excellent low-temperature properties, good lubricity, and low evaporation rates at moderate temperatures. Top temperature range for greases compounded with these diesters is about 275° F.

Characteristics of several of the diester-type fluids and petroleum oils, of about the same viscosities, are given in table 2.

It is evident that the characteristics of the diester-type fluids are more suitable for low-temperature applications than are petroleum oils.

In the postwar years, the rapid advance of aircraft and space equipment dictated the need for lubricants operable for moderate to long periods at temperatures between 400° to 600° F. It was hoped initially that fluids possessing suitable low-temperature properties would also function at the higher temperatures. This hope was short lived, because the volatility, viscosity, and stability (both thermal and oxidative) of those fluids required for high-temperature operation were, in most cases, in direct contrast to those needed for use at low temperatures.

The search for fluids satisfactory for high-temperature operation covered evaluation of conventional and highly refined hydrogenated petroleum oils, esters, silicates, silicones, ferrocenes, silphenylenes, phosphorized, sul-

TABLE 1.—*Petroleum Oil Characteristics*

Viscosity, SUS		V.I.	Pour point, °F	Aniline point	Aromatics, percent	Naphthenes, percent	Paraffins, percent
100° F	210° F						
100 to 4000	40 to 210	95 to 100+	0 to +15	210 to 260	2 to 8	21 to 35	63 to 70
125 to 1250	40 to 85	50 to 60	−10 to −55	190 to 230	4 to 7	35 to 44	52 to 58
160 to 2500	40 to 100	15 to 30	0 to −60	165 to 200	13 to 14	35 to 45	42 to 53

TABLE 2.—*Diester Fluids and Petroleum Oil Characteristics*

Diester	Viscosity, SUS			V.I.	Pour point, °F
	100° F	210° F	~−65° F		
Di-2-ethylhexyl sebacate	68.6	37.3	37 000	150	−80
Diisooctyl adipate	57.7	35.5	26 500	147	−80
Di-2-ethylhexyl adipate	52.8	34.2	22 600	121	−80
Diisooctyl azelate	68.6	37.4	32 000	155	−85
Di-2-ethylhexyl azelate	62.4	36.2	29 300	140	−100
Low pour-low V.I. petroleum oil	58.3	34.2	139 000	51	−70
High pour-high V.I. petroleum oil	57.8	34.6	70 000	96	10

furized, chlormatic and fluorinated materials, silicones, and polyphenyl ethers. Of these, only a high phenyl content silicone, a fluorinated fluid, and a polyphenyl ether looked attractive at the high-temperature end. The high-viscosity and low-viscosity index of the polyphenyl ether eliminate this type of fluid. The fluorinated fluid initially seemed attractive but showed corrosive properties at high temperature. Perhaps this undesirable characteristic has been mitigated or eliminated in more advanced types.

Characteristics of several of the best materials examined are given in table 3.

Thickener Phase

Because metallic soaps constitute the thickener phase for most greases, the following deals with them.

The soap phase, formed by the reaction of alkali or positive metals with various fats or fatty acids, is also complex for several different reasons. First, the metallic oxides or hydroxides contain minor amounts of impurities. For example, analytical grades of $Ca(OH)_2$ contain NH_4OH, Cl, Fe, Pb, or Mg; of NaOH contain Cl, Fe, Ag, N, Si, or Na_2CO_3; of $Ba(OH)_2$ contain Ca, Cl, Fe, or Pb; and of LiOH contain Na, Ca, CO_2, Fe_2O_3, SO_4, Al_2O_3, or Cl_2. It should be remembered also that grease manufacturers do not ordinarily use analytical grades of these materials in large-scale production, and larger amounts of impurities may be found in commercial grades of the same materials.

Second, the fats or glycerides such as beef or mutton tallow usually contain predominantly five distinct fatty acids; i.e., stearic, palmitic, oleic, linoleic, and myristic acids. In some cases, materials other than natural tallows or glycerides may be used as extenders by suppliers. Typical beef tallows in general contain 48 percent oleic acid, 32 percent palmitic acid, 15 percent stearic acid, 3 percent linoleic acid, and 2 percent myristic acid.

TABLE 3.—*High-Temperature Fluid Characteristics*

Fluid	Viscosity, SUS			Pour point, °F	Evaporation, percent (500 hr at 400° F)
	100° F	210° F	~−65° F		
Silicones:					
A	332	89	38 000	−55	8
B	292	100	8 300	−100	4
C	321	112	8 300	−100	19
D	296	105	7 400	−95	21
E	284	100	7 600	−75	7
F	929	91.6	58 000 000	25	7
Polyphenyl ethers:					
A	1567	69.5	[a] 90 000 000+	35	7
B	8565	118	[b] 90 000 000+	70	4
Silphenylene	303	85	36 000	−80	15
Ferrocene derivative	84.5	42.2	10 400		30+
Fluorinated fluid:					
A	440	62.8	4 000 000	−45	
B	1251	124.6	10 000 000+	−30	

[a] At −30° F.

[b] At 10° F.

Concentrations of the above may well vary depending on the origin of the animals and their respective menus.

Typical tallow purchase specifications can call for rather rigid adherence to requirements for gravity, melting point, viscosity, flash, cloud and pour, titer, color, odor, sulfur, water, carbon residue, as well as neutralization, saponification, and iodine values. Despite these controls, a batch of tallow occasionally pops up that will not produce satisfactory greases. One lot in our experience defied all efforts to detect reasons for its poor performance.

Third, the commercial grades of fatty acids are by no means pure products. Stearic acid always contains some portion of palmitic acid. Oleic acid, if stored for some time in iron tanks, may contain iron soaps. Composition varies depending on the source, refining, and blending processes. Typical examples of fatty acid distribution in several commercial products are given in table 4.

Control tests may cover determinations of flash, titer, odor, sulfur, water, carbon residue, corrosion, neutralization, saponification and iodine values, and chromatographic analysis. In general, the properties of fatty acids are more consistent than those of glycerides and also yield greases of more consistent characteristics.

Fourth, the hydrocarbon chains of the fats or fatty acids used in greases may contain from 2 to about 22 carbon atoms.

Finally, the fats or fatty acids may be of the unsaturated or saturated series, or a combination of both.

Additives

In general, additives used in greases may be broken down into six main categories: oxidation inhibitors, rust preventives, extreme-pressure (EP) and/or antiwear agents, oiliness agents, friction modifiers, and sealants. In general, the amounts of these agents required to perform a specific function will exceed those required to do a similar job in an oil. The masking effect caused by adsorption on, or reaction with, the thickener may be responsible for reduced effectiveness.

A wide variety of materials are used, singly or in combination, to impart a specific characteristic or a combination of properties. Some of the most common are antioxidants, which include phenolic and amine types, phenothiazine, selenides and diselenides, and zinc dithiophosphates; antirust agents, which include sulfonates, phenates, amines or amine derivatives, dithiophosphates, sorbitan monostearate, or oleates; EP and antiwear agents, which include sulfurized materials, lead naphthenate and oleate, phosphorus, chlorine, and antimony compounds, metallic dithiocarbamates, and many combinations of the foregoing; friction modifiers, which include graphite, molybdenum and tungsten disulfide, Teflon, nylon, and mica; sealants, which include lead, zinc, and copper powders, and asbestos floats; structure modifiers, which include latex, isobutylene

TABLE 4.—*Fatty Acid Distribution*

Composition, percent	Animal fatty acids		Fish fatty acid	Hydrogenated	
	1	2		Tallow glyceride	Fish glyceride
Stearic	35 to 95	37 to 83	27	65	21
Palmitic	5 to 53	11 to 54	35	28	31
Pentadienoic	0 to 1	0 to 0.5	.5	0.5	.5
Myristic	0 to 2.5	1 to 3	11	3	4
Margaric	0 to 2.5	1 to 2	2	1	1.5
Oleic	0 to 1	0.5 to 4	2	2	6
Linoleic	0 to 1	----------	----------	----------	----------
Lauric	----------		1	----------	----------
Arachidic	----------	----------	17.5	Trace	23
Behenic	----------	----------	4	0	13
Palmitoleic	----------	0 to 2.5	----------	----------	----------

polymers, alpha olefin polymers, polyethylene, and polypropylene; and metal deactivators, which include heterocyclic S–N compounds, zimates, trialkyl and triaryl phosphites, and diamines.

Selection of any one or combination of additives to perform either a specific function or combination of functions can be a time-consuming and frustrating experience. In many cases, certain additives will effect the specific improvement required but in the process degrade other properties. Properties more generally affected are yield, shear stability, water resistance, consistency-temperature characteristics, high-temperature performance, or any combination thereof. The most sensitive of the additives are generally antirust and EP materials. Ultimately, if one specific property is of prime importance, a compromise on other properties may be necessary.

Generally, exploratory work may be carried out in one grade of grease. If the same level of performance is required for all grades, it cannot be safely assumed that the identical concentration of additive or additives will perform the same in all grades. Neither can it be assumed that the same additive package will perform in other grease types. Even in the same type of grease, variations in acidity or alkalinity or ratios of saponifiable materials can upset the effective balance of components. To further complicate the picture, processing conditions can have a profound effect.

To summarize, the resultant grease consists of the reaction product of the metallic oxides or hydroxides and the fats or fatty acids (essentially a metallic soap), plus minor amounts of free acid, alkali or metals, glycerin and water, possibly in one of several states, dispersed in the fluid component. Add to this the materials required to provide oxidation stability, antirust, EP, antiwear, tackiness, etc., and you have a conglomerate mass or mess depending on how it is viewed.

From the foregoing, it is quite evident why some investigators have decided that a combination of the oil and soap phases of a grease may contain from 500 to 1000 different chemical compounds.

The soap phase of a grease may be considered to have little or no lubricating qualities, but being a solid or semisolid, it does possess, to some extent, the property of resistance to flow. Oil alone, while having the quality of lubricity, being mobile will flow, thus deserting the job for which it was intended, if bearing seals are inadequate. A combination of the two phases results in a product combining to a great extent the desirable properties of both ingredients. Figuratively speaking, a grease may be defined as an oil storage system in which the soap phase constitutes the reservoir while at the same time being an integral part of the lubricant.

WHY GREASES ARE USED

The main function of either oils or greases is to reduce friction, to prevent adhesion or seizure between moving metal surfaces, and to provide between these surfaces a film of sufficient consistency that can be easily sheared and that, in some cases, may act as a heat transfer medium.

When comparative qualities of oils and greases are discussed, consideration must be given to the mechanical aspects of the problem and to the relative adaptability of each type of lubricant to the problems involved.

The question, therefore, of where and when to use greases or oils requires some knowledge of the operating conditions and mechanics of the mechanism to be lubricated and of the technology of lubrication.

Greases possess certain characteristics that give them a decided advantage over oils. The fact that greases are solid or semisolid materials capable of resisting deformation to some extent and the fact that they have considerable ability to remain put accounts for their usefulness in some applications.

Lubrication with fluids at particularly high speed and temperatures has progressed more rapidly than with greases mainly for one reason: mobility. A fluid will flow into a bearing under its own head, feed through a wick, be picked up and distributed by slinger rings; it can be jetted as a fluid or supplied as an air-oil mist; it can be pumped, filtered, and cooled with relative ease. Possibly most of the design work on bearings has been predicated on the use of fluids as lubricants.

The property of a grease that most recommends it as a substitute for fluid lubricants is its resistance to flow. This property enables the designer to eliminate certain accessory equipment and reduce the size and weight of other components. This same property, however, can be a double-edged sword because resistance to flow, if too high, can result in inadequate lubrication and consequently in rapid failure of bearings.

Because of this property, bearings may be required to operate on very minute amounts of grease retained in the races and ball-retainer contact areas. The same situation applies to plain bearings of various types. These thin films must therefore resist thermal and oxidative degradation, prevent excessive wear, and lubricate adequately for the time required. The point of no return is reached when the initial film fails to perform these functions and the bulk grease fails to flow or separate oil into the contact areas to replenish or replace the initial film.

In general, where flood lubrication is not required, where limited space prohibits the use of cumbersome oiling systems or sumps, or where temperatures do not call for heat transfer mediums, the use of greases has been found particularly suitable.

In the field of lubrication engineering, certain operating conditions will be met that are not adaptable to oil lubrication, and in some cases it is often found desirable or imperative to resort to grease lubrication.

Some cases for which greases have been found particularly suitable are—

(1) Where products in the process of manufacture were contaminated by oil dripping or being splashed into the products by oil-lubricated machinery. These conditions are experienced chiefly in the food processing, textile, and papermaking industries.
(2) Where oil cannot be retained in bearings because of faulty or inadequate seals.
(3) Where it is necessary to insure positive lubrication using a comparatively small amount of lubricant and yet have a sufficient reserve to allow the bearings to operate for long intervals with little or no attention.
(4) Where bearings may be subjected to repeated shocks or suddenly reversed bearing pressures, as found in motor vehicle chassis, crank pins, recoil mechanisms, etc.
(5) Where there is danger of dust, abrasive materials, or water entering bearings. Grease may form a protective seal at the extremities of bearings preventing entry of these contaminants.
(6) Where it is desirable that a lubricant adhere, whether the mechanism is in motion or idle.
(7) Because greases are normally heavier than oils, they may leave a better protective film on bearing surfaces for prevention of rust and corrosion under severe operating conditions.

Greases are usually preferred to oil for any application where the condition, design, or service renders frequent lubrication difficult or impossible.

A few of the disadvantages of grease lubrication are—

(1) Greases are not stable when stored. If a grease is not of the best quality, storage for long periods may cause separation, hardening or

softening, change in color and oxidation resistance, and an undesirable odor.

(2) Greases are not as resistant to oxidation either in storage or in operation as are oils.

(3) Greases are not as uniform in character as are oils. The grades of different manufacturers often differ widely in regard to consistency, melting point, physical and chemical stability, and other properties.

GREASE CLASSIFICATION AND TYPES

Lubricants of the grease type can be classified on two different bases, by consistency and by type of thickener.

Consistency.—The NLGI set up a numbering system for greases similar to the Society of Automotive Engineers (SAE) number for motor oils. According to the NLGI system, the grade number of a grease is based on its worked penetration. The grade numbers range from 000 to 6, and the corresponding penetrations from 475 to 85. This classification holds true for all types of greases falling within this penetration range.

Type of Thickener.—Thickeners may be of the soap, soap-salt, inorganic, complex inorganic and organic types, or combinations of these.

The properties of all greases initially are dependent on the nature of the thickener, the concentration of thickener, the characteristics of the fluid component, the types and amounts of additives, and the compounding conditions.

In the case of soap base greases, classification is ordinarily based on the predominating metal of the soap. Since greases of the soap type constitute by far the largest production, these will be discussed first.

Calcium Base Greases

These can be divided into three types: those dependent on appreciable amounts of water to maintain their structure, the anhydrous type, and the calcium complex.

Hydrous Type

The most commonly used greases for general applications are of the lime soap type. They are ordinarily referred to as industrial cup greases. In general, the oil content may range from 65 to 95 percent, and the soap content from about 5 to 35 percent, depending on the consistency desired. Consistency depends on the soap content, the oil viscosity, water content, and compounding procedure and may vary from a fluid to a plastic solid. The viscosity of the oil used in ordinary industrial cup greases may range from 100 to 500 SUS at 100° F. However, lime base greases intended for heavy-duty service may contain oils of much higher viscosity. Hydrous calcium base greases all contain water and are dependent on the water content to maintain structural stability and texture. This dependency on water, which may range from about 0.2 to 2 percent, is a limiting factor in the usefulness of the calcium base greases, as will be indicated later on. Microscopic examination shows that calcium base greases contain microfibers that may account for the smooth, homogeneous, and butterlike texture of these greases.

Calcium base greases are usually characterized by low dropping or melting points ranging from 150° to 220° F, relatively high water content ranging from approximately 0.2 to 5 percent, a high change of consistency with temperature, good water resistance, a fair resistance to oil separation at moderate temperatures, and poor structural stability if maintained for prolonged periods at temperatures in excess of 150° to 160° F. Poor stability can be attributed to the fact that because this type of grease is dependent on water content to maintain the soap and oil in a combined state, loss of water due to evaporation at elevated temperatures will cause the lubricant to revert to the original phases.

Conventional calcium greases will function satisfactorily at normal speed and at normal operating temperatures and are to be desired where water is a problem. They are used generally in applications where the normal conditions are slow speeds and relatively low temperatures. Fortified with suitable EP additives, they are used extensively in applications where pressures are high and ordinarily in systems where frequent or periodic lubrication is prevalent.

Anhydrous Type

As the name implies, the anhydrous calcium greases contain negligible amounts of water. In the majority of cases, fatty acids are used as the saponifiable material. Stearic acid, various combinations of fatty acids, 12-hydroxy stearic acid, alone or in conjunction with various modifying agents such as glycerol, long-chain alcohols, naphthenates, etc., have been employed.

Dropping points are somewhat higher than those of the conventional greases and may range from about 225° to 290° F. Greases compounded with calcium hydroxy stearate in general have higher dropping points and are usable over a wider temperature range than those containing soaps of stearic or other fatty acids. Greases of this type compounded with low-viscosity oils have been used extensively to meet the requirements of military specification MIL–G–10924 B. Their use has been extended also into many other applications.

Complex Type

Patent No. 2,197,263 (ref. 2) issued in 1940 covered an "improved lime base grease characterized by stability at temperatures in excess of 200° F, comprising a lubricating oil and lime soaps of fatty acids and in addition thereto a small proportion of the calcium salt of a monobasic fatty acid having not more than 6 carbon atoms." By 1960 approximately 50 additional patents had been issued on the calcium-complex type of grease.

Calcium-complex greases may consist of an infinite number of possible formulations of petroleum lubricating oil thickened with a variable ratio of calcium salt of a low-molecular-weight organic acid to calcium soap of fatty acids. Acetic acid is widely used for the low-molecular-weight component because of commercial availability and relatively low cost. The specific peformance properties desired and cost considerations dictate a selection of options for formulating and processing a commercial calcium-complex grease product. The ratio of the various acid components in the thickener, the total amount of thickener, and the time extent and temperature level of heat treatment of the grease govern the degree to which specific characteristics are developed in a particular formulation.

In general, the calcium-complex greases have a much higher thickener content than do greases of other types. Thickener concentrations of about 15 to 25 percent are not uncommon for an NLGI Grade 1 consistency. Although many of the complex greases used industrially are of this soft consistency, their excellent consistency-temperature characteristics mitigate excessive leakage or drainage even at high temperatures.

Calcium-complex greases are usually characterized by dropping points above 500° F, good to fair shear stability, excellent water resistance and rust preventive characteristics, good resistance to oxidation if inhibited, and high load-carrying capacity and antiwear properties. These characteristics are, however, dependent on ratios of the components used.

Age hardening in storage and a tendency to separate when held under pressure in centralized lubrication systems was very prevalent with some of the early products but less so today. These characteristics seem to be pertinent to specific compositions or processing conditions.

The calcium-complex greases are used for the lubrication of many types of equipment used in the steel, paper, cement, rubber, refractories, and chemical industries. Specific applications are conveyors, molding presses, hot gas fans and blowers, paving machines, and laundry and drycleaning equipment.

Sodium Base Greases

These are commonly referred to as sponge or fiber greases and are so designated because of their fibrous or spongy texture. However, sodium base greases can be prepared that are quite similar in appearance and texture to cup greases.

Some factors controlling the fiber length or structure of sodium greases are—

(1) *Nature of the soap stocks.*—Soaps of the glycerides such as beef or mutton tallow are more apt to be fibrous than the soaps prepared from fatty acids.

(2) *Character of the petroleum oils used.*—Greases made from low-viscosity oils are usually less stringy or spongy than greases prepared from heavier oils.
(3) *Compounding temperatures and cooling rates.*—High compounding temperatures followed by quick cooling usually reduce the fiber length.
(4) *Ratio of caustic to saponifiable material.*—Greases slightly on the alkaline side are more apt to be smoother than slightly acid products.
(5) *Extent of dehydration.*

The soap content, depending on the type of application and operating conditions, may range from 5 percent in transmission or gear grease, 10 to 30 percent in ball- or roller-bearing greases, or to 60 percent in railroad driving journal compounds.

The oil viscosity may range from 50 to 200 sec at 100° F for textile applications, to 3000 to 4000 sec at 100° F for heavy-duty gear to transmission applications.

Sodium base greases are usually characterized by—

(1) Rather fibrous or spongy texture, although fiber length and structure can be modified by milling.
(2) Relatively high melting points of approximately 250° to 450° F, depending on soap content, water content, soap stocks, and processing methods.
(3) Low water content, usually from 0.0 to 0.5 percent.
(4) Good structural stability. Unlike the cup greases, the sodium base greases are not dependent on water to maintain equilibrium and can be held at fairly high temperatures for prolonged periods without undue breakdown from oil-soap separation or structural breakdown.
(5) Poor water resistance at elevated temperatures. Rust prevention, however, is good.

The applications for sodium base greases are numerous and varied. Uses may range from lubricants for textile mill machinery to such rough applications as drier rolls of paper and cement mills. They have been used extensively for automotive wheel bearings and other antifriction bearings. For many years, several high-soap-content sodium greases were almost the unanimous choice as factory fill for antifriction bearings. They may be used where high operating temperature conditions prohibit the use of the lower melting and less mechanically stable calcium greases, but should not be used where resistance to water is a major factor.

Lithium Base Greases

As late as 1938, there appeared to be no published account of the use of lithium soaps for greases. However, it should have been expected that lithium would produce greases similar in properties to sodium base greases, possibly having equivalent or higher melting points and greater resistance to water. In all probability, the development of lithium base greases was initially retarded by the abnormally high cost of lithium hydroxide ($2/lb) in comparison with caustic soda or lime, the relatively small amounts of lithium hydroxide produced at that time, the unavailability of fats or fatty acids having optimum properties for combination with lithium, and the lack of compounding techniques or processing equipment suitable for the production of satisfactory lithium greases.

In the early part of World War II, advances in design and performance of aircraft necessitated the development of greases that would render certain aircraft accessories operable over a temperature range of −65° to about 250° F and that would be resistant to the washing action of water. The water solubility of the sodium base greases and their high-torque characteristics at low temperatures, which possibly is a function of fiber structure, ruled them out of the picture. The low dropping point and instability of the calcium and aluminum base greases at elevated temperatures made them unsuitable for this application.

A patent applied for in 1940 and granted in C. E. Earle (ref. 3) in 1942 covered the use of lithium soaps in greases. Since no prior claims were cited, Earle's development was possibly the first on record. In 1941, the U.S. Air Corps Specification for Grease, Lubricating, Aircraft, Low Temperature (MIL–G–3588 B) was issued. Experimental work indicated that the requirements of this specification could be met only by lithium base greases. Possibly the specification was written around one of Earle's compositions. By early 1942 several companies were producing limited quantities of lithium stearate, and in all probability most of the greases sold initially against this specification contained the preformed soap. Expansion of plants for the production of lithium hydroxide probably contributed to the rapid development of other lithium soaps by various companies.

Some of the first greases compounded to contain lithium soaps of conventional fatty acids required fairly high soap contents. This was necessary to obtain adequate resistance to oil separation and shear. Since lithium hydroxide was considerably more expensive than sodium or calcium hydroxide, the lithium greases were also expensive.

About 1946 to 1948 the use of lithium soaps of 12-hydroxy acid or glyceride, either alone or in combination with other fatty acids or glycerides, was proposed (ref. 4). Greases so compounded proved to have excellent shear stability, adequate resistance to oil separation, and good yield.

Since that time, production and use of lithium base greases as specialized aircraft lubricants, multipurpose automotive greases, and industrial lubricants have increased tremendously. Today, lithium greases comprise about 50 percent of the total market. The adaptability of these greases to a wide variety of applications has justified this growth. One major use is as a multipurpose automotive-type lubricant. They are used extensively in many major industrial applications. Steel mills furnish a large outlet for lithium grease production.

In general, the lithium greases combine the adhesiveness, shear stability, and water resistance of the calcium greases and the high-temperature properties of the sodium greases.

Aluminum Base Greases

Complex Type

One of the more recent developments in the lubricating grease industry is the aluminum-complex grease (ref. 5). Generally, the thickener is formed by the reaction of a combination of stearic and benzoic acids with a reactive aluminum compound such as aluminum isopropoxide or a variation of this compound. To maximize yields and optimum properties requires careful balancing of the different thickener components and selection of the fluid component. In general, thickener contents required for the various NLGI grades are low and similar to those required for lithium greases.

Some of the important characteristics of aluminum-complex greases are dropping points of about 500° F; good mechanical stability; excellent consistency-temperature properties; low oil separation both under static conditions and under pressures found in centralized lubrication systems; and adequate oxidation stability, rust preventive, EP, and antiwear properties if so compounded.

They are recommended especially for the lubrication of equipment exposed to high temperatures in the steel, glass, rubber, and paper industries. They also perform well as automotive chassis and wheel-bearing lubricants.

Conventional Type

The sale of aluminum base greases would probably skyrocket if women were to replace men as lubrication engineers or purchasing agents for industrial concerns because these greases have a very attractive appearance, being clear, transparent, and of jellylike consistency.

As with other greases, oil and soap content and the oil viscosity may be varied to meet specific applications.

Aluminum base greases are usually characterized by dropping points between 150° to 220° F, excellent water resistance, zero water content, low starting and running torques at normal temperatures and also at subzero temperatures if the proper viscosity oil has been used, adhesion and cohesion as their melting point is approached and the exhibition of a tendency to creep, and rather good mechanical stability. If heated above their melting point and then permitted to cool, the majority of aluminum base greases will set to a somewhat harder consistency, and exhibit considerable oil separation.

In the past, aluminum greases were widely used as chassis lubricants, for some applications in the textile and food industries, as lubricants for recoil mechanisms, cash registers, and other business machines. Today they constitute only a very small part of the total market.

Miscellaneous Greases

Barium and Strontium

Although both types have been known for about 30 years, neither attained the stature of the calcium, sodium, and lithium greases. The basic barium- and strontium-complex greases, depending on specific components, ratio of components, and processing conditions, can be compounded to provide high dropping points, excellent water resistance, and good high-temperature performance. Rather complicated compounding procedures, high soap contents compared to lithium, and consequently higher materials cost, mitigated against widespread acceptance.

Barium base greases have been used as multipurpose automotive chassis and wheel-bearing lubricants. One of the main uses today is as a lubricant for automotive ball joint and steering-gear linkages. The author knows of no applications where strontium greases are employed at present. There is, however, some indication that interest in this area is again developing.

Mixed Base

With regard to the mixed-base greases, the patent literature abounds with them, and this entire paper could be used to discuss them. The mixed-base greases consist of petroleum oils, plus two or more of any of the metallic soaps discussed previously or the soaps of lead, zinc, magnesium, etc. Greases containing lead soaps alone or in conjunction with sulfur, chlorine, or phosphorus have been used extensively for years as EP lubricants. Relatively small amounts of calcium soaps have been used with sodium base greases to reduce fiber length. Mixed-base greases usually are compounded to improve some property of the single-base grease or to meet specific requirements for which the properties of both bases might be advantageous.

Bentone

The bentone greases are unique because the gelling agent is not a metallic soap but rather a reaction product of bentonite and various organic cations. By a method in which the sodium atoms of the bentonite are replaced by certain ammonium compounds, the bentonite is changed from a material dispersible in water to one dispersible in organic liquids.

Bentone greases, if compounded properly, are characterized by good working stability and consistency-temperature properties, excellent resistance to the washing action of water and adhesion to metal, fair rust-preventive properties if inhibited, high water absorption (with little effect on consistency at least up to 100-percent absorption), no dropping point, low oil separation, fair high-temperature performance if relubrication is frequent, antiwear properties equivalent to conventional greases, and good low-temperature properties depending on base oil.

Bentone greases appear to be very sensitive to the types of materials used to impart adequate rust prevention and EP properties. Many have a serious degelling effect. The problem is aggravated if both of the above characteristics are required.

Bentone greases have been used in both automotive and industrial applications, and their use appears to be expanding. Their resistance to dropping, melting, or leaking at high temperatures renders them suitable for use in certain applications in the steel, glass, and rubber industries.

Silica and Carbon-Black

Neither silica nor carbon-black greases are used extensively in this country, although both types, if compounded properly, have desirable high-temperature characteristics. The low bulk density and extreme dusting characteristics of both materials are objectionable.

Water resistance and rust prevention of greases compounded with conventional silica are poor. Resistance to washing action of water can be corrected by either precoating the silica particles or by use of certain additives, but inhibition against rusting is difficult.

The carbon- or acetylene-black greases have adequate water resistance, but also may be difficult to inhibit against rusting. Silicone carbon-black greases are used in high-temperature applications such as paint-baking ovens, kiln and drying oven equipment, and glass-drawing equipment.

Specialty Greases

As mentioned previously, the rapid advance of aircraft and space equipment dictated the need for greases operable for reasonable periods of time at temperatures up to 600° F and speeds up to 45 000 rpm. Most of the grease development work in this area has been sponsored by the military.

Initial work quickly demonstrated that petroleum oils and the diester-type fluids were unsatisfactory for use at temperatures much above 300° F. The same situation applied to greases containing the above fluids and thickeners of the conventional soap or inorganic types. At 350° F, performance life of such greases ranged from about 10 to 250 hr.

In the search for suitable grease components, 70 to 100 fluids of various types, viscosities, and combinations and about 300 potential thickeners were evaluated. Of the fluids, several silicones proved to have the best resistance to excessive thickening or gelling. Of the following types of materials tested as thickeners, only several produced greases having a reasonable performance life at 600° F. These included several triazines, arylureas, and dyes (ref. 6).

Inorganic materials tested as thickeners were silicas and clays, treated and untreated, metallic oxides and hydroxides, silicates, and colloidal metals. Organic compounds tested were amides, imides, arylureas, high-melting-point acids and derivatives, substituted polyphenyls, and triazines.

With the exception of the silicas, modified clays, several organic compounds, salts, and complexes, the other materials tested showed little thickening action even in concentrations up to 40 percent. With few exceptions, the organic compounds were thermally or oxidatively unstable and showed excessive volatility, sublimation, agglomeration, fusion, or decomposition.

In general, greases containing inorganic materials showed very short performance life. The high concentrations required to yield a product of greaselike consistency, poor shear stability at test temperatures in bearings, possible abrasive tendencies, and catalytic effect on the stability of the fluids probably contributed to short life.

The best efforts in this area produced a grease, comprised of a high-phenyl-content silicone thickened with ammeline plus a minor amount of silica, which had a performance life of about 150 to 200 hr at 600° F and 20 000 rpm. At 30 000 and 45 000 rpm and 600° F, maximum life was about 50 and 20 hr, respectively.

Table 5 is based on replies of 68.42 percent of the companies contacted for production information. Full participation in this study would have resulted in a larger total production but may have not altered the individual percentage figures appreciably.

MANUFACTURING METHODS FOR SOAP BASE LUBRICATING GREASES

The commercial processes for manufacturing conventional soap-thickened greases generally follow three basic steps.

First, the soap-forming ingredients are saponified or neutralized at an elevated temperature in a minor proportion of the lubricating oil required in the finished grease. Some of the factors controlling the rate and completeness of saponification are the amount of material, temperature, ratio of saponifiable material to caustic, water content, oil viscosity, and efficiency of the stirring mechanism.

Second, the soap concentrate is reduced by the addition of oil at a controlled rate, accompanied by simultaneous cooling of the kettle.

Third, final adjustment of the soap content is made by small additions of oil and inclusion of additives, if required. This general procedure applies to the preparation of sodium, calcium, or lithium soap greases.

Milling or homogenizing may be an optional step.

Two methods of saponification are employed in the commercial manufacture of grease: pressure saponification in a closed reaction vessel or atmospheric saponification in an open vessel. The soapmaking ingredients,

TABLE 5.—*Approximate U.S. Grease Production (1969)*

Grease type	Production, thousands of pounds	Percent of total production
Aluminum soap:		
Conventional	5 463	1.07
Complex	6 473	1.27
Total	11 936	2.34
Calcium soap:		
Hydrated	72 688	14.24
Anhydrous	27 575	5.40
Complex	27 817	5.45
Total	128 080	25.09
Lithium soap:		
Conventional	255 273	50.00
Complex	7 542	1.48
Total	262 815	51.48
Sodium soap	48 218	9.44
Other soap	13 188	2.58
Nonsoap	46 289	9.07
Total	510 526	100.00

fats or fatty acids and the appropriate alkali, are charged to the saponification vessel with part of the lubricating oil base.

Atmospheric Saponification.—An open-type grease kettle equipped with counterrotating paddles and wall scrapers and a jacket for application of heat serves as the saponifier. After substantial saponification and dehydration have been accomplished by stirring and heating at a temperature sufficiently low to prevent excessive foaming, the soap is heated to a much higher temperature level to complete the reaction and drive the remaining traces of moisture from sodium or lithium soaps. The addition of consecutive small increments of water may be necessary to stabilize the gel structure of calcium soap during the same heating period at an elevated temperature.

Pressure Saponification.—The pressure vessel may be a closed-type grease kettle with conventional stirrers and wall scrapers or a closed contactor capable of circulating the soap concentrate at high velocity. The pressure saponification step is essentially the same in kettle or contactor except for a substantially shorter time required to heat the contactor to the desired maximum temperature. The concentrates of sodium or calcium soap are discharged at maximum temperature into an open kettle by the steam pressure generated by water of reaction. A large amount of moisture is evaporated rapidly by this sudden pressure drop. Sodium soap concentrates are reheated to effect complete dehydration. Calcium soap concentrates are held at a constant temperature level for a sufficient time to evaporate excessive water content. Lithium soap concentrates are held in the pressure vessel at maximum temperature until internal steam pressure is released by venting and vacuum is applied for complete dehydration. The soap concentrate is then pumped to an open grease kettle for reduction of the soap content.

The soap reduction step consists of simultaneously diluting and cooling the soap concentrate by adding oil at a controlled rate. The rate of oil addition varies with the type of metallic soap, the stirring speed of the kettle, and the temperature of grease base at any particular time. As a general rule, addition of oil is started slowly into the soap concentrate at maximum temperature and gradually increased as the mass of grease in the kettle becomes larger and the temperature falls.

The final adjustment step is made for most formulations below 200° F, at which point required additives are also dispersed in the grease. Pilot samples are removed directly from the kettle or passed through a grease mill or homogenizer to determine specification test properties. After adjustments are made to satisfy all requirements, the finished batch is filled from the kettle or through a mill into shipping containers or into a storage vessel for later filling into bulk-delivery vehicles.

The processing steps for calcium-complex greases follow the general pattern for conventional soap-thickened greases in open kettles with the exception of saponifying the thickener content in the presence of a major part of or all the lubricating oil present in the finished grease. Additives are usually mixed into the grease at a lower temperature before the mill-finishing step. A single grease kettle may serve for the entire kettle process if adequately equipped for both heating and cooling, or the batch may be transferred, after heat treatment is completed, to a finishing kettle with the proper cooling facility. Milling is necessary for most formulas to obtain the smoothest texture and maximum efficiency from the thickener.

MANUFACTURING METHODS FOR NONSOAP LUBRICATING GREASES

The manufacture of grease from nonsoap thickeners is accomplished by two basic steps: preparation of a uniform slurry of the preformed thickener in the oil base and maximum dispersion of the thickener by passing the slurry through a mill or homogenizer.

Nonsoap thickener types most commonly used in commercial greases include silica gels and an organophilic bentonite.

In preparing the slurry of thickener in fluid lubricant, a coupling agent is required, and intimate mechanical dispersion of the solid material before milling promotes maximum gelling effect in the finished grease. Heat treatment of the slurry may be required in some cases, depending on the nature and amount of coupling agent used and the nature of the thickener. When it is necessary to heat the slurry, only a part of the oil is used with the premix of thickener and coupling agent. The remainder is added to dilute and aid in cooling the batch before milling.

The conditions for milling nonsoap greases are more critical than for conventional soap greases. Maximum dispersion of the thickener in most cases is aided by cooling the preslurry to a temperature near room ambience before passing through the mill at a slow rate. The clearance setting between the rotor and stator of the mill is also restricted to a small tolerance and is predetermined for any specific formula.

In general, there are no set rules or procedures to be followed in grease production. The methods employed are those that have resulted in the production of suitable lubricants for various applications. Grease making does not appear to be a process in which temperature and time limits can be rigidly specified and adhered to, with resultant products rolling off the assembly line with clockwork precision.

DEVELOPMENT AND EVALUATION OF GREASES

The development of a new grease usually begins with the determination of the desired performance characteristics and the preparation of experimental samples.

The experimental samples are then evaluated in the laboratory and compared, if necessary, with leading competitive products.

Pilot-plant lots are prepared and compared with laboratory size samples.

Full-scale production is begun and compared with pilot-plant production.

Field testing is made and, if satisfactory, commercial manufacture and sale are begun.

Preparation and comparative laboratory evaluation of experimental greases enables laboratory personnel to eliminate obviously unsatisfactory compositions. When development work reaches the stage at which laboratory tests indicate the experimental samples to possess the required performance characteristics, and when pilot-plant lots substantiate the initial results, laboratory testing ceases to be of further value and field testing is required. Field testing and service performance are the final criteria of any product. Monitoring of important characteristics of production lots, however, is required to assure that consistent quality is maintained.

There are numerous standard ASTM grease tests available to the developer, producer, consumer, and analyst that can be applied as production controls for properties and quality, guidelines or benchmarks for service specifications, and fingerprints which may aid in identification of a grease of unknown composition. It is evident that the functions or use of the methods may well overlap as shown in table 6.

The speed with which greases can be produced, packaged, and shipped depends not only on processing and packaging time but also on the number and types of control tests necessary to assure adequate and consistent quality. The time and cost of control tests may well eat into the margin of profit.

Thus in general, once the properties of a specific grease have been established by exhaustive testing of laboratory, pilot-plant, and plant trial batches, inspection tests are reduced to the minimum consistent with predetermined limits for quality control and/or limits set by purchase specifications. The first phases of quality control are realistic specifications for all raw grease components, plus prescribed and adhered-to requirements for both composition and processing conditions.

Quality control tests used depend to some extent on the type of grease, critical properties pertinent to service and, in some cases, prior history on either performance in service or in storage. Some of the control tests used may be seen in table 7.

Because of the test time required, rust and other lengthy oxidation tests are ordinarily not run on every batch.

GREASE TESTS AND SIGNIFICANCE

Grease Analysis

The analytical tests used depend on the amount of information required and the end use of the information. In the majority of cases, greases may be analyzed for three main reasons: to determine what the competition is doing, to determine how consistently one's own plant is operating, and to determine possible reasons for the failure of a lubricant in service.

Dropping point, water resistance, or simple heat tests often supply an initial clue as to grease type. Spectrographic ash analysis is used to substantiate the type or types of thickeners present and the presence of contaminants. Separation of the fluid and thickener components permits determination of their respective characteristics. Decomposition of the thickener, if of the soap type, and further analysis yield clues as to the composition of the fatty component. Examination of the fluid phase by infrared or other sophisticated techniques may determine the presence of oxidation inhibitors, polymers, EP or antiwear agents, and rust preventives that are preferentially soluble in the liquid media, either oil or solvent. If additives are not detected in the fluid and if the product exhibits characteristics ordinarily attributed to the foregoing types of additives, then the assumption can be that they are tied up with or entirely dependent on the thickener. In that case further analysis of the thickener may be in order.

TABLE 6.—*Grease Test Uses*

Tests for lubricating greases	ASTM No.	A	D	P	U	Production control	Significant to service
Analysis	D128–64	×	------	------	------	------	------
Lead in new and used greases	D1262–55	×	------	------	------	------	------
Cone penetration	D217–68, D1403–69	------	×	×	×	×	------
Dropping point	D566–64, D2265–67	×	×	×	×	×	×
Oil separation	D1742–64	------	×	×	×	×	------
Leakage tendencies	D1263–61	------	×	×	------	×	×
Roll stability	D1831–64		×	×	------	×	×
Oxidation stability	D942–70	×	×	------	------	------	------
Rust prevention	D1743–64	------	×	×	------	------	×
Water washout	D1264–63	------	×	×	------	------	×
Apparent viscosity	D1092–62	------	×	------	------	------	×
Evaporation loss	D972–56, D2595–70	------	×	------	------	------	×
Low-temperature torque	D1478–63	------	×	------	------	------	×
EP properties:							
Timken	D2509–68	------	×	×	×	×	×
4-ball	D2596–69	------	×	×	×	×	×
Wear-preventive properties	D2266–67	------	×	×	×	×	×
Effect of copper on oxidation rate	D1402–58	------	×	------	------	------	------
Functional life	D1741–64	------	×	------	------	------	×

A = analyst; D = developer; P = producer; U = user.

TABLE 7.—*Grease Control Tests*

Grease type	Conventional calcium	Complex calcium	Lithium	Lithium EP	Special lithium
Dropping point	×	×	×	×	×
Penetration:					
Unworked	×	×	×	×	×
Worked	×	×	×	×	×
60 strokes	----------	×	×	×	×
10 000 strokes	----------	×	----------	×	×
Water, percent	×	----------	----------	----------	----------
Acidity or alkalinity	×	×	×	×	×
Color	×	×	×	×	×
Copper strip corrosion	----------	×	----------	----------	×
Timken	----------	×	----------	×	----------
Oil separation	----------	×	----------	----------	×
Rust prevention	----------	×	×[a]	----------	×
Water washout	----------	×	----------	×	----------
Oxidation stability	----------	×	×[a]	×	×
Water stability	----------	----------	----------	----------	×

[a] Selected lots only.

Analytical methods such as ASTM D128 and supplementary or modified procedures are time consuming and costly. Currently ASTM Technical Division G is investigating infrared techniques as possible analytical tools for greases. If successful, analyses of these very complex systems might be simplified.

Cone Penetration, Dropping Point, Oil Separation

It is generally agreed that results of these tests are valuable as plant control measures, but from the performance angle may have little practical significance.

The effects of temperature on consistency, however, may give a fair indication of the temperature range over which a grease can be used, of structure changes that occur on heating, and extent of oil separation. Table 8 shows data on several representative types of greases. These data, obtained under static conditions, could indicate to the uninitiated that (1) the hydrous calcium grease is unsuitable for use much above 150° F, (2) the upper temperature limits for the sodium and lithium greases may be about 350° and 250° F, respectively, and (3) both the calcium- and aluminum-complex greases may be usable up to 500° F.

Case (1) could be a safe assumption; case (2) could be correct if leakage from bearings under static conditions were of prime consideration but

TABLE 8.—*Effects of Temperature on Consistency*

	Penetration				
	Calcium		Sodium DP = 370° F	Lithium DP = 380° F	Al complex DP = 570° F
	Hydrous DP = 220° F	Complex DP = 570° F			
Temperature, °F:					
77	290	330	255	270	270
100	305	330	270	305	285
150	$\underline{380}$	$\underline{307}$	330	$\underline{345}$	310
200	460+	295	$\boxed{355}$	360	320
250	----------	303	$\boxed{355}$	$\underline{405}$	325
300	----------	$\boxed{325}$	$\boxed{365}$	435	335
350	----------	$\boxed{375}$	415	460+	340
400	----------	$\boxed{390}$	460+	----------	345
450	----------	350	----------	----------	$\underline{305}$
500	----------	$\underline{335}$	----------	----------	325
550	----------	460+	----------	----------	460+

DP = dropping point.

erroneous if leakage under dynamic conditions is important. In general, shear resistance of lithium grease is superior to that of sodium grease. Case (3) may indicate only that the calcium- and aluminum-complex greases, again depending on their shear stability characteristics, should resist leakage over a wider temperature range. Although dropping points are high and consistency-temperature characteristics excellent, instability of the fluid component could well limit grease life if temperatures are much above 300° F.

Structure changes before liquefaction can be detected by rather abrupt rise or decrease in consistency or stabilization of consistency over a fairly wide temperature range. Underlined or boxed-in figures indicate transition temperatures. Visual observations of oil separation at various temperature levels can also be of value.

Shear Stability

In all probability, the majority of people intimately connected with the development, production, and ultimate use of greases will agree that the ability of a grease to remain at the point of application depends on its original consistency and its resistance to change in consistency.

Anyone thoroughly familiar with greases will probably also agree that other individual factors or combination of factors, in addition to pure mechanical working, can and do affect the consistency of greases either in laboratory performance tests or in field service.

Two tests used currently to evaluate shear stability are ASTM methods D217, "Procedure for Prolonged Worked Penetration," and D1831, "Roll Stability of Lubricating Grease."

In D217 a grease sample is subjected to working or shearing by forcing a perforated plate through the grease a number of times (usually 100 000). Change in penetration following the normal 60 strokes and 100 000 strokes (passes of the perforated plate) is taken as a measure of shear stability. In D1831 a grease sample is placed in a cylinder containing a weighted roll that is free to roll as the cylinder is rotated. Passage of the roll over the grease during rotation subjects the grease to shear. Again shear stability is gaged by the extent of change in penetration.

Although many industrial and military specifications place limits on penetration change when subjected to either or both tests, it is questionable whether there is much correlation with service in most applications. There are too many other variables that can affect the mechanical or chemical characteristics of grease in service.

Oxidation Stability

In the early days of prepacked bearings, the chemical stability of greases left much to be desired. As a result, excessive gumming or hardening of the lubricants during storage necessitated removal of the crud and cleaning and relubrication of the bearings before use. Development and use of ASTM method D942, "Oxidation Stability of Lubricating Greases by the Oxygen Bomb Method," greatly accelerated the development of greases having adequate resistance to oxidation under static conditions and was at least partially responsible for elimination of the above storage problem. The same method, however, does not predict or correlate with service performance.

Oxidation stability of greases is of prime concern in the antifriction bearing field. Grease-lubricated antifriction bearings may be required to operate for long periods with little attention or relubrication.

Our observation of bearing tests on greases indicates that the majority of greases will decrease in consistency during some stage of operation. A large decrease will cause excessive leakage from the bearings. This decrease in consistency is normally attributed to shear instability, but it may also be associated with the formation of acidic or other initial oxidation products, which are detrimental to gel structure. As oxidation proceeds, the greases harden and eventually wind up as very gummy or cokelike products.

A screening test run under dynamic conditions that will eliminate obviously undesirable greases on the basis of rapid oxygen absorption, consistency degradation, and undesirable reactions with various metals is useful. A test procedure and equipment whereby a relatively thin film of grease can be exposed to shearing action under oxidizing atmosphere in the presence of common metals of construction seemed to be a logical starting point. These conditions might approximate those encountered in the operation of plain or antifriction bearings.

The bomb used for dynamic oxidation tests is very similar to that specified by D942, with the exception that a weighted steel or brass roller is inserted in the bomb along with 20 g of the test grease. The bomb is pressurized with oxygen to 110 psi, inserted in an oven controlled at test temperature, and rotated at a fixed speed by an external drive. The rolling action of the weighted roller during rotation of the bomb subjects the grease to shear and exposes fresh surfaces continuously to the oxidizing atmosphere.

Rust Prevention

Although D1743 is run primarily under static conditions, some degree of correlation was initially established between results of these tests and rusting of wheel bearings of aircraft operated under wet conditions followed by idle periods. The test can differentiate between greases having poor and good antirust properties, but precision is poor on borderline products.

Water Washout

Method D1264 provides a means to estimate the resistance of a grease to washout by water from an antifriction bearing under dynamic conditions. It is a useful tool for comparing greases of various types and consistencies. Determinations are usually made at 100° and 175° F. By modifications in the equipment, temperatures can be varied from the typical and fluids other than water can be used. For example, we have used modified equipment to determine the resistance of greases to aqueous solutions of acids, caustic, and other materials.

Precision of the test is poor. Loss by emulsification and by grease leakage, per se, from the bearing cannot be separated, nor is normal leakage for any grease under dry conditions considered. The latter is dependent on the type, structure, and consistency of each grease. Consequently, although defined as a procedure to evaluate washout by water, test results from D1264 are combinations of grease loss by emulsification, leakage due to changes in consistency, adhesiveness, or structure, and normal leakage that may occur even under dry conditions.

Water Absorption

Water absorption tests run in conjunction with consistency measurements will predict to some extent the effects that the addition of water will have on greases under dynamic conditions. The primary effect of the addition of water to greases will be a decrease in consistency. The extent of the decrease will depend on the type of soap, oil viscosity, and additives present in the grease. A secondary effect may be the change in the rust-preventive qualities. The latter may depend on whether an oil-in-water or a water-in-oil emulsion occurs.

Water absorption tests are run by working specified increments of water into a grease and determining the change in consistency by standard methods.

Apparent Viscosity

ASTM D1092, "Apparent Viscosity of Lubricating Greases," describes a procedure for measuring in poises the apparent viscosity of greases in the temperature range of —65° to 100° F at shear rates between 10 and 1500 reciprocal seconds. Unlike many other test methods, results of apparent viscosity tests can be used to predict, at least approximately, the ease with which a grease can be transferred through pipe or tubing. There also may be some relationship between apparent viscosity and torque characteristics. Since viscosity and torque tests are run initially on fresh uncontaminated grease samples, there may be correlation between results of the two tests for only a short period in service. Physical and chemical changes or presence of contaminants produced in service may render initial results of little value.

Apparent viscosity tests are quite useful also for determining the effects of oil viscosity, thickener content, and type of thickener on potential pumpability or transfer problems.

EP and Antiwear Tests

Generally, EP properties are determined by either the Timken (ASTM D2509) or the four-ball (D2596) procedures, and antiwear properties by the four-ball method (D2266). These tests are useful for differentiating between greases having different degrees of EP or antiwear properties. The extent of correlation between results of these tests run under standard test conditions and service performance may be open to question. However, by adjusting conditions of the tests, such as shape and materials of the test specimens, temperatures, loads, test periods, etc., we may approach service conditions and obtain more meaningful results.

Performance Tests

Performance testing in antifriction bearings can be the most costly, time-consuming, and frustrating experience for those engaged in grease development and evaluation. Basic cost of the most uncomplicated tester may exceed $2500. Instrumentation ordinarily required can increase the cost considerably. Cost of test bearings, depending on test temperature and speed, may range from $3 to $30 or more each. Length-of-performance-life tests, if run under moderate conditions of temperature, speed, and load, can be excessively long, thus necessitating a number of test units to compile information within a reasonable time. To reduce both time and equipment expenditure, temperature and speed may be raised to increase severity of operation.

Either the military directly or the Coordinating Research Council (CRC) under sponsorship of the military has been responsible for the development of equipment and procedures for evaluating performance life of greases in antifriction bearings, generally under severe conditions. ASTM is currently attempting to standardize one of the test procedures originally developed by the CRC. Despite very extensive cooperative work by various groups of capable people, precision of test results is extremely poor. This is not too surprising because in bearing performance testing, not only the grease but also the test bearings, test equipment, instrumentation, and even the operator are involved. Despite their shortcomings, bearing tests may still show better correlation with performance in service than will any other single test or combinations of other tests used currently.

Compatibility

On several occasions, it has been proposed that ASTM Technical Division G attempt to develop a method for determining the compatibility of greases. The extreme complexities inherent in such a study discouraged any attempt in this direction.

Grease compatibility is a complex phenomenon because of the many variables and changing conditions involved. At one end of the scale, mixing a fresh lubricant with a severely oxidized portion of the same lubricant may effect immediate or progressive physical or chemical changes in the mixture. At the other end of the scale, a non-soap-thickened grease containing mineral oil may be admixed with a soap-thickened grease containing a synthetic fluid. Add to this diverse operating conditions of time, temperature, and various contaminants, and the complexities of measuring and predicting compatibility of greases are apparent. Little information has been published on this matter, and factual data on compatibility may not be available. This alone may indicate that actual field compatibility problems are either rare in occurrence or not recognized as such.

However, grease compatibility is of more than academic interest, especially when an actual or potential customer questions or resists a grease recommendation on the basis of compatibility alone. Compatibility characteristics should not generally deter a proper change in lubricating grease; product performance and overall economics of use should be the primary determinants of lubricant selection. In changing from one grease type to another, the ideal of thoroughly removing all the old grease before applying new grease is often impractical or economically unfeasible. However, all efforts toward that end should be recommended and pursued. Short of physical dismantling and cleaning, purging with the new lubricant will assist in removal of the old. This can be done initially or progressively by temporarily increasing application intervals and quantity of grease applied.

ASTM, NLGI, CRC, and individual oil companies have done a tremendous amount of work on the development of chemical, physical, and performance test methods to aid the producers and consumers in the selection of lubricants that should be satisfactory in service.

It is rather unfortunate that in spite of the information available on greases, service performance still cannot be accurately predicted on the basis of physical and chemical laboratory tests alone because of unforeseen changes that may occur under actual operating conditions. These changes may be caused by high temperatures, contact with metals, contamination by dirt or moisture, bearing pressure and stresses, etc. Unexpectedly high operating temperature alone would produce changes in a lubricant. The primary effect would be oxidation, with resultant consistency changes, decrease in dropping point, separation or bleeding, change in color and appearance, and structural changes.

Most physical and chemical tests for greases stress initial characteristics such as dropping point, penetration, shear stability, water content, EP properties, and oxidation stability, acidity or alkalinity, etc. These requirements are all right as a yardstick by which the possibilities of a new product can be measured or for production control. But these products are not going to remain in the containers forever, and use will change the initial characteristics within possibly short periods. For this reason, abnormally close ranges should not be specified for those characteristics or properties that will soon be obliterated in service.

The limitations of the ordinary physical and chemical tests are recognized, and the trend is toward the development of test methods that simulate service conditions.

FUTURE OF GREASES

Grease production has declined steadily since 1961. The primary reasons for this are the advent of and the expanding use of factory lubricated and essentially sealed auto chassis components, and the extended relubrication intervals for chassis components advocated by the car manufacturers.

In the automotive field, I believe that this decline may have reached the bottom and that a slow but steady increase in production and use of greases can now be expected. My reasons for this belief are several. First, increased passenger car sales are projected. Second, cars of 1965 or earlier model years will require relubrication at more frequent intervals to maintain them in operable condition. Also, in this affluent society, two- or three-car families are becoming more prevalent. Finally, safety is being stressed, and proper lubrication is related to safe operation. I expect a decrease rather than an increase in the recommended time periods for relubrication.

In the industrial field, assuming a no-growth period, the market for greases could be expected to decline also, as the result of better greases and more efficient and economical lubrication practices. Bulk handling and centralized lubrication systems would contribute to the latter.

In the heavy industries, the day of the so-called grease monkey may be past. Very capable and efficient men are taking over the lubrication jobs. Many of them are well aware of the problems in their particular area and are capable of determining the properties of lubricants required for operation of their equipment. They are cognizant of the necessity for economy and will demand the best lubricants that can be used in the smallest amounts at the lowest cost.

On the brighter side, population growth will increase the demand for all types of products and services. Industrial growth in all directions will be needed to meet the demand. The overall market for greases can be expected to increase. Technological advances in equipment may require lubricants capable of operating under more severe conditions of speed, temperature, and load for longer periods than are now prevalent. More diversified and specialized greases may be required to lubricate future equipment. Such lubricants, although possibly low in volume, could be expected to yield a greater margin of profit.

Underdeveloped countries now on the move could represent a high potential market for all products including greases. Companies having access to and willing to gamble on these countries might be able to establish lucrative markets for the future.

I believe that if the grease industry is to advance or remain competitive in the lubricant field, it must—

(1) Be amenable to change. New products must be developed or current products modified to adjust to changing requirements and markets.
(2) Keep informed about the development of new machinery, their lubrication requirements, and the methods proposed for applying the lubricants.
(3) Continue to evaluate new raw materials, processing equipment, and methods with the view to improving products and reducing costs.
(4) Diversify into specialty product lines where volume could be low but profits high. Diversification should not be excessively hampered by complaints that manufacturing facilities can be operated efficiently and economically only when the number of types of products processed are held to the bare minimum.
(5) Expand if possible into underdeveloped countries that show signs of developing.

Technological changes that may affect the manufacturing, types, volumes, and use of greases are many. A few examples of possible changes are:

(1) Construction and use of continuous, fully automated grease-making facilities will be expanded. This type of operation is most

amenable to production of high-volume items. Manufacturing costs could be reduced. Accelerators to reduce reaction time may be required.

(2) Regulations for adequate removal of spent lubricants from industrial sewage before discharge into public waters will become more stringent. Greases that are either biodegradable or more easily removed from sewage effluent will be required and developed.

(3) Prior specifications for automotive greases have been primarily of the composition type. Many of the test requirements specified showed little or no correlation with performance. Automotive companies now are spearheading a drive for realistic test procedures that will correlate with performance in service. Once developed, these procedures will be incorporated in specifications. To meet the specifications, greases having better antiwear, antirust, and antisquawk properties will be required.

(4) Heavy construction machinery will become more massive and complex. Use of centralized lubrication systems may reduce the number of lubricants required. Current and future building programs will necessitate accelerated construction and full utilization of all types of equipment. Full utilization requires a minimum of downtime for repairs. Equipment owners will become more cognizant of the need for preventive maintenance and will insist on better lubricants and lubrication schedules.

(5) Mass transportation problems in all major cities are critical. A vast expansion program in transit equipment and facilities will occur. Because mass transit systems ordinarily appear to operate in the red, all preventive maintenance required to maximize operational time is required. Lubrication schedules will become more stringent, and relubrication, more frequent. Operation at high speeds and possibly higher temperatures may require greases having better shear, antiwear, and oxidation properties.

(6) Obsolete textile machinery will be replaced. Centralized lubrication systems will replace hand lubrication practices and will affect both the volume and types of greases required. A new breed of lubricants, very resistant to separation and plugging, will be required for the industry.

(7) New tire fabrics will require processing of components at higher temperatures. To prevent excessive downtime due to bearing failures, use of high-temperature synthetic lubricants will increase.

(8) The railroads are moving heavier loads at higher speeds. Some bearing companies believe that improvement in the antiwear properties of the current AAR M–917–63 greases is required and that a separate grease is needed for the lubrication of diesel locomotive bearings.

(9) Adequate sealing of traction gear cases to prevent leakage of lubricants has been a major problem. To offset the leakage problem, very heavy, viscous lubricants extremely difficult to handle and having poor lubricating properties at low temperatures are used. Extensive work in the area of improved gear cases is in progress. Preliminary tests indicate that design changes can reduce leakage considerably and that improved lubrication is afforded by lower viscosity lubricants.

(10) Aircraft of the future will require greases capable of lubricating for long periods under severe environmental and mechanical conditions. Conventional lubricants give short life at temperatures above 300° F. Temperature range for lubricants needed for the future will be at least −100° to 600° F. Current fluids such as the silicones and polyphenyl ethers used in greases are unsatisfactory at low temperatures. At 600° F, life may range between 100 to 200 hr. Greases composed of certain highly fluorinated materials have better low-temperature properties but are extremely corrosive at high temperatures. I expect that this deficiency will be corrected by modification of the structure or development of effective additives. Fluids appear to be the weak link, and extensive work in this area may be necessary.

(11) Regulations covering use of additives with adverse toxicological effects will become more stringent. Government agencies, unions, and the public in general will become increasingly aware of the need to upgrade health standards. A more detailed study of the toxicological effects of various additives to be used in lubricants may be required before approval. Use of some lead compounds, used for years as EP and antiwear agents, may be outlawed.

(12) In the communications, electronic, space, and weaponry fields, lubricants that will contribute to cleanliness and resistance to pickup of moisture and debris will be in demand. Lubricants particularly of the bonded type fit this category. Their primary deficiency at present is short life at high speeds and even moderate loads. In applications where loads are light and operational time required is short, current bonded films may be satisfactory. Further development work to increase life under adverse conditions is required.

(13) Polytetrafluoroethylene type of lubricants are used extensively in the missile and space programs because they are most resistant to the current fuels and oxidizers. Changes in the characteristics of the propellants may require changes in types of lubricants.

In general, I believe that a greater variety of better greases will be needed to satisfy the demands of the automotive, aircraft, and light and heavy industries.

AREAS OF NEEDED RESEARCH

Grease Lubrication Under Severe Conditions

Space equipment and possibly supersonic aircraft may require greases capable of lubricating for long periods under severe conditions. Temperatures may range from −100° to 600° F, and speeds possibly to 50 000 rpm or above. So far in this area we have just scratched the surface, and the scratches are nearly indiscernible. Several thickeners having the required stability are available. The limiting factor on grease life is probably the thermal and oxidative stability of the fluid component. A fertile field for future study is the development of new and improved fluids. In conjunction with work on lubricants, a program on development of antifriction bearings for grease lubrication at high speeds and temperatures seems to be needed.

Oxidation Stability Under Dynamic Conditions

A cursory study has indicated that a number of the oxidation inhibitors used in greases to meet the standard D942 oxidation test are not effective under dynamic conditions. Expanded research in this area may uncover new additives that will increase life in service.

Adhesion and Cohesion

One of the most important characteristics of a grease is its ability to remain at the point of application under either static or dynamic conditions. This property is related to the inherent adhesive and cohesive characteristics of the grease. Despite the importance of these characteristics, a literature survey conducted recently by ASTM Technical Division G showed little or no information on this subject. An investigation of the factors pertinent to these individual characteristics and their interaction could possibly be a difficult but rewarding assignment.

EP Characteristics of Calcium-Complex Greases

In general, EP properties can be obtained only by including in grease formulations those additives imparting such characteristics. Usually additives containing active materials such as sulfur, chlorine, and phosphorus alone or in conjunction with lead, antimony, etc., are required. Although certain calcium-complex greases do not contain additives of the foregoing types, they do possess excellent EP and antiwear properties. Why and how these work would be interesting and useful questions to have answered.

Migration of Oil in Greases

A limited study has shown that if two layers of grease containing the same type and concentration of a soap but compounded with oils of different viscosities are placed in contact, cross-migration of the oils will occur. Establishment of the relationship of this phenomenon to performance life in fully packed cartridge-type bearings would be informative and useful.

DISCUSSIONS

T. Salomon (OMER, Israel)

Mr. McCarthy states that "In general, the properties of fatty acids are more consistent than those of glycerides and also yield greases of more consistent characteristics." This statement is correct when the lubricating grease prepared with fatty acids contains a structure modifier like water or alcohol. It is important to emphasize that greases of the same soap type prepared with fatty acid and a structure modifier or with glycerides (where the glycerol freed by the saponification acts as the structure modifier) may not be compatible one with another.

With reference to additives, no EP agent like chlorinated paraffin is used in lubricating greases, only antiwear agents.

Mr. McCarthy has not mentioned lead-complex greases, which are used in Europe. Moreover, mixed calcium-lithium greases are not mentioned. They are largely used in Europe especially for roller bearings. There is an SKF specification for this type of grease.

Finally, with regard to test methods, the DTA test for the characterization of the structure of the grease is not mentioned.

A. Dyson (Shell Research Ltd., Thornton Research Center, Chester, England)

The nature and behavior of the lubricating fluid is a question that has not been raised in the discussion. Mr. McCarthy speaks of a grease as "an oil-bearing sand or shale that releases the fluid component only under certain conditions . . .," but the fluid component differs from the mineral oil used in making the grease. It contains enough filler and other components, either unchanged or as their degradation products, to modify the behavior in very important respects. We do not know whether we have a fluid with the best possible properties, and if we do not have such a fluid, we do not know in which direction and by what means we should modify the properties of the existing fluid.

This point may be illustrated by some measurements of the capacitance between rolling steel disks (ref. 7). The minimum thickness of the lubricant film may be estimated from these measurements. The lubricant is applied once only, without replenishment, as drops of oil or lumps of grease on the end of a glass rod or of a spatula, to the inlet to the conjunction.

Figure 1 shows that the thickness of the films formed by the mineral oil is approximately constant and that the grease film is initially thicker than the oil film but rapidly becomes thinner. The oil is that from which the grease was made. Poon, in his discussion of reference 7, reported a similar result obtained by a completely different method of measuring film thicknesses.

Results similar to those shown for the grease were obtained with a polymer solution, as shown in Dr. Lansdown's paper, and it therefore seems plausible to attribute the behavior of the grease-lubricated disks to

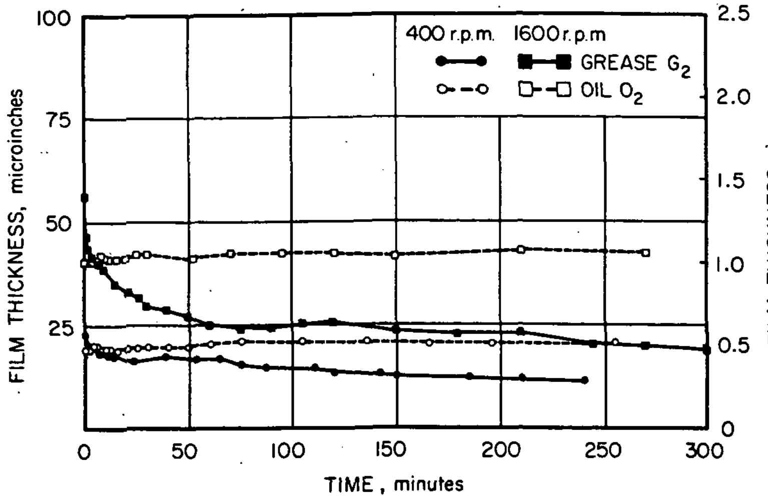

FIGURE 1.—Variation with time of film thickness of grease G_2 and base oil O_2 (60° C, 2200-lb$_f$ load).

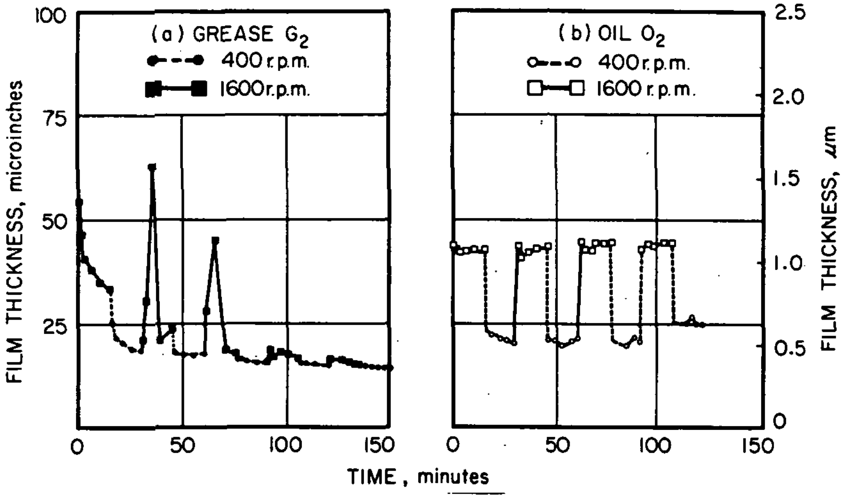

FIGURE 2.—Effect of variation of speed on film thickness (60° C, 2200-lb$_f$ load). (*a*) Grease G_2. (*b*) Base oil O_2.

the viscoelastic nature of the lubricating fluid released by the grease. The exact mechanism is not understood.

Figure 2 shows that the thickness of the oil film can respond apparently indefinitely to changes in the speed of the disks, whereas that of the grease film cannot. After a few cycles the thickness remains at a steady value appropriate to the lower speed.

The geometry of the disk machine is rather different from that of a rolling-contact bearing, but I suggest that differences in the behavior of greases and oils, illustrated by these results, must have important effects on the operation of mechanisms lubricated by greases. The nature of these differences is not understood, and I suggest that this aspect of grease behavior be added to the list of areas of needed research that Mr. McCarthy gives at the end of his paper.

A. J. Groszek (British Petroleum Co., Sunbury-on-Thames, England)

A new form of graphite has been developed at the BP Research Center that can be used to thicken mineral oils and other organic liquids to a grease consistency (ref. 8). The graphite is in the form of very thin flakes about 100 Å thick and has a surface area of 100 m^2/g. The greases thickened with this graphite hold promise of becoming outstanding high-temperature lubricants for use in bearings and transmission systems operating under a wide range of speeds and pressures.

Notable properties of these greases are high drop points (above 400° C), excellent mechanical stability, good EP action, and outstanding performance under boundary lubrication conditions at least up to 300° C.

It seems at present that the greases thickened with graphite would offer important advantages over existing commercial greases when used at temperatures above 150° C under high loads.

Some properties of a typical graphite grease not containing any additives are given in table 9.

TABLE 9.—*Typical Graphite Grease Properties*

Oil in grease	500 Middle East pale
Graphite in grease, percent wt	15
Penetration, mm $\times 10^{-1}$:	
Unworked	330
60 strokes	348
Drop point	>400° C
SKF 4A	
Bearing test (500 hr at 120° C)	Good pass
Mean Hertz load, kg	40

High-temperature performance of the greases can be considerably improved by the incorporation of appropriate oxidation inhibitors to protect the mineral oil.

G. H. Kinner (Royal Aircraft Establishment, Farnborough, England)

I very much agree with Mr. McCarthy's remarks about the need for more development work on grease lubrication under severe conditions. The following notes are intended to illustrate the present unsatisfactory situation with regard to certain miniature bearings used in aircraft applications.

We use servomotors for the control of aircraft instruments and the position of surfaces. Correct and reliable functioning is very important, so much so that systems are often installed in triplicate.

Typically, the servomotors have miniature stainless-steel precision bearings of 0.125-in. bore and 0.375-in. outside diameter. They have to start up at low voltage ($\simeq$3 V), and low torque is essential. This rules out the use of thick greases.

A first class of servomotor has a working temperature of about 100° to 110° C and functions satisfactorily on present standardized aircraft greases.

The next class operates in the temperature range of 140° to 160° C. We find that most aircraft greases fail to meet this condition, but one grease has been shown to be satisfactory.

The third class of motor has a working temperature in the range 200° to 220° C. The requirement is that it shall give a minimum life of 1000 hr when tested at 200° C under a journal load of 250 g at a speed of 3000 rpm. We have not found any grease that will meet this requirement. On the other hand, systems using dry self-lubricating cages without oil or grease have proved satisfactory.

This situation exists despite the fact that military specifications for greases include performance tests at temperatures that may be as high as 232° C, as in the case of specification DTD 5585 (MIL–G–25013D). One notes, however, that these performance tests invoke the use of 20-mm-bore ball bearings.

We also find that whereas a product supplied by one manufacturer to a given military grease specification will meet the performance laid down for an electrical machine, an alternative supply from another manufacturer may prove to be inferior. This is an unsatisfactory technical situation that may cost something like £1000 to make the necessary proving tests.

We therefore feel we have some way to go before we are satisfied either that we have adequate greases and grease specifications or that we know properly how to evaluate greases and use them to best advantage in certain specialty applications.

You will note that I am only speaking about shortcomings in grease performance. Grease storage is another problem area and not dealt with here.

In an attempt to resolve some of the above difficulties, we have been sponsoring work with the objective of finding out why aviation greases have lower maximum operating temperatures in miniature ball bearings than would perhaps be predicted from their performance in the larger rigs quoted in military specifications.

In general terms, we recognize that as the size of a bearing is decreased there will be an increase in the ratio of surface-to-volume effects. Put in another way, one would expect the grease in a miniature bearing to offer a larger free surface area per unit weight of grease and that this would tend to accentuate degradation due to volatility and thermal or oxidative instability.

We ran a selected variety of greases in servomotor bearings housed in ovens maintained at a fixed temperature. We incorporated a flywheel in the system so that a periodic check on rundown time could be made to monitor grease performance. Failure was deemed to occur when the motor stalled during running or when it failed to restart after a rundown check. We somewhat arbitrarily selected a life of 3000 hr as indicating satisfactory performance.

Table 10 shows our observed maximum operating temperatures for satisfactory performance with a variety of grease types. You will see that only one grease operated satisfactorily at a temperature higher than 150° C.

All bearings and greases were suitably examined after test. As a result we have made the following observations:

(1) Failure of greases based on hydrocarbons and esters was mainly due to the high volatility of the base fluid. This resulted in a hard dried-out residue. There was no evidence of grease or oil leakage causing failure.

(2) Failure of greases based on conventional silicones was associated with high volatility of the base fluid. These greases also allowed wear to occur, and the wear particles may have contributed to catalytic degradation. Another contributory factor was the increase in grease stiffness due

TABLE 10.—*Observed Upper Temperature Limits of Greases in Miniature Ball Bearings*

Grease	Upper temperature limit
Clay/ester, DTD 825 B	90° to 120° C
Clay/ester, DTD 5598	≃90° C
Lithium soap/ester/mineral oil, DTD 825 B	90° to 100° C
MIL–G–81322A, grease A	<150° C
Dye/MS 510/50 silicone	<150° C
Dye/MS 510/50 silicone (DTD 5585)	120° to 150° C
MIL–G–81322A, grease B	<150° C
Clay/ester/mineral oil, DTD 5579	>120° to 150° C
Lithium soap/MS 510/50 silicone	>120° to 150° C
Lithium soap/MS 550 silicone	>120° to 150° C
Fluorosilicone grease	>150° to 175° C

to oxidation. This remark is based on the fact that enhanced performance was obtained by running the bearings in an atmosphere of nitrogen.

(3) Failure of the fluorosilicone grease was attributed to volatilization of the base fluid. Wear was not a contributory factor.

(4) The performance of greases in miniature bearings cannot be predicted with accuracy by reference to the high-temperature performance requirement in the appropriate specification.

Further work will be required to identify more clearly the relative importance of the various factors leading to grease failure in miniature bearings. We have the subject under active consideration.

I am sure you will all agree that the formulation and development of specialty high-temperature greases is a difficult subject. Great advances have been made over the past 30 years or so. However, I feel there is a need to know much more about the fundamentals of grease structure and formulation and the ways in which the structures change during use. We have tried to interest various schools of surface chemistry in this subject, but without success. Such schools appear to be largely preoccupied with studying more simple disperse systems and also largely to confine their work to systems based on aqueous media.

We are grateful to Shell Research Ltd. who carried out much of the practical work on this subject under contract to the Ministry of Defence.

E. L. Armstrong (Mobil Research and Development Corp., Princeton, N.J.)

Mr. McCarthy's paper on lubricating greases comprehensively reviews the many advances that the industry has made in developing improved products to satisfy the needs of automotive, railroad, industrial, and space-age equipment. A remarkable variety of fluids, gelling agents, and additives have been studied and evaluated since World War II, and many interesting changes have occurred to this class of lubricants.

My comments are supplementary to McCarthy's concluding topic of areas of needed research. His presentation emphasizes the research needed from a viewpoint of the application requirements and the improved materials, such as fluids, oxidation inhibitors, and EP additives, required to provide better stability under more severe conditions. In addition to studies of better materials, research is also needed on many of the mechanisms that are important to the performance of lubricating grease: how it is applied and retained in place and yet releases sufficient lubricating liquid to minimize friction and wear where rolling, sliding, and vibrating motions are taking place. Among the most important mechanisms (refs. 9 and 10) that affect operation in grease-lubricated systems are mechanisms of grease lubrication, mechanisms of grease flow and structure, and mechanisms of grease oxidation. Some of the complexities of these mechanisms and their interactions are illustrated in tables 11 and 12.

TABLE 11.—*Grease Mechanisms for Further Research—Flow/Structure Studies*

Flow (structure) mechanisms	Non-Newtonian nature	Shear rate for viscometric studies, sec^{-1}	Method of observation	Method of collecting particle size statistics
(1) Network elasticity (gross structure)	+++	10^{-3} to 1.0	Optical microscopy	
(2) Network breakage (fine structure)	++	1.0 to 10^5	Electron and scanning electron microscopy	Coulter counter
(3) Particle breakage (internal structure)	+	10^6 to 10^7		
(4) Oil phase	0			

TABLE 12.—*Flow (Structure)/Lubrication Performance Interactions*

Flow (structure) mechanisms	Grease properties affected	Application and bearing speed aspects
(1) Network elasticity	Consistency, stringiness, and oil release	Application devices (pumps and pipelines); resistance to end leakage; slow-speed bearings (DN to 10^4)
(2) Network breakage	Consistency, stringiness, oil release, evaporation, water resistance, mechanical stability, load support (viscoelasticity), elastohydrodynamic lubrication and starvation effects, boundary lubrication, adhesion (particle/substrate interactions), and work breakdown (leakage past seals)	
(3) Particle breakage	Evaporation, water resistance, mechanical stability, load support (viscoelasticity), and elastohydrodynamic lubrication and starvation effects, boundary lubrication, adhesion (particle/substrate interactions, and work breakdown (leakage past seals)	Normal-speed bearings (DN to 4×10^5); high-speed bearings (DN to 4×10^6)
(4) Oil phase		

Table 11 indicates four differing types of grease flow mechanisms. These can be studied in viscometers at varying shear rates from 10^{-3} to 10^7. The gross structure responsible for network elasticity is observable by optical microscopy techniques; the fine structure and internal particle structure, by electron and scanning electron microscopy.

In table 12, lubrication performance aspects are related to the grease flow-to-structure mechanisms. It is shown that network elasticity and network breakage (occurring at low-shear-rate regimes) affect certain grease properties and related behavior in application devices and bearings.

Particle breakage and oil-phase properties (exhibited at much higher shear rates) affect performance properties such as elastohydrodynamic (EHD) or boundary lubrication and the behavior of a grease in high-speed bearings.

Oxidation mechanisms important to grease lubrication life can be divided into two categories. Specific to lubricating greases are particle catalytic effects, particle network degradation, and particle degradation. Common with other liquid lubricants are antioxidant degradation, degradation of other additives, and oil degradation. The importance of effects caused by the gelling agent particles and particle network that are specific to lubricating greases as distinguished from other liquid lubricants should be noted.

The mechanisms noted in tables 11 and 12 and the text and others such as surface migration phenomena all contribute to the end result of how well and how long a grease lubricates a bearing. Research on these mechanisms will greatly assist the identification and development of improved greases for the future.

H. Schwenker (Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio)

Mr. McCarthy's lecture on lubricating greases is primarily devoted to soap-thickened petroleum oil greases and their state of the art. The reason for this as given by the author is that 99 percent of the greases produced by industry have a petroleum oil base and approximately all but 8 percent of these are soap thickened. Unfortunately (in this discussor's opinion), they do not represent the highest level of grease technology or state of the art with respect to properties and performance. It is most misleading to base industry's top capability with respect to grease products and their capabilities to meet stringent and critical applications like those used in the aerospace industry or specific commercial applications on the soap-thickened petroleum oil greases. I am stressing this point primarily for those who are not thoroughly familiar with grease technology and the overall state of the art. The author, who is one of the most capable and active grease experts in the industry, is quite cognizant of this (for example, one of the best high-temperature nonsoap thickeners, ammeline, resulted from his efforts). The writing of a paper or presenting of a lecture on a subject that contains many facets is most difficult, and the author must therefore select and reject certain areas for discussion which in his opinion are most pertinent. The author has done well in this respect of his coverage of the soap-petroleum oil greases.

The rest of my discussion contains specific comments on the contents of the lecture or material that I would have liked to have seen covered within the author's framework.

Basic Components of Greases.—With respect to the fluid phase, the author should have included perfluoroalkyl ethers and synthetic hydrocarbons. These fluids are finding increasing usage in the aerospace industry. The synthetic hydrocarbon base greases are being used most effectively in wheel bearings of military aircraft, and the perfluoroalkyl ether greases in high-temperature applications, space greases, and where chemical resistance is required. It would have been helpful if the author had devoted more time in this area concerning base fluid characteristics and their selection for specific needs because the limitations and capabilities are influenced primarily by their base oil component. The author stresses the fact that the petroleum oil phase of a grease is complex; however, he does not mention that with synthetic hydrocarbon and other nonpetroleum fluids this undesirable complexity can be avoided.

The discussion on the thickener phase should include nonsoap thickeners because they are primarily responsible for advancing the state of the art with respect to high-temperature capability, chemical resistance, and long-term storage and operation stability. While they may make up only a small portion of the total grease market, they are absolutely essential to the operation of the aerospace industry.

Advantages and Disadvantages.—The author covers most of the advantages of using greases. However, there are other important factors not mentioned that should be covered. Grease lubrication has become more and more the favorite method of lubricating aerospace equipment because of the need for minimizing weight and space of equipment used in aircraft, missiles, satellites, and spacecraft. A greater range of additives can be used in larger amounts than with liquids, thereby providing greater load-carrying ability, rust protection, etc. Seals are easier to design and are not as likely to cause increased friction and power consumption as in the case of liquid lubrication. Maintenance is either eliminated or greatly minimized. Elements such as ball and roller bearings can be prepacked, providing lifetime lubrication and insuring correct selection of lubricant. Requirements of various different types of elements within aerospace equipment often require lubricants with different characteristics. This can be accomplished by the use of grease lubricants without the complicated design required for oil lubricants. The author points out that one of the disadvantages of grease lubricants is their lack of uniform character and that grades of greases of different manufacturers often differ widely in their physical and chemical properties. This can be eliminated by the use of strict specifications such as those employed by the military. One disadvantage of grease lubrication not mentioned is its inability to remove debris and degradation products from contact areas. It cannot be purified like liquid lubricants in circulatory systems. There are a limited number of methods of grease application and few devices to accomplish it.

Grease Classification and Types.—The author does not present a great detail of information on nonsoap synthetic oil base greases. The following information on these types of greases will help to provide a more complete picture of the state of the art of grease technology.

Nonsoap Synthetic Hydrocarbon Greases.—These greases have an overall temperature range of −80° to 350° F in an oxidizing atmosphere. Since the synthetic hydrocarbon base fluids are very susceptible to improvement by additives, they can be made to have improved oxidation stability and load-carrying ability over ordinary petroleum oils by the use of antioxidants and EP additives. There are two military specifications covering this type of grease: MIL–G–81322, which is intended specifically for use in wheel bearings in internal brake assemblies, antifriction bearings, gear boxes, and plain bearings over a −65° to 350° F temperature range; and MIL–G–81827, intended for use in heavily loaded bearing and gear application over a −80° to 350° F temperature range. This material contains MoS_2 as an EP additive. Many nonsoap thickeners are available that will allow full exploitation of the synthetic hydrocarbon base fluids such as ammeline, Teflon, arylurea, clays, and silicas.

Ester Base Greases.—The state of the art in this class is well represented by the lithium soap or non-soap-thickened dibasic acid ester greases conforming to MIL–G–23827. This grease is intended for use in ball, roller, and needle bearings, gears, and on sliding and rolling surfaces of such equipment as instruments, cameras, electronic gear, and aircraft control systems. It is particularly suitable for equipment that must operate at both low and high temperatures. Its extremely low volatility is of advantage in preventing oil fogging in optical instruments. This grease is also intended for general use on aircraft gears, actuator screws, and other equipment requiring a high load capacity over −65° to 250° F. It will function for short periods up to 300° F.

Non-soap-thickened pentaerythritol greases have worked satisfactorily in ball- and roller-bearing applications over the −40° to 350° F temperature. Short excursions up to 450° F can be tolerated.

Silicone Greases.—Soap-thickened silicone greases consist essentially of two types of base fluids, methylphenyl silicones and chlorophenylmethyl silicones. Soap thickeners used are lithium octoate, lithium 12-hydroxystearate, and lithium stearate. The majority of these soap silicone greases are used in lightly loaded antifriction bearings and cover various temperature ranges depending upon the soap thickener and silicone fluid used. The top temperature these greases can obtain is 350° F when lithium octoate is used as the thickener and the lowest temperature is −100° F when a methylphenyl silicone base fluid is used. Chlorophenylmethyl silicone soap-thickened greases give slightly improved wear characteristics over methylphenyl silicone grease and can be used in some applications where increased load-carrying ability is required.

Non-soap-thickened silicone greases comprise the bulk of military specification greases and are used as extreme high-temperature or extreme wide-temperature range lubricants. Examples of these type lubricants are: MIL–G–25013(D) (−100° to +450° F). The base fluid is a methylphenyl silicone, and thickeners are of the nonsoap types such as arylurea and indantherene dyes. These greases are used primarily in antifriction bearings under light loads and at moderate to high speeds. They are used in instruments, electric motors, generators, guidance and control mechanisms, camera, radio and radar equipment, wheel bearings, and engine accessories. MIL–G–83261 is a polytetrafluoroethylene-thickened fluorosilicone grease with a temperature range of −100° to 450° F. It is intended for use in gear trains and antifriction bearings under heavy loads. It has exceptionally good wear characteristics for a silicone-type grease. Ammeline-thickened high-phenyl content greases covered under MIL–G–38227 will perform in antifriction ball bearings at temperatures from 0° to

600° F. A polytetrafluoroethylene-thickened fluorosilicone grease (MIL–G–27617) is used in ball and roller bearings, on plug valves, fittings, sliding surfaces, and other applications where fuel, oil, and liquid oxygen resistance is required. The low volatility characteristics of nonsoap silicone greases have made them desirable lubricants for space applications when used in conjunction with specially designed sealed bearings.

Perfluoroalkyl Ether Greases.—Polytetrafluoroethylene-thickened perfluoroalkyl ether grease have found use in (MIL–G–38220) antifriction bearing applications up to DN values of 400 000 and over a temperature range of −40° to 400° F. They are also used in the missile and aircraft industry (MIL–G–27617) for use in ball and roller bearings, on plug valves, fittings, sliding surfaces, and other applications where fuel, oil, and liquid oxygen resistance is needed. They are also desirable lubricants for use in space applications where low volatility is of primary consideration.

Manufacturing Methods for Nonsoap Greases.—In addition to the normally used method outlined by the author, some nonsoap greases such as the aryl ureas are prepared by the in-situ-type process normally associated with soap greases.

The Future of Greases.—The author's discussion on the future of greases presents a worthy challenge to those working in this area of lubrication. While the subject of ecology is touched upon, one aspect of possible increased usages of grease might be as a substitute in applications where waste oil presents an ecology problem. The use of grease here would eliminate the necessity of continually getting rid of the waste oil.

Areas of Needed Research.—Rather than pointing out a specific path to be followed here, I feel that significant contributions to grease technology and advancements in the state of the art can be made that will greatly increase the use and importance of grease lubrication by expending efforts in the areas of the basic factors involved in gel formation and stability, additives, thickeners, base oils, application methods, and special bearing design.

Of these areas, the one the grease researcher has probably the least opportunity to make contributions in is that of base fluid development. Generally he is dependent upon the efforts of others to provide advances in the state of the art here. It is therefore necessary for grease research effort to be devoted to reaching the maximum potential from other grease components, formulation, and preparation. Concepts should not become ironclad, or progress will be impeded. An example of this can be best illustrated by the successful use of ammeline as a thickener in high-temperature, high-speed greases. Thermal stability has been the No. 1 criterion for high-temperature thickeners; however, in this case the ammeline degrades slowly, without harmful degradation products, keeping pace with the diminishing oil supply and thereby maintains a favorable thickener-to-oil balance over a substantial period of time. Grease formulated from this type of material outperformed other greases formulated from more thermally stable thickeners. In 20 years we have seen men progress from breaking the sound barrier to walking on the moon. I believe that similar progress can be made in grease technology if the effort is made.

LECTURER'S CLOSURE

The author thanks the various discussers and will attempt to answer each individual's comments and questions.

As pointed out in the oral presentation of this paper, both Boner and Klemgard have covered very extensively many phases of the grease field. A paper on greases can cover rather broadly a specific phase or rather narrowly a number of aspects. The paper presented was of the latter type and consequently many areas of specific interest to various individuals were, of necessity, omitted.

In reply to Professor Salomon, I have the following comments.

It is not essential that greases prepared from fatty acids contain structure modifiers such as water or alcohols to produce consistent greases. There always is the possibility that greases compounded from different components may not be compatible.

Chlorinated materials have been used and can, depending on type, impart both EP and antiwear properties.

Discussion of mix-base greases was very brief. My statement "The mixed-base greases consist of petroleum oils, plus two or more of any of the metallic soaps discussed previously or the soaps of lead, zinc, magnesium, etc." covers, by inference, mixed calcium-lithium greases. The author's experience with lead-complex greases is negligible and explains lack of discussion.

Personal experience with DTA tests yielded negligible information of practical value.

As proposed by Mr. Dyson, investigation of the nature and viscoelastic properties of lubricating fluid released from greases could well be added to the long list of areas of needed research. Information of this nature could be of academic interest. Its importance to performance might be very difficult to assess.

Based on the data presented, the special form of graphite used as a thickener by Mr. Groszek appears to warrant further investigation.

With reference to Mr. Kinner's comments, the author agrees that results of performance life tests in size 204 bearings cannot be used as a firm basis to predict life in miniature (1/4 smaller bore) bearings. The types of bearing tests specified by various military specifications can, however, differentiate between greases, assuming that a sufficient number of tests are run under closely controlled conditions. The extremely small amount of grease available to a miniature bearing is probably the limiting factor in life. Use of a single-shield bearing, changes in design of equipment to provide grease storage space adjacent to the unshielded side, and use of a grease with adequate high-temperature properties and a controlled bleed rate in the cavity would probably prolong life.

Mr. Armstrong has proposed very pertinent areas for fundamental research, and the author agrees that, with the proper guidance, the studies proposed could provide invaluable information as to how and why greases function or fail to function as they should. To be of value, however, the practical aspects and eventual end use of information to be developed should be of prime consideration. Unfortunately, sufficient emphasis is not placed on these areas in many fundamental research projects.

Mr. Schwenker's area of immediate concern is the development and evaluation of greases intended for the lubrication of aircraft and space components exposed to severe environmental conditions. He chides the author for failure to devote more discussion to this phase.

As mentioned previously, a paper can cover in depth only a small area. The author chose the bread-and-butter areas that help to support investigation of the more exotic phases. Investigation of many fluids, thickeners, and additives as potential grease components and evaluation of the individual components and greases have been covered extensively by the author and others under Air Force contracts. A limited amount of this information has been published, but much of the meat is buried in technical reports. Ready access to the latter could eliminate replowing of old fields, including some of the areas indicated for needed research.

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Theory of Rheology

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For many lubrication problems, the lubricant can be considered to be a Newtonian liquid with a viscosity that depends only on temperature and pressure. On the other hand, since most lubricants are viscoelastic, operating conditions will be found in which the Newtonian approximation will no longer be valid. Then the main questions for a tribologist are how the consequences of viscoelasticity can be predicted and how lubricants can be formulated to give control over viscoelastic properties. As a contribution to the answering of these two questions, this paper discusses the theory of rheology from two different standpoints.

First, rheology is discussed as a branch of continuum mechanics. The discussion is about relationships between stress, strain, and strain rate (constitutive equations), which will give a better representation of lubricant properties than the Newtonian flow equation. The simpler, so-called small-strain, linear models, such as the Maxwell model, are discussed first because these will be fairly familiar. Then the problem of dealing with large-strain viscoelasticity is introduced. This is a complicated matter but essential to understand if the first of the above-mentioned questions is to be answered properly. Following this, the responses of the simpler models to large-strain simple shears are calculated and shown to be at variance with experiment. More advanced models and ways of improving the simpler models are then treated to show how their development has followed a logical progression from basic ideas.

Second, rheology is discussed as a branch of chemical physics. Consideration is limited to those theories of nonpolymeric and polymeric liquids that have some ability to represent viscoelasticity in terms of identifiable and measurable molecular characteristics.

Last, two additional paragraphs deal with the possibility that elastic liquids may rupture in shear and linear tension in an analogous way to solids and the Deborah number, which is a dimensionless group containing viscoelastic material parameters.

This paper is concerned with the structure of the modern theory of rheology, with its assumptions and limitations. It is concerned with those branches of the subject that will be needed in answering the two above-mentioned questions. It is not concerned with applications to lubrication theory, past or future, although certain applications are mentioned in passing to provide a link with lubrication theory.

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THIS REVIEW has turned out to be a lengthy one. One reason for this length is that rheology has been a science in its own right for a long time and during this period there has been considerable progress. The requirements of industry have played a large part in this, and this fact is no better illustrated than in the field of polymer rheology. A lot is known about polymer rheology because of the vast industry that needs to know about it. And this leads to the second reason, namely, that in the lubrication industry theoretical rheology has not often been applied to the solution of problems as rigorously as it might have been: this suggests that there may be a lack of appreciation of the basic principles. Of course, the Newtonian approximation with, perhaps, a temperature and pressure dependence of viscosity is adequate in numerous instances, and there is no need to add complications to an already complicated situation. But there are indications that at the limits of lubrication with Newtonian oils, as well as with polymer-containing oils, viscoelastic effects are being observed.

This review is not intended to be complete, but it covers the basic reasoning behind much of continuum theory and molecular theory. It covers many of the aspects that are likely to be relevant in lubrication. Also, if a few of the references were to be followed up, the rest of the subject would soon be revealed.

Two major and related topics have been omitted. Lubricating greases are mentioned here and there, but grease rheology has not been discussed. Also, there is no mention of the approach to the rheology of anisotropic liquids originated by Ericksen (refs. 1 and 2). This is a continuum theory in which the stress tensor is taken to be a function not only of the rate of strain tensor but also of a vector that is a measure of the direction and degree of orientation of the structure. The theory has been taken up, so far, by those interested in liquid crystals, but it should have a more general application.

An attempt has been made to achieve a degree of continuity throughout the paper. This has been done, first, by using a consistent notation and, second, by linking together the several approaches to rheology theory through the stress relaxation function and its close relative, the relaxation time spectrum. These functions are introduced early in the treatment. It should, however, be pointed out that although these functions are to be found in all valid theories, they are strictly linear and are not to be found exclusively in the higher order terms of finite-strain theory. The higher order terms will contain material functions that are nonexistent in the linear theory.

SHEAR ELASTICITY IN LIQUIDS

The coexistence of elastic and viscous properties in certain materials has been recognized for many decades. Usually it has been thought that most of the common materials are either purely elastic solids or purely viscous liquids and that the viscoelastic [1] materials are rather scarce special cases. For some time a few rheologists, notably Weissenberg, have insisted that the converse of this statement is true and that there are few materials which behave according to the mathematical abstractions known as the elastic solid (Hooke model) and the viscous liquid (Newtonian or Navier-Stokes model). We hope to show in the next few paragraphs that greases, mineral oils, and synthetic oils are all viscoelastic.

Lubricating greases are materials that can be characterized in the linear approximation by a viscosity and a yield stress. Measurements made by Vinogradov and Klimov (ref. 3) and by the author (ref. 4) at stresses below the yield stress have shown that the creep properties of greases can be analyzed in terms of three components: a pure elastic deformation, a delayed elastic deformation, and an irreversible deformation. These results are typical of the viscoelastic solid. Greases have also been studied in oscillatory shear. This type of testing, in which the amplitude and phase relations between the input motion and the output stress are measured, is complementary to creep testing. As will be discussed later, the results can be expressed in terms of two shear moduli: G', the in-phase modulus that is an elastic modulus, and G'', the out-of-phase modulus that is related to the viscosity. Forster and Kolfenbach (ref. 5), using two coaxial cylinders with grease contained in the intervening space, and Harris and Bogie (ref. 6) and Yousif and Bogie (ref. 7), using a rheogoniometer, have demonstrated that greases have a finite value of G'. Typical values at low frequencies are in the vicinity of 1 $\mathrm{kN/m^2}$.

Lubricating oils containing polymeric viscosity index (V.I.) improvers are elasticoviscous liquids. Oscillatory shear experiments, mentioned in more detail later, have demonstrated the presence of elasticity, but the determination of elastic parameters in continuous shear is not easy in these oils because at moderate to high operating temperatures, the elasticity is small. Most experiments have been designed to find the variation of viscosity of polymer-containing oils with rate of shear. For example, in the early days a number of investigations (ref. 8) showed the decrease of viscosity with increasing rate of shear. Later work by Horowitz (ref. 9) showed a more convenient correlation of viscosity with shear stress, the results for solutions of different concentration and temperature lying on the same curve. Philippoff (ref. 10) has shown that instruments of basically different design give results that must be suitably treated to give a unique viscosity-shear stress relationship independent of the apparatus. Hence the treated results are properly invariant characteristics of the oils. The problem of invariance is discussed later.

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[1] The word "viscoelastic" is used in a general sense for materials having combined viscous and elastic behavior. It is also used for solids that can be made to flow. The word "elasticoviscous" refers to liquids that can be made to deform elastically.

The fact that viscosity varies with rate of shear is not conclusive evidence that the liquid is elasticoviscous but is a strong indication of this. Conclusive evidence of elasticity is provided in a number of ways, one of which is the phenomenon of recoil. If an elastic liquid is rotated or stirred and the motion is suddenly stopped, there is an instantaneous reverse shear in the liquid that can be made visible by the presence of a bubble or a suspended solid particle. Other indicators of elasticity are the generation of normal stress components in shear and the Weissenberg effect; that is, the rise of liquid up a rotating rod dipping into a shallow bowl of liquid. The Weissenberg effect is a consequence of the existence of normal stresses that will be discussed later. All of these elastic effects have been demonstrated in motor oils containing polymeric additives, particularly at low temperatures.

Molten polymers are elastic liquids that have been studied widely because of the importance of the rheological properties in the polymer-processing industry. A molten polymer that is also of interest in lubrication is the silicone fluid. The dimethylsiloxanes have been shown to be non-Newtonian, and the normal stress components have also been measured (ref. 11) in liquids of this type of medium to high viscosity.

The next class of liquids to consider is that of the low-molecular-weight mineral and synthetic oils. The demonstration that such liquids are elasticoviscous requires some very sophisticated apparatus and experimental technique. The now classic paper in this field is that of Barlow and Lamb (ref. 12), who studied the response of three straight, conventionally refined, lubricating oils of low, medium, and high V.I. to oscillatory shear at frequencies in the range 6 to 78 MHz. For details of the technique, the reader must refer to the literature (ref. 13). The results showed that the oils were elastic with the in-phase shear modulus G' rising to values of about 700 MN/m^2 at 30° C. Similar oils have been investigated more recently (ref. 14) in the same frequency range, while other work (ref. 15) has been done at rather lower frequencies. Many liquids, pure ones and mixtures, have now been studied (refs. 16 to 18). Those representative of synthetic lubricants include di(2-ethylhexyl) sebacate, dioctyl adipate and *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether. These liquids, as well as quite simple hydrocarbons such as *n*-propylbenzene (ref. 16) and heptamethylnonane (ref. 19), have all been shown to be elasticoviscous.

Lamb and his coworkers have used another technique operating in the kHz frequency region to study liquids rather more elastic than straight mineral oils. Their work has shown elastic effects in the silicone fluids with viscosities of 100 to 100 000 cs at 30° C (ref. 20) and in dilute polymer solutions such as polystyrene in toluene (ref. 21). Polyisobutylene solutions in hydrocarbons have also been studied in oscillatory shear at rather lower frequencies (ref. 22).

A very important difference between the simple liquids, on the one hand,

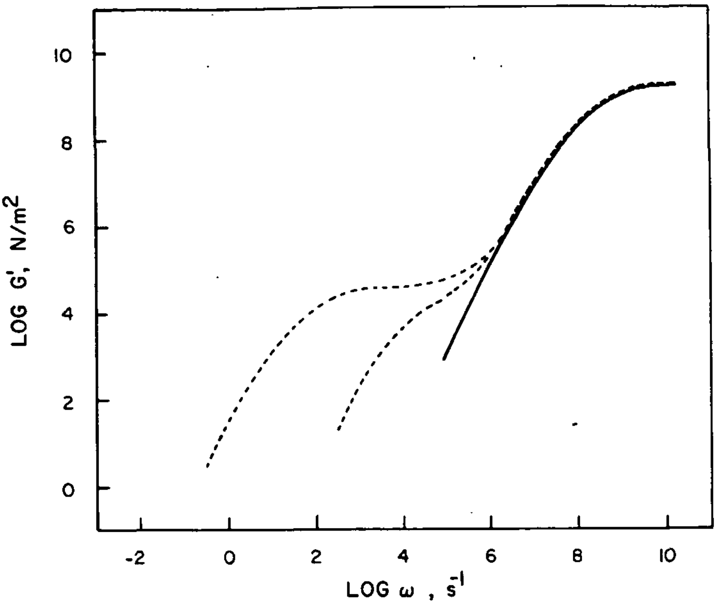

FIGURE 1.—Schematic diagram based on experimental results showing how the variation of the in-phase shear modulus of simple liquids with frequency ω (full line) differs from that for polymer melts and solutions (dashed line).

and the molten polymers and polymer solutions, on the other, can be noted by comparing the results of oscillatory shear experiments. The difference is illustrated schematically in figure 1. Whereas for both classes of material the modulus rises with increasing frequency to reach an ultimate level of the order of 1 GN/m^2, for the polymeric materials there is an additional plateau where the modulus levels out. The extent of the plateau and the value of the modulus for the plateau depend on the molecular weight and concentration of the polymer, but the deviation from the curve for a simple liquid occurs at a shear modulus of the order 100 kN/m^2, that is about four orders of magnitude lower than the limiting value for the simple liquid. This low modulus is characteristic of high polymers. The origin of this low modulus in molecular terms is fundamentally different from that of the high modulus in all liquids, as will be discussed later.

CONSTITUTIVE EQUATIONS OF CONTINUUM MECHANICS

With the elasticoviscous nature of most lubricants established, the next problem is to find out whether or not the elasticity is important in lubrication and in what way. This can be approached experimentally, but a theoretical calculation of what to expect would greatly assist the interpretation of results. To carry out the calculation it is necessary to have a relationship between stress and strain and the rates of change of these; i.e., a constitutive equation, sometimes known as a rheological equation of state. In general terms, the constitutive equation will relate the state of stress to changes of shape that have occurred up to the instant considered. Temperature should also be considered as a variable in a completely general case, but in rheology isothermal conditions are usually assumed. It is also usual to consider the material as incompressible.

Constitutive equations can be divided conveniently into two classes: for conditions of infinitesimally small strains and for conditions of finite strain. Although the latter class contains the former as special cases, it is a less familiar class; therefore, it may be more enlightening to deal with the special cases first.

SMALL-STRAIN LINEAR VISCOELASTICITY

The Maxwell Model

If a small shear strain γ is considered to be made up of a viscous component γ^v and an elastic component γ^e, we have

$$\gamma = \gamma^v + \gamma^e \tag{1}$$

Then from Hooke's law of elasticity and Newton's law of viscosity, the Maxwell model can be derived for shear stress σ by

$$\sigma + \tau\dot{\sigma} = \eta\dot{\gamma} \tag{2}$$

where the dot refers to the ordinary differential with respect to time, $\tau \equiv \eta/G$ is a material constant with the dimension of time, η is a viscosity, and G is a shear modulus of elasticity.

In steady shear with a constant rate of shear ($\dot{\gamma} = D$ and $\dot{\sigma} = 0$), the shear stress is constant and equal to $\sigma_0 = \eta D$: the Maxwell model has a constant viscosity in steady shear. If the shear is suddenly stopped at a time t', then $\dot{\gamma} = 0$ for $t > t'$ and equation (2) becomes

$$\sigma + \tau\dot{\sigma} = 0$$

By integrating between t' and current time t, the current value of the stress is obtained:

$$\sigma(t) = \sigma_0 \exp\left[\frac{-(t-t')}{\tau}\right] \tag{3}$$

The stress therefore relaxes exponentially to 0 after an infinite elapsed time and with a characteristic decay constant τ, which is known as the relaxation time.

For a sinusoidal oscillatory shear of the form

$$\gamma = \gamma_0 e^{i\omega t'}$$
$$\dot{\gamma} = i\omega\gamma$$

it can be derived readily that the real and imaginary components of a complex shear modulus defined as

$$G^* \equiv G' + iG'' \equiv \frac{\sigma}{\gamma}$$

are given by

$$\left.\begin{aligned} \frac{G'(\omega)}{G(\infty)} &= \frac{\omega^2\tau^2}{1+\omega^2\tau^2} \\ \frac{G''(\omega)}{G(\infty)} &= \frac{\omega\tau}{1+\omega^2\tau^2} \end{aligned}\right\} \tag{4}$$

Hence, G' and G'' are functions of the angular frequency ω. In these relationships, G of equation (2) has been rewritten $G(\infty)$ because it is the value of the shear modulus $G'(\omega)$ at infinite frequency of oscillation. We have already referred to G' and G'' in the previous sections as the in-phase and out-of-phase moduli. $G'(\omega)$ is sometimes known as a storage modulus and $G''(\omega)$ as a loss modulus. If a complex viscosity is defined as the ratio of shear stress σ to rate of shear $\dot{\gamma}$, the real part $\eta'(\omega)$ is found to be related to $G''(\omega)$ by

$$\eta'(\omega) = \frac{G''(\omega)}{\omega} = \frac{\eta(0)}{1+\omega^2\tau^2} \tag{5}$$

where $\eta'(\omega)$ is known as the dynamic viscosity.

In this relationship, η of equation (2) has been rewritten $\eta(0)$ because it is the value of $\eta'(\omega)$ at zero frequency.

Thus, we see that the two parameters of the Maxwell model, $G(\infty)$ and $\eta(0)$, represent elastic or viscous behavior at limiting high or low frequencies. At intermediate frequencies the behavior is mixed; i.e., elasticoviscous. We also see that the dynamic viscosity decreases with frequency rather rapidly to 0 (eq. (5)), with most of the decrease occurring over the frequency range given by $0.1 < \omega\tau < 10$. The shear modulus $G'(\omega)$ increases from 0 to $G(\infty)$ over the same frequency range. This is also a more rapid change than is generally observed. It can be seen in figure 1 that in both the high- and low-frequency regions the main changes in G' occur over much more than two decades of frequency, whereas the Maxwell model predicts that such changes should occur in about two decades. It can be said that the transition from viscous to elastic behavior depends on the value of the relaxation time. The larger the relaxation time is, the lower the mean value of the frequency about which the transition occurs. Clearly the two parameters $\eta(0)$ and τ are the sufficient and most useful pair for characterizing a liquid that conforms to the Maxwell model.

The Distributed Maxwell Model

Very few liquids behave according to the Maxwell model. This model predicts a stress relaxation that is too rapid and a variation in $G'(\omega)$ and $\eta'(\omega)$ that is more precipitous than that shown by experiment. To overcome these difficulties it is convenient to postulate the existence of a number of relaxation processes, each with a characteristic time. A distribution function of relaxation times, sometimes known as a relaxation spectrum, is preferred to a set of discrete relaxations. The distribution function $H(\tau)$ can be defined by rewriting equations (4) as

$$\left.\begin{aligned} G'(\omega) &= \int_0^{\infty} \frac{H(\tau)\omega^2\tau^2}{1+\omega^2\tau^2}\, d\tau \\ G''(\omega) &= \int_0^{\infty} \frac{H(\tau)\omega\tau}{1+\omega^2\tau^2}\, d\tau \end{aligned}\right\} \tag{6}$$

In these expressions $H(\tau)\, d\tau$ represents the contribution to the modulus of the processes with relaxation times lying in the interval τ and $(\tau+d\tau)$. By putting $\omega=\infty$, we see that

$$\int_0^{\infty} H(\tau)\, d\tau = G(\infty) \tag{7}$$

Thus, the area under the spectrum is equal to the limiting shear modulus. In the literature, use has been made of other distribution functions that are all essentially equivalent. For example, Walters (ref. 23) uses a spectrum $N(\tau)$ and in the treatment of results for mineral oils (refs. 12 and 14), a relaxation frequency spectrum H (log F), where $F=1/2\pi\tau$, has been used. The relationships between these functions are

$$\frac{N(\tau)}{\tau}\, d\tau = H(\tau)\, d\tau = H\ (\log F)\ d(\log F)$$

By simple substitution, equations (6) can be written in terms of any of the spectra. The low-frequency limit is

$$\eta(0) = \int_0^{\infty} N(\tau)\, d\tau = \int_0^{\infty} \tau H(\tau)\, d\tau = \int_{-\infty}^{\infty} \frac{H\ (\log F)}{2\pi F}\, d\ (\log F) \tag{8}$$

Hence, the zero shear viscosity is equal to the first moment of the relaxation spectrum $H(\tau)$ and to the area under $N(\tau)$. It will be seen later that for large-strain viscoelasticity, higher moments of the relaxation spectrum become important. This fact places a burden on the experimental rheologist investigating liquids composed of small molecules because the long-time (hence low-frequency) end of the spectrum is not easy to measure with accuracy, yet this is the end of the spectrum that carries ever-increasing weight in successively higher moments.

The Barlow-Erginsav-Lamb (BEL) Model

Although the distributed Maxwell model cannot be completely characterized by a single relaxation time, it is nevertheless convenient to normalize time and frequency with respect to the ratio $\eta(0)/G(\infty)$. This ratio can be considered as an average Maxwell relaxation time for the distribution. Similarly, moduli are normalized with respect to $G(\infty)$. A few years ago Lamb and his coworkers (refs. 16 and 17) discovered that the experimental results for many different liquids, when plotted on the normalized coordinates, fell on the same pair of curves. Instead of plotting moduli, Lamb generally plots the related quantities, shear impedance R and X. The interrelations are

$$\left.\begin{aligned} G'(\omega) &= \frac{R^2 - X^2}{\rho} \\ G''(\omega) &= \frac{2RX}{\rho} \end{aligned}\right\} \tag{9}$$

where ρ is the density of the liquid. The reduced frequency is $\omega\eta(0)/G(\infty)$. Figure 2 shows the results for liquids covering a wide range of molecular structures and for a wide range of temperatures.

The lack of any systematic deviation from the unique curves for the real and imaginary components is remarkable. It is, therefore, tempting to regard all nonpolymeric liquids as having identical relaxation behavior. However, there is some evidence that this would be too sweeping a generalization (ref. 18).

Nevertheless, there is a regularity about the results that suggested to Lamb and his colleagues that perhaps a simple model would fit them. Their model (ref. 17) can be expressed simply as follows: the admittance Y (equal to the reciprocal of the impedance) of the liquid is the sum of the admittances of a viscous element Y^v and an elastic element Y^e:

$$Y = Y^v + Y^e \tag{10}$$

This can be contrasted with the Maxwell model in which the strains, or compliances, of the ideal elements are added. (See eq. (1).) By algebraic manipulation it can be shown that, for the BEL model

$$\sigma + \tau\dot{\sigma} + (4\tau\sigma\dot{\sigma})^{\frac{1}{2}} = \eta(0)\dot{\gamma} \tag{11}$$

where σ is the shear stress, the dot refers to the ordinary differential with respect to time, $\eta(0)$ is the zero shear viscosity, and τ, the relaxation time, is equal to $\eta(0)/G(\infty)$. This equation is directly comparable with equation (2) for the Maxwell model from which it differs by the term in the square root. For oscillatory shear motion, the real and imaginary components of the shear modulus can be derived (ref. 17). However, the expressions are complicated, and it is neater to quote for the shear compliance, defined by

$$J^* = J' - iJ'' = 1/G^* = 1/(G' + iG'')$$

Then the BEL model gives

$$J'(\omega) = \frac{1}{G(\infty)} + \frac{1}{[\omega\eta(0)\,G(\infty)/2]^{\frac{1}{2}}} \tag{12}$$

$$J''(\omega) = \frac{1}{\omega\eta(0)} + \frac{1}{[\omega\eta(0)\,G(\infty)/2]^{\frac{1}{2}}} \tag{13}$$

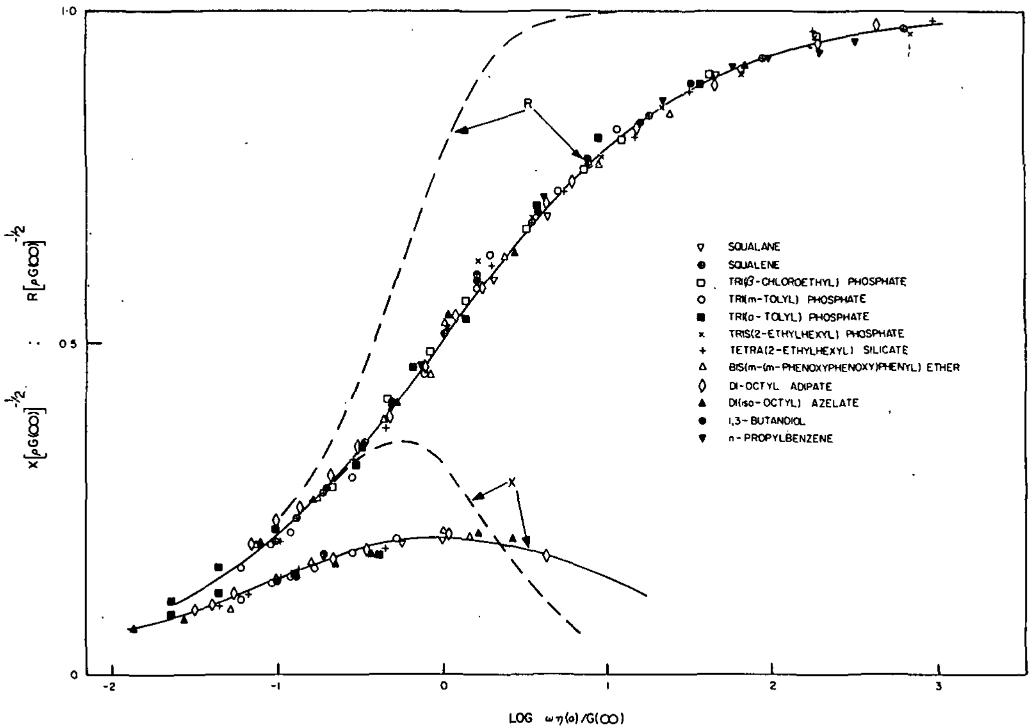

FIGURE 2.—Plots of values of $R[\rho G(\infty)]^{-\frac{1}{2}}$ and $X[\rho G(\infty)]^{-\frac{1}{2}}$ against $\omega\eta(0)/G(\infty)$ for a number of simple liquids. The solid lines are calculated according to the BEL model, and the dotted lines are for the Maxwell model. Data are provided by Prof. J. Lamb.

The first terms on the right-hand side are those given by the Maxwell model. The expressions for R and X are readily derivable from the model, and the full lines in figure 2 are obtained in this way.

It can be seen in figure 2 that the BEL model is very successful in representing the data, in contrast with the Maxwell model, which gives the dotted-line curve. This has been confirmed by independent studies (ref. 19). Moreover, only two material constants, $\eta(0)$ and $G(\infty)$, are required. While $\eta(0)$ is measurable in a straightforward way, $G(\infty)$ has to be determined by high-frequency techniques, and an extrapolation procedure is also required in some part of the temperature and pressure range. This extrapolation is discussed in the literature (ref. 19).

The Stress Relaxation Function

Equation (3) expressed the stress as a function of elapsed time in a relaxation experiment following continuous shear of a Maxwell model fluid. In another type of relaxation experiment, a strain is suddenly applied and held constant. The stress decays according to equation (3) in which σ_0 is now equal to the product of the constant strain γ_0 and the shear modulus G of the Maxwell model. The stress function divided by the strain is called the relaxation function ϕ.

If a strain γ_0 be applied to a distributed Maxwell model at time t', the stress in the nth element, according to modified equation (3), has the value at current time t of

$$\sigma_n(t) = \gamma_0 G_n e^{-(t-t')/\tau_n}$$

where G_n and τ_n are the constants of the nth element. The total stress on the model fluid is obtained by integrating over the distribution. Hence, the relaxation function is obtained:

$$\phi(t-t') = \frac{\sigma(t)}{\gamma_0} = \int_0^\infty H(\tau) e^{-(t-t')/\tau}\, d\tau \tag{14}$$

At $t' = t$,

$$\phi(0) = \int_0^\infty H(\tau)\, d\tau = G(\infty) \tag{15}$$

Consider now an increment of strain $d\gamma(t')$ applied at a time t' to any model liquid. Then by the Boltzmann superposition principle, the current stress is given by

$$\sigma(t) = \int_{-\infty}^{t} \phi(t-t')\, d\gamma(t') \tag{16}$$

and for a varying strain history

$$\sigma(t) = \int_{-\infty}^{t} \phi(t-t')\, \frac{d\gamma(t')}{dt'}\, dt' \tag{17}$$

where $d\gamma(t')/dt'$ is the rate of strain. Equation (17) gives the stress explicitly in an integral form. We shall see later some examples of constitutive equations expressed in this way. All the models so far mentioned can also be cast in this form.

It is of interest to consider the response of a general model to the sinusoidal shear $\gamma = \gamma_0 e^{i\omega t'}$. From equation (17)

$$\sigma(t) = \int_{-\infty}^{t} \gamma_0 i\omega e^{i\omega t'} \phi(t-t') \, dt'$$

Then, from the definition of the complex shear modulus, we get

$$G^*(\omega) = \frac{\sigma(t)}{\gamma(t)} = i\omega \int_{-\infty}^{t} e^{i\omega(t-t')} \phi(t-t') \, dt' \tag{18}$$

If the stress relaxation function is substituted in equation (18), the integration can be performed to give $G^*(\omega)$. As an example, if we introduce the relaxation function for the distributed Maxwell model (eq. (14)) and integrate to give $G^*(\omega)$, this then can be separated into real and imaginary parts to yield equations (6).

We see also that equation (18) is a Laplace integral transform in the complex variable $p = i\omega$. It follows that the relaxation function is obtainable by Laplace inversion of the function $G^*(\omega)/i\omega$, and because $G^*(\omega)/i\omega$ equals $\eta^*(\omega)$, the relaxation function is obtainable by inversion of the complex viscosity function. This inversion has been accomplished recently for the BEL model by Phillips (ref. 24) to give

$$\frac{\phi(s)}{G(\infty)} = \left[1 + 2\left(\frac{s}{\tau}\right)\right] \exp\left(\frac{s}{\tau}\right) \operatorname{erfc}\left(\sqrt{\frac{s}{\tau}} - 2\sqrt{\frac{s}{\pi\tau}}\right) \tag{19}$$

in which s is written for $(t-t')$ and erfc (x) is the complementary error function

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} \exp(-u^2) \, du$$

It can also be seen that equation (14) is a Laplace integral transform in $1/\tau$, hence in relaxation frequency F. Therefore, the relaxation spectrum $H(F)$ is in principle obtainable by Laplace inversion of the relaxation function. However, there is an alternative way of obtaining H. Gross (ref. 25) gives an inversion procedure (due to Fuoss and Kirkwood) for obtaining the relaxation spectra directly from $G^*(\omega)$. Again, for the BEL model this procedure (ref. 19) leads to

$$\frac{H(\tau)}{G(\infty)} = \frac{2}{\pi\sqrt{\tau}\,(1+\tau)^2} \tag{20}$$

Gross (ref. 25) discusses in detail the interrelationships between the various functions that appear in small-strain linear viscoelasticity. While the transforms are applicable to models for which certain of the functions are known in analytic form, they cannot be applied directly to numerical data. Thus, for a real material $G'(\omega)$ and $G''(\omega)$ may be known as tables of numbers. The conversion of these to a relaxation spectrum requires the use of an approximation procedure, of which there are a number (refs. 26 and 27). Published spectra for lubricating oils (refs. 12 and 14) were obtained by an approximation technique.

FINITE-STRAIN VISCOELASTICITY

The central problem in dealing with large strains and strain rates is that of invariance. By invariance is meant that constitutive equations, and in particular the constants characteristic of the material, must not change under changes of geometrical coordinates or of units of measurement. This is a fundamental principle of physics that has been recognized in elasticity theory for at least a century. Nevertheless, many rheologists and most engineers making use of rheological results take no notice of it. Weissenberg, Reiner, and Rivlin were pioneers in applying the principle to elasticoviscous liquids, but Oldroyd (ref. 28) was the first to state clearly what its consequences for rheology are. He has given the transformations required as well as the principles for generalizing constitutive equations.

The solution of the invariance problem is insured by using tensors of the second rank. The necessity for this complication is apparent once it is recognized that a stress, defined as a force per unit area, requires two directions, that of the force and that normal to the surface element, for its complete specification.

The notation we use follows that of Oldroyd and the treatment is taken from his papers and modified in the light of works by Truesdell (ref. 29) and Lodge (ref. 30).

The Strain Tensors

If a material is given a pure translational motion or a pure rotational motion, it suffers no distortion. This is an experimental observation. Therefore, the constitutive equations, which are relations in terms of distortion, must be independent of such motions. Sometimes this principle is called material objectivity or material indifference. A shear motion involves translation, rotation, and distortion; hence, the invariance problem is to set up usable relationships that are independent of translation and rotation.

It is convenient to consider the existence of two manifolds, one consisting of the material and the other of the space through which the material moves. Points in the material manifold are material particles, and points in the spatial manifold are places. The constitutive equation is written with reference to coordinate axes embedded in the material and that translate, rotate, and distort with the material. Since the shear is generated by boundaries moving in the space manifold, and forces are also measured in this manifold, the most convenient procedure is to transform the constitutive equation to the space manifold, although the reverse procedure is possible. This transformed equation is then used in conjunction with the conservation equations (mass, momentum, energy) to solve the flow problem.

There are many ways of expressing strain; two major ways are in terms of the change of separation between particles and between planes. In certain conditions these definitions are equivalent; in others they are not. The results obtained depend on the definition used.

Consider two points in a spatial coordinate system x^i ($i=1, 2, 3$) separated by a distance dS. Then the relationship[2]

$$(dS)^2 = g_{ij}(x)\, dx^i\, dx^j \tag{21}$$

defines a metric tensor $g_{ij}(x)$ that is a function of the coordinate system x^i. It is a measure of the separation normalized with respect to the coordinate system. In a rectangular Cartesian system, $g_{ij}(x)$ equals the Kronecker delta δ_{ij}, which has the values 1 for $i=j$ and 0 for $i \neq j$.

The separation between the same two points in material coordinates[3] ξ^i is

$$(dS)^2 = \gamma_{mn}\,(\xi, t)\, d\xi^m\, d\xi^n \tag{22}$$

Hence, from equations (21) and (22),

$$\gamma_{nm} = \gamma_{mn} = \frac{\partial x^i}{\partial \xi^m} \frac{\partial x^j}{\partial \xi^n}\, g_{ij}(x) \tag{23}$$

Equation (23) is a transformation relating the spatial metric tensor g_{ij} to the material metric tensor γ_{mn}, which is a function of the coordinate system and time. In this branch of rheology, we consider shear fields in which the coordinate system of the material does not change with time; hence, a line or a surface drawn in the material contains the same particles in the same relative positions throughout the motion (fracture and self-diffusion are thus excluded).

Consider two instants of time, the current time (a constant) t and some instant in the past (a variable) t'. At t', the coordinate systems can be written x'^i and ξ'^i, and at t they are x^i and ξ^i. Since, as stated above, ξ does not change with time, $\xi'^i = \xi^i$. It is clear from the definition of the metrics that the material strain is given by the difference between the metric tensors of the material at the two times.

$$\text{Strain} \equiv \epsilon_{ij} = \gamma_{ij}(\xi, t) - \gamma_{ij}(\xi, t') \tag{24}$$

A transformation to spatial coordinates gives

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[2] In relationships between tensorial components, if an index letter, e.g., i, is repeated and appears as both a superscript and subscript, it signifies summation over all values ($i = 1, 2, 3$) of the repeated index.

[3] As a rule, a Greek letter in this notation refers to the material and a Roman letter to the spatial manifold.

$$\epsilon_{ij} \rightarrow e_{ij} = \frac{\partial x^m}{\partial \xi^i}\frac{\partial x^n}{\partial \xi^j} g_{mn}(x) - \frac{\partial x'^m}{\partial \xi^i}\frac{\partial x'^n}{\partial \xi^j} g_{mn}(x') \qquad (25)$$

where the arrow sign means that the material tensor on the left transforms to the spatial tensor on the right.

Since the choice of coordinates is arbitrary, we choose that the spatial and material manifolds coincide at current time t, at which measurements are to be made. Then $\xi^i = x^i$, and

$$e_{ij} = g_{ij}(x) - \frac{\partial x'^m}{\partial x^i}\frac{\partial x'^n}{\partial x^j} g_{mn}(x') \qquad (26)$$

It is understood that for each pair of indices i and j, the quantities marked by the dummy indices m and n are to be summed over $m, n = 1, 2, 3$. The tensor e_{ij} is sometimes referred to as the Green-Almansi strain tensor, and $[g_{ij}(x) - e_{ij}]$, written C_{ij}, is called the Cauchy deformation tensor. The transformation process is shown diagrammatically in figure 3.

It has been mentioned that another measure of strain is given by changes in separation between planes drawn in the material. Such spacings are best described in terms of reciprocal base vectors. The metric tensors γ^{ij} and g^{ij} are written with superscripts to indicate that they are expressed in terms of reciprocal vectors and the components, known as the contravariant components, transformed in the inverse way to the covariant components. Thus

$$\gamma^{mn} = \frac{\partial \xi^m}{\partial x^i}\frac{\partial \xi^n}{\partial x^j} g^{ij}(x) \qquad (27)$$

The strain tensor in contravariant components ϵ^{ij} transforms as

$$\epsilon^{ij} \rightarrow e^{ij} = \frac{\partial x^i}{\partial x'^m}\frac{\partial x^j}{\partial x'^n} g^{mn}(x') - g^{ij}(x) \qquad (28)$$

The first term on the right-hand side is called the Finger deformation tensor B^{ij}.

Oldroyd (ref. 28) has also given rules for transforming the time derivatives of strain, but they apply for any tensorial quantity. The rules for the first differential of any material tensor τ_{ij} are

$$\frac{\partial \tau_{ij}(\xi, t)}{\partial t} \rightarrow \frac{\mathfrak{d} T_{ij}(x, t)}{\mathfrak{d} t} = \frac{\partial T_{ij}(x, t)}{\partial t} + v^m T_{ij,m} + v^m{}_{,i} T_{mj} + v^m{}_{,j} T_{im} \qquad (29)$$

$$\frac{\partial \tau^{ij}(\xi, t)}{\partial t} \rightarrow \frac{\mathfrak{d} T^{ij}(x, t)}{\mathfrak{d} t} = \frac{\partial T^{ij}(x, t)}{\partial t} + v^m T^{ij}{}_{,m} - v^i{}_{,m} T^{mj} - v^j{}_{,m} T^{im} \qquad (30)$$

The meaning of these equations, illustrated by considering equation (29), is that if the partial derivative occurs in the constitutive equation referred to material coordinates, it is transformed to spatial coordinates by replacing $\partial/\partial t$ by $\mathfrak{d}/\mathfrak{d}t$ (called the convected derivative by Oldroyd), which is related to derivatives in the spatial frame by the expression given. In the expressions above, v^m is the velocity vector, m is a dummy index (summed

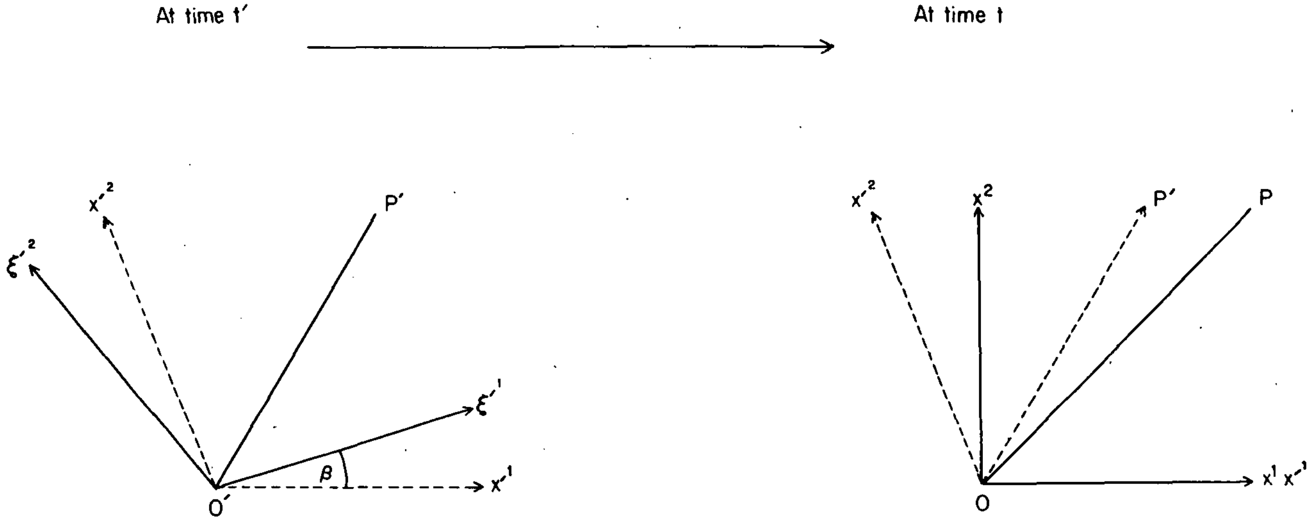

FIGURE 3.—A finite simple shear flow. During flow in which points in the liquid are constrained to move in planes, a vector drawn in the liquid moves from $O'P'$ at a time t' to OP at a time t. In the same interval the material coordinate system $O'\xi'^1\xi'^2$ undergoes a translation from O' to O, a rotation through an angle β, and a distortion to the system Ox^1x^2 when the material and spatial coordinates coincide. The strain, represented by the change OP' to OP, is also represented by the change in spatial coordinates from $Ox'^1x'^2$ to Ox^1x^2, and the purely geometrical effects of the translation and rotation have been thereby eliminated.

over all values), and the comma denotes covariant differentiation which, for an isotropic material, reduces to the partial derivative with respect to x^i.

The (first) rate of strain tensor $\epsilon^{(1)}{}_{ij}$, according to the above rules, transforms as

$$\epsilon^{(1)}{}_{ij}=\frac{1}{2}\,\frac{\partial\gamma_{ij}\,(\xi,\,t')}{\partial t'}\rightarrow e^{(1)}{}_{ij}=\frac{1}{2}\,\frac{\mathfrak{b}g_{ij}\,(x)}{\mathfrak{b}t} \tag{31}$$

and from equation (29),

$$e^{(1)}{}_{ij}=\tfrac{1}{2}\,(g_{mj}v^m{}_{,i}+g_{im}v^m{}_{,j})$$

or

$$e^{(1)}{}_{ij}=\tfrac{1}{2}\,(v_{j,i}+v_{i,j}) \tag{32}$$

since

$$v^m=g^{mj}v_j$$

Similarly for the contravariant components

$$e^{(1)ij}=\tfrac{1}{2}\,(v_{j,i}+v_{i,j}) \tag{33}$$

The rate of strain tensor is symmetric. An antisymmetric tensor known as the vorticity tensor can be defined:

$$\omega_{ij}\equiv\tfrac{1}{2}\,(v_{j,i}-v_{i,j}) \tag{34}$$

Then from equations (32) and (34),

$$v_{j,i}=e^{(1)}{}_{ij}+\omega_{ij} \tag{35}$$

$$v_{i,j}=e^{(1)}{}_{ij}-\omega_{ij} \tag{36}$$

These relations show that in large strains the velocity gradient $\partial v_j/\partial x^i$ does not equal the rate of shear. They can also be used to eliminate the velocity gradients from the differentials in equations (29) and (30) to give relationships in the partial derivative, the velocity vector, the vorticity, and the strain rate. Oldroyd (ref. 31) has listed the series of derivatives that can be obtained from this relationship by putting certain terms equal to 0. The list in covariant components is

$$\frac{\partial T_{ij}}{\partial t} \tag{37}$$

$$\frac{DT_{ij}}{Dt}=\frac{\partial T_{ij}}{\partial t}+v^m\,\frac{\partial T_{ij}}{\partial x^m} \tag{38}$$

$$\frac{\mathfrak{D}T_{ij}}{\mathfrak{D}t}=\frac{DT_{ij}}{Dt}+\omega_{im}\,T_{mj}+\omega_{jm}\,T_{im} \tag{39}$$

$$\frac{\mathfrak{b}T_{ij}}{\mathfrak{b}t}=\frac{\mathfrak{D}T_{ij}}{\mathfrak{D}t}+e^{(1)m}{}_i\,T_{mj}+e^{(1)m}{}_j\,T_{im} \tag{40}$$

Relationship (38) is the classical time derivative following the translational motion; equation (39) is the Jaumann derivative, which refers to a rigid set of axes that translate and rotate; equation (40) is the total derivative discussed above.

Higher order strain rate tensors can be derived from the following generalization:

$$e^{(n)}{}_{ij}=\frac{1}{2}\,\frac{\mathfrak{d}^n g_{ij}(x)}{\mathfrak{d}t^n} \tag{41}$$

The set of strain rate tensors known as the Rivlin-Ericksen tensors (ref. 32) are given by

$$A^{(n)}{}_{ij}=2e^{(n)}{}_{ij} \tag{42}$$

The Stress Tensor

The usual convention with regard to the sign of the components of the stress tensor, written π_{ij} in the material frame and p_{ij} in the spatial frame, is to consider tractions directed outward from the element of material to be positive and those directed inward to be negative. By reference to a unit cube of material (fig. 4), it can be seen that there are nine components of stress: three normal components, $i=j$, and six shear components, $i\neq j$. In figure 4 only the components on one of each pair of surfaces are shown. By considering the couples exerted on the unit cube by the shear components and the requirement that the total couple must be 0, it can be shown that

$$\pi_{ij}=\pi_{ji} \tag{43}$$

Hence the number of independent shear components is reduced to three. If a hydrostatic pressure p is applied to the cube (fig. 4), the total stress tensor can be written (in covariant components)

$$\pi_{ij}=\pi'_{ij}-p\gamma_{ij} \tag{44}$$

Since it is normally assumed that the liquid is incompressible, the material properties are unaffected by the presence of p. Hence, the individual normal stress components π_{ii} cannot be determined absolutely: they are indeterminate to within p. Furthermore, the constitutive equation is a function only of π'_{ij} (or p'_{ij}), which is sometimes referred to as the extra stress.

The transformation rules for the stress tensor and its time derivatives are analogous to those for the strain and strain rate. However, since the stress is normally taken to be the independent variable, the stress tensor is not required to be transformed. Thus,

$$\pi^{ij}\rightarrow p^{ij} \tag{45}$$

On the other hand, the first time derivative is transformed according to the rules given in relationships (38) to (40) with T_{ij} replaced by p'_{ij}, the components of the stress tensor in the space coordinates at current time t.

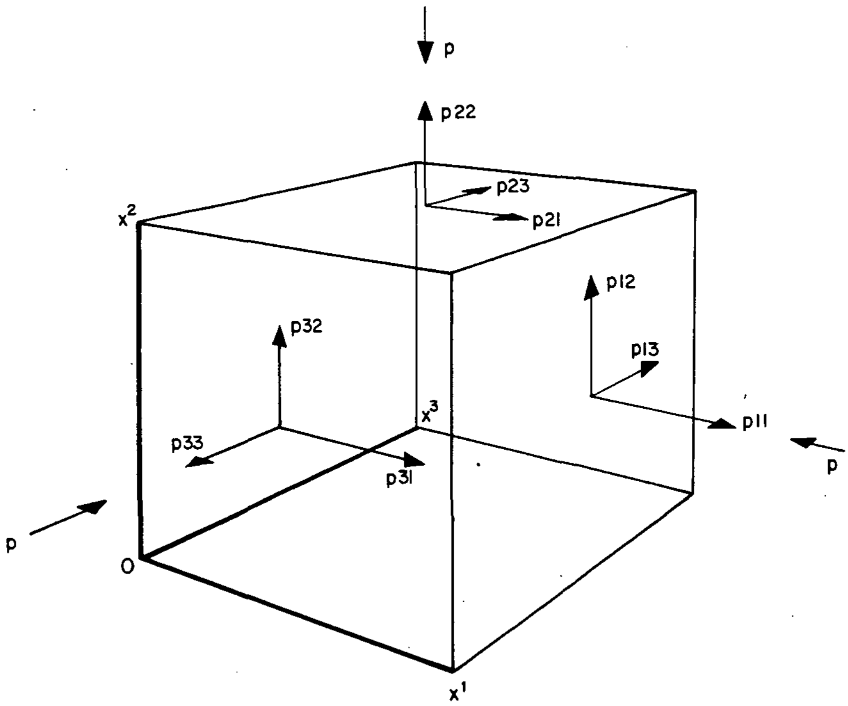

FIGURE 4.—Components of the stress tensor acting on a unit cube of material with a superimposed isotropic pressure p. Only the components on one of each pair of surfaces are shown.

Physical Components

The physical components of vectors and tensors are the quantities actually measured along coordinate axes. They are recovered from tensor components through

$$P_{ij}=\frac{p_{ij}}{(g_{ii})^{\frac{1}{2}}\,(g_{jj})^{\frac{1}{2}}}=p^{ij}\,(g_{ii})^{\frac{1}{2}}\,(g_{jj})^{\frac{1}{2}}$$

$$V_i=\frac{v_i}{(g_{ii})^{\frac{1}{2}}}=v^i\,(g_{ii})^{\frac{1}{2}}$$

In some papers physical components are written in terms of the coordinate axes, e.g., $\langle r\theta\rangle$ means the force acting on the surface $r=$constant and in the direction θ in a cylindrical coordinate system. In a Cartesian system, the physical and tensor components are equal; in a curvilinear system they are not necessarily equal. In the rest of this paper, the stresses calculated for particular models are calculated for simple shears and hence are expressed in Cartesian coordinates. The physical components then equal the tensor components, and covariant components equal contravariant components.

MODIFICATION OF SMALL-STRAIN MODELS

The Modified Maxwell Model

A number of workers have extended the use of the small-strain models, e.g., Maxwell and BEL, to large strains by replacing the strain γ and strain rate $\dot{\gamma}$ by C_{ij} and $e^{(1)}{}_{ij}$ or by any other valid measures of finite strain. Likewise, the time derivative of stress that appears in these models is replaced by one of the derivatives of equations (38), (39), and (40). Of these derivatives, the most general is that given by equation (40), since it takes into account all changes in the coordinate axes that are irrelevant to the material properties, namely, translation, rotation, and change of length scale. On the other hand, that given by equation (39) takes into account the rigid body translation and rotation of axes and hence is acceptable, whereas equation (38) is not of much use in rheology.

The following example using the Jaumann derivative is interesting for the use that has been made of it in lubrication theory.

In a steady simple shear flow, for which the velocity vectors are

$$v^1 = Dx^2$$

$$v^2 = 0$$

$$v^3 = 0$$

the components of the stress tensor in spatial coordinates for the Maxwell model may be written (refs. 33 and 34) as

$$p_{ij} = p'_{ij} - p\delta_{ij} \tag{46}$$

$$p'_{ij} + \frac{\mathfrak{D}p'_{ij}}{\mathfrak{D}t} = 2\eta(0)e^{(1)}{}_{ij} \tag{47}$$

Also, from the description of the motion,

$$\omega_{12} = \frac{-D}{2}$$

$$\omega_{21} = \frac{D}{2}$$

$$e^{(1)}{}_{12} = \frac{D}{2}$$

$$e^{(1)}{}_{21} = \frac{D}{2}$$

and the other components are 0.

By substitution and rearrangement, it is readily shown that

$$p_{21} = p_{12} = \frac{\eta(0)D}{1+\tau^2 D^2} \tag{48}$$

$$p_{11}-p_{22}=\frac{2G(\infty)\tau^2D^2}{1+\tau^2D^2} \tag{49}$$

$$p_{11}=-p_{22} \tag{50}$$

and all other components are 0.

It is interesting to compare equation (48) with equation (5) for the dynamic viscosity of a Maxwell model fluid in small-strain oscillatory shear, and to compare equation (49) with the equation (4) that refers to the in-phase component of shear modulus. The forms of the equations are identical, with ω equivalent to D, $\eta(D)\equiv p_{21}/D$ equivalent to $\eta'(D)$, and $(p_{11}-p_{22})/2$ equivalent to $G'(D)$.

Rheologists refer to this equivalence as the analogy between continuous shear and oscillatory shear. For the Maxwell model and a few others, the variation in viscosity with rate of shear can be deduced from the variation with frequency, with ω replaced by D. The analogy has been found to apply reasonably well to polymer solutions and molten polymers (refs. 22, 35 to 37), as long as the departures from the zero shear viscosity are not too great, no more than 20 percent. A better agreement between continuous shear and oscillatory shear results is obtained if ω is replaced by KD. For polymer solutions, K lies between 1 and 0.2, while for other liquids it seems to be greater than 1: 2.4 for silicones (ref. 38) and 7 for mineral oils (ref. 39). Introduction of K is an empirical procedure, but it can be derived analytically by a suitable choice of generalized finite-strain constitutive equations, discussed later. Dyson (ref. 40) has used the analogy in predicting the viscosity of oils at the high rates of shear encountered in elastohydrodynamic (EHD) lubrication conditions from a knowledge of the viscosity measured in high-frequency, small-strain conditions. The reason for doing this is that the direct measurement of any variation of viscosity with shear rate for mineral oils is bedeviled by viscous heating, which produces a decrease in viscosity of the same magnitude as, or greater than, the expected shear rate effect. A number of attempts have been made to make the continuous shear measurement, but with only moderate success (refs. 41 and 42). On the other hand, the small-strain oscillatory test is carried out with negligible viscous heating.

Before the Maxwell model is put aside, it should be pointed out that equation (48) for shear stress predicts a maximum value equal to $G(\infty)/2$ at $\tau D=1$, followed by a decrease. This may indicate an instability, but more probably it is indicative of the unsuitability of the model at other than low values of τD. The result of equation (50), $p_{11}=-p_{22}$, is a relationship between normal stress components that has never been observed experimentally. Hence, the model is rather limited in application.

If another differential, equation (40), is used in equation (47), the modified Maxwell model thus obtained has a constant viscosity. The normal stress components are realistic if the contravariant form of the model is used.

In general, the Maxwell model modified to take finite strains into account is unsatisfactory. On the other hand, it is mathematically relatively simple, and if the main aim is to predict a trend due to a variation of viscosity with rate of shear, it is acceptable. Tanner (ref. 43) and Mitchell (ref. 44) have applied this model to hydrodynamic lubrication theory and have considered only the viscous effects; that is, the shear components of the stress tensor. The normal stress components were not regarded as being significant.

The Modified BEL Model

Extension of the BEL model to large strains gives unsatisfactory results. Thus, if the Jaumann derivative (eq. (39)) is used, the shear stress in simple shear has a term in $\sqrt{-1}$; on the other hand, the total derivative, equation (40), leads to a viscosity independent of rate of shear.

An alternative approach to the extension of linear models to large-strain shears is to modify equations (16) and (17), which give the stress in terms of the stress relaxation function. For example, in spatial coordinates, equation (17) becomes, for the extra stress in covariant components,

$$p'_{ij}=\int_{-\infty}^{t} \phi(t-t')\,\frac{dC_{ij}(t')}{dt'}\,dt' \tag{51}$$

In the simple shear motion considered above, the coordinates at t and t' are

$$\left.\begin{aligned} x^1&=x'^1-Dx'^2\,(t-t') \\ x^2&=x'^2 \\ x^3&=x'^3 \end{aligned}\right\} \tag{52}$$

Hence the strain rates can be deduced and the products with the stress relaxation function determined. The integral for ϕ_{BEL} (eq. (19)) is not a simple one, but it leads to the simple result that $p_{21}=\eta(0)D$; that is, a constant viscosity. On the other hand, the integral for p'_{11}/D^2 gives a value of infinity. This last result has been obtained in an equivalent but slightly different way (ref. 19) by integrating the second moment of the relaxation spectrum, equation (20). (Compare also with eqs. (77) and (80) for the second-order simple fluid to be discussed later.)

It follows that the BEL model fails in continuous shear by not predicting an analogy between oscillatory and continuous shear and by predicting an infinite normal stress coefficient[4] and, incidentally, infinite higher order rheological properties. The reason lies in the failure of the model at long relaxation times. Methods for adjusting the model have been proposed by Phillips (refs. 24 and 45).

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[4] Strictly, this refers to the first normal stress coefficient N_1, defined as $(p_{11} - p_{22})/D^2$.

THE OLDROYD FAMILY OF MODELS

A number of useful constitutive equations are directly descended from Oldroyd's pioneering work (ref. 28). While most of them are expressed in a differential form, they are not exclusively so; the integral equations of Walters are true members of the family. The starting point is a very general relationship between, on the one hand, stress and successive time differentials of stress and, on the other, strain rate and successive time differentials of strain rate. Thus

$$p_{ij}=-pg_{ij}+p'_{ij} \tag{53}$$

$$\left(1+\lambda_1\frac{d}{dt}+\mu_1\frac{d^2}{dt^2}+\cdots\right)p'_{ij}=2\eta(0)\left(1+\lambda_2\frac{d}{dt}+\mu_2\frac{d^2}{dt^2}+\cdots\right)e^{(1)}{}_{ij} \tag{54}$$

where $\eta(0)$ and the λ, μ, etc., are material constants. The first approximation, obtained by neglecting the time differentials, is the Newtonian model, while the second, obtained by neglecting the second and higher time differentials, is known as the Jeffreys model.

It should not need mentioning that the differentials can take any of the forms in equations (38) to (40) and the tensors can be in either covariant or contravariant components.

The Oldroyd model A is equation (53) and

$$\left(1+\lambda_1\frac{\mathfrak{d}}{\mathfrak{d}t}\right)p'_{ij}=2\eta(0)\left(1+\lambda_2\frac{\mathfrak{d}}{\mathfrak{d}t}\right)e^{(1)}{}_{ij} \tag{55}$$

Model B is the contravariant form.

Another series of models is obtainable by adding models A and B together (ref. 46). Since the resulting equations must give the same low shear viscosity $\eta(0)$, this parameter remains the same in both equations, but in, for example, model B, λ_1 and λ_2 can be replaced by two new constants $K_1\lambda_1$ and $K_2\lambda_2$, where K_1 and K_2 are scalars. Then by adding models A and B and lowering suffixes by means of such standard tensorial relationships as

$$p'^{ij}\,g_{ii}g_{jj}=p'_{ij}$$

$$v_m p'^{m}{}_{j}=v^m\,p'_{mj}$$

we obtain equation (53) and

$$\left[1+\lambda_1\,(1+K_1)\,\frac{\mathfrak{d}}{\mathfrak{d}t}\right]p'_{ij}-2\lambda_1 g_{mm}[e^{(1)}{}_{im}p'_{mj}+e^{(1)}{}_{jm}p'_{im}]$$
$$=2\eta(0)\left[1+\lambda_2\,(1+K_2)\,\frac{\mathfrak{d}}{\mathfrak{d}t}\right]e^{(1)}{}_{ij}-8\eta(0)\lambda_2 g_{mm}e^{(1)}{}_{im}e^{(1)}{}_{mj} \tag{56}$$

This model is a form of that known as the Oldroyd five-parameter model. It contains cross-product terms in stress and strain rate in addition to a relationship of the model A type. A further generalization can be made by including all cross-products of second degree, as long as symmetry and invariance are preserved. This process has given rise to the Oldroyd eight-parameter model (ref. 31). By related arguments Spriggs (ref. 47) and Roscoe (ref. 48) have developed other equations that contain a number of material parameters.

The eight-parameter Oldroyd model is defined by equation (53) and

$$\begin{aligned} p'_{ij}+\lambda_1 \frac{\mathfrak{D}p'_{ij}}{\mathfrak{D}t}+\mu_0 p'_{mm}g_{mm}e^{(1)}{}_{ij}-\mu_1 g_{mm}[e^{(1)}{}_{im}p'_{mj}+e^{(1)}{}_{jm}p'_{im}] \\ +\nu_1 p'_{ml}g_{mm}e^{(1)}{}_{ml}g_{ll}g_{ij} \\ =2\eta(0)\left[e^{(1)}{}_{ij}+\lambda_2 \frac{\mathfrak{D}e^{(1)}{}_{ij}}{\mathfrak{D}t}-2\mu_2 e^{(1)}{}_{im}g_{mm}e^{(1)}{}_{mj}+\nu_2 e^{(1)}{}_{ml}g_{mm}e^{(1)}{}_{ml}g_{ll}g_{ij}\right] \end{aligned} \tag{57}$$

in which $\eta(0)$ is the zero shear viscosity and λ_1, λ_2, μ_0, μ_1, μ_2, ν_1, and ν_2 are the material parameters with the dimension of time.

It can be shown that in the steady simple shear motion defined by equations (52), the nonzero components of the stress tensor are

$$p_{21}=\eta(0)D\,\frac{1+\sigma_2 D^2}{1+\sigma_1 D^2}\equiv\eta(0)DF(D) \tag{58}$$

$$p_{11}-p_{22}=2\eta(0)D^2\,[\lambda_1 F(D)-\lambda_2] \tag{59}$$

$$p_{22}-p_{33}=\eta(0)D^2\,[(\lambda_2-\mu_2)-(\lambda_1-\mu_1)\,F(D)] \tag{60}$$

where

$$\sigma_2\equiv\lambda_1\lambda_2+\mu_0\left(\mu_2-\frac{3\nu_2}{2}\right)-\mu_1(\mu_2-\nu_2)$$

$$\sigma_1\equiv\lambda_1{}^2+\mu_0\left(\mu_1-\frac{3\nu_1}{2}\right)-\mu_1(\mu_1-\nu_1)$$

In small-strain oscillatory shear the dynamic viscosity is

$$\eta'(\omega)=\eta(0)\,\frac{1+\lambda_1\lambda_2\omega^2}{1+\lambda_1{}^2\omega^2} \tag{61}$$

The forms of the relationships (61) for $\eta'(\omega)$ and (58) for $p_{21}/D=\eta(D)$ are similar, but whether or not there is an exact analogy between oscillatory and continuous shear with ω replaceable by D, or an analogy of the type in which ω can be replaced by KD depends on the values of the time constants of the liquid. Hence, the eight-parameter model should be capable of representing many more real liquids than any of the models considered hitherto. Similarly, as regards the normal stress differences, the model will represent a wide range of observable behavior including the generally observed deviation from the dependence on the square of the rate of shear. Unfortunately, insufficient experimental work has been done to determine the eight time constants for elastic liquids and comparatively few checks have been made on the validity of the eight-parameter model. It is probably true to say that equations (58), (59), and (60) are satisfactory as long as the observed deviations of shear stress from a linear dependence on D and of normal stresses from a quadratic dependence on D are not too great.

Nally (ref. 49) has calculated the performance of a wide journal bearing using the Oldroyd eight-constant model to represent the rheology of the lubricant. He ignored normal stresses as being of minor importance and took into account only the variation of viscosity with rate of shear as given by equation (58). He found, in common with Tanner (ref. 43), a reduction in both friction and load-carrying capacity.

Walters (ref. 50) contributed to the development of constitutive equations by replacing some of the time constants in the Oldroyd equations by the relaxation time spectrum. Starting with the stress relaxation function of equation (17) and generalizing to finite strains in the manner given above in developing equation (51), he substituted for the Cauchy deformation tensor by using equations (26) and (31) and arrived at the results

$$p_{ij}=p'_{ij}-pg_{ij} \tag{62}$$

$$p'_{ij}(x,t)=2\int_{-\infty}^{t}\phi(t-t')\,\frac{\partial x'^m}{\partial x^i}\,\frac{\partial x'^n}{\partial x^j}\,e^{(1)}{}_{mn}(x',t')\,dt' \tag{63}$$

where

$$\phi(t-t')=\int_{0}^{\infty}\frac{N(\tau)}{\tau}\,e^{-(t-t')/\tau}\,d\tau \tag{64}$$

in which the relaxation spectrum $N(\tau)$ is identical with the one discussed in equation (8).

These relationships have been named "liquid model A′," and in the contravariant form they are known as "liquid model B′." The model A of Oldroyd is a special case obtainable by substituting in equation (64)

$$N(\tau)=\eta(0)\,\frac{\lambda_2}{\lambda_1}\,\delta(\tau)+\eta(0)\,\frac{\lambda_1-\lambda_2}{\lambda_1}\,\delta(\tau-\lambda_1)$$

in which δ denotes the Dirac delta function.

Walters has also studied a constitutive equation that is analogous to the Oldroyd eight-parameter model but, again, with the differential terms replaced by the relaxation integral. In the contravariant form (ref. 50), it is equation (62) together with

$$\begin{aligned}p'^{ij}-\mu_0 p'^{k}{}_{k}\,e^{(1)ij}-\mu'[e^{(1)kj}p'^{i}{}_{k}+e^{(1)ki}\,p'^{j}{}_{k}]+\nu_1 p'^{kl}\,e^{(1)}{}_{kl}g^{ij}\\ -4\eta(0)\mu_2\,e^{(1)i}{}_{k}\,e^{(1)kj}-2\eta(0)\nu_2\,e^{(1)kl}\,e^{(1)}{}_{kl}g^{ij}\\ =2\int_{-\infty}^{t}\phi(t-t')\,\frac{\partial x^i}{\partial x'^m}\,\frac{\partial x^k}{\partial x'^n}\,e^{(1)mn}\,(x',t')\,dt'\end{aligned} \tag{65}$$

where k, l, m, and n are all dummy indices that take on values 1, 2, 3 for each pair of i, j, and $\phi(t-t')$ is given in equation (64). The behavior in simple shear and other situations has been worked out (ref. 50).

Finally, in the Oldroyd family of models, we include one due to Tanner (ref. 51) and a similar one due to White and Metzner (ref. 52). It can be argued that these models should not be included in this group. However, any system of classification is arbitrary, and it is convenient to mention them here. The basic idea behind the models is the generalization of the Maxwell model by use of the Oldroyd differential (see eq. (39)) and also by the replacement of the constant viscosity $\eta(0)$ by a viscosity function $\eta(\mathrm{II})$. Since the equations must remain invariant in shear, the viscosity function must be a scalar and the argument II must, therefore, be a function of the components of the rate of shear tensor, which itself is invariant. There are three rate of shear invariants. The one chosen, and written as II, is the second, defined by

$$\mathrm{II}=g_{ik}\,g_{mn}\,e^{(1)im}\,e^{(1)kn} \tag{66}$$

summed over all values of the indices. For the simple shear of equations (52), $\mathrm{II}=D^2$. Hence a function of viscosity in D^2 is permissible.

Tanner (ref. 51) used his form of generalized Maxwell model to analyze squeeze-film lubrication and chose a power-law relationship in the invariant II to represent the viscosity function. Normal stresses were regarded as unimportant.

THE COLEMAN-NOLL SIMPLE FLUID MODELS

The notion of the simple fluid was introduced by Noll (ref. 53) as being a fluid for which the current stress is determined by the entire history of the strain. If the fluid is also incompressible and if the effects of deformation occurring in the recent past are greater than those that occurred in the distant past, we have an incompressible simple fluid with fading memory (refs. 54 to 56). This long name is usually abbreviated by rheologists to "simple fluid."

The constitutive equations in material coordinates can be written, in the present notation

$$\pi_{ij}=-p\gamma_{ij}+\pi'_{ij} \tag{67}$$

$$\pi'_{ij}\,(\xi,\,t)=\mathfrak{F}^{t}{}_{-\infty}[\gamma_{ij}\,(\xi,\,t')-\gamma_{ij}\,(\xi,\,t)] \tag{68}$$

and in spatial coordinates

$$p_{ij}=-pg_{ij}+p'_{ij} \tag{69}$$

$$p'_{ij}\,(x,\,t)=\mathfrak{F}_0{}^{\infty}[C_{ij}(x,\,s)] \tag{70}$$

where C_{ij} is the deformation tensor of equation (26) and $s=(t-t')$ is the elasped time. $\mathfrak{F}$ is a tensor-valued functional, and $\mathfrak{F}(0)=0$.

The idea of a fading memory is explicitly introduced by specifying that an influence function $h(s)$ must approach 0 monotonically and faster than

$s^{-3/2}$ as s goes to infinity. The influence function defines a norm $\|C_{kl}\|$ of the strain history where

$$\|C_{kl}\|^2=\int_0^\infty C_{kl}(s)C_{kl}(s)h(s)^2\,ds \tag{71}$$

The limitation on $h(s)$ insures that the norm vanishes when there has been no strain and for an arbitrary history of strain places the greatest emphasis on the recent past (small s). The forms of the operator $\mathfrak{F}$ are restricted to those that are smooth and, in practice, to those that conform to a theorem of Frechet. As a consequence of this, the functional can be expressed as a series of integrals so that

$$\begin{aligned} p'_{ij}=&\int_0^\infty M_1(s)C_{ij}(s)\,ds \\ &+\int_0^\infty\int_0^\infty[M_2(s_1,\ s_2)C_{im}(s_1)C_{mj}(s_2)+N_2(s_1,\ s_2)C_{mm}(s_1)C_{ij}(s_2)]\,ds_1\,ds_2 \\ &+O(\|C_{kl}\|^3) \end{aligned} \tag{72}$$

in which $O(\ )$ means terms of the order of the argument. The series can be truncated at the nth term if the $(n+1)$th power of the norm can be considered small. Coleman and Noll (ref. 56) have shown that smallness of the norm is insured by small strains at any time in the history, by any size of strain as long as the strain in the recent past was small, by low rates of shear, and by a short memory; that is, a small relaxation time. However, as pointed out by Truesdell (ref. 57), there is no way of deciding a priori whether or not a small norm is small enough for the approximation involved.

In an alternative approximation, applicable in the case of retarded motions, that is, when the velocities and accelerations are small, Coleman and Noll replaced the functional in equation (70) by functions of the rate of strain tensors. By truncation of the series, the following equations up to the third order are obtained for the extra stress.

For the first order,

$$p'_{ij}=2\alpha_1e^{(1)}{}_{ij} \tag{73}$$

For the second order,

$$p'_{ij}=2\alpha_1e^{(1)}{}_{ij}+2\alpha_2e^{(2)}{}_{ij}+4\alpha_3e^{(1)}{}_{im}e^{(1)}{}_{mj} \tag{74}$$

For the third order,

$$\begin{aligned} p'_{ij}=&2\alpha_1e^{(1)}{}_{ij}+2\alpha_2e^{(2)}{}_{ij}+4\alpha_3e^{(1)}{}_{im}e^{(1)}{}_{mj}+8\beta_1[e^{(1)}{}_{ml}e^{(1)}{}_{lm}]e^{(1)}{}_{ij} \\ &+2\beta_2e^{(3)}{}_{ij}+4\alpha_5[e^{(1)}{}_{im}e^{(2)}{}_{mj}+e^{(1)}{}_{jm}e^{(2)}{}_{mi}] \end{aligned} \tag{75}$$

In some texts the rate of strain tensors are written as Rivlin-Ericksen tensors (eq. (42)). The α and β are material constants that are related to the functions M of equation (72). It can also be shown (ref. 57A) by comparing the first-order term in equation (72) with the equations derived earlier in terms of the stress relaxation function (eqs. (17) and (51)) that $-M_1$ is equal to the time differential of the stress relaxation function and, consequently, by putting the stress relaxation function in terms of the relaxation time spectrum by equation (14), that $-M_1$ is also equal to the relaxation time spectrum. Thus,

$$\alpha_1 = -\int_0^\infty M_1(s)s\,ds = \int_0^\infty H(\tau)\tau\,d\tau = \eta(0) \tag{76}$$

$$-\alpha_2 = -\frac{1}{2}\int_0^\infty M_1(s)s^2\,ds = \frac{1}{2}\int_0^\infty H(\tau)\tau^2\,d\tau \tag{77}$$

$$\beta_2 = -\frac{1}{6}\int_0^\infty M_1(s)s^3\,ds = \frac{1}{6}\int_0^\infty H(\tau)\tau^3\,d\tau \tag{78}$$

The other parameters are functions of M_2 and M_3 (ref. 58).

It can be seen that the first-order simple fluid (eq. (73)) is Newtonian and has only one material parameter given by the relaxation spectrum (eq. (76)). The second-order simple fluid (eq. (74)) has three material parameters, two of which are calculable from the relaxation spectrum (eqs. (76) and (77)), while the other is not. In simple shear (eqs. (52)), this fluid requires the following stress components to maintain the shear:

$$p_{21} = \alpha_1 D = \eta(0)D \tag{79}$$

$$p_{11} - p_{22} = -2\alpha_2 D^2 \tag{80}$$

$$p_{22} - p_{33} = (2\alpha_2 + \alpha_3)D^2 \tag{81}$$

The normal stress difference that in all experiments is found to be the larger, $p_{11} - p_{22}$, is therefore related to the relaxation time spectrum which is measured in low-amplitude oscillatory shear. The other normal stress difference is quite unrelated to anything measurable in low-amplitude oscillatory shear. A shear rate-dependent viscosity is obtained with the third-order simple fluid for which

$$\eta(D) = \frac{p_{21}}{D} = \alpha_1 - (-\alpha_5 - 2\beta_1)D^2 \tag{82}$$

Unfortunately, this dependence leads to a negative viscosity at a high enough rate of shear. On the other hand, to the third order in rate of shear, this result for the shear stress is the same as that obtained with the Maxwell and Oldroyd models.

In passing, we note that a special case of the second-order simple fluid model, obtained when $\alpha_2 = 0$, is identical with the so-called Reiner-Rivlin model (refs. 59 and 60). This model has been used in many engineering calculations, but its predictions are generally inconsistent with experiment. Another class of models, the Rivlin-Ericksen models (ref. 61), are also special cases of the Coleman-Noll fluids.

It is permissible in the simple fluid models, as mentioned in earlier sections on other models, to choose any strain or rate of strain measure and also to choose the material parameters as scalar functions of the invariants of strain or strain rate.

A COMPARISON BETWEEN CONSTITUTIVE EQUATIONS

It will already have become clear that many of the constitutive equations discussed are very similar if not identical. Although the generalization of equations to apply not only in the small-strain approximation but also in finite strain leads to an infinite number of possibilities, the desire to retain simplicity makes it certain that different approaches will lead to similar results. The comparison of constitutive equations has been taken up by Walters (ref. 58), and he draws the conclusions that in almost all circumstances the Green-Rivlin models (not discussed here) are equivalent to the Coleman-Noll models and that the Rivlin-Ericksen models are approximations thereto. The Oldroyd family of equations (refs. 28, 31, and 62) is also a special case of *n*th-order viscoelasticity.

MOLECULAR THEORIES OF ELASTICOVISCOUS LIQUIDS

Nonpolymeric Liquids

The most basic type of liquid theory is a statistical theory that considers the liquid to be an assembly of molecules in continuous motion (refs. 63 to 65). The thermal energy of the molecules is the sum of kinetic energy and potential energy. The kinetic energy is determined by the momentum carried by each molecule, while the potential energy is determined by intermolecular forces and hence, for a given force law, by the relative positions of the molecules. Therefore, a phase space distribution function that expresses the momentum and coordinates of every molecule will characterize the liquid. The extent to which the intermolecular force term exceeds the kinetic energy term determines the extent by which the liquid differs from an ideal gas. Hence in a liquid theory the specification of the coordinates of the molecules is of supreme importance.

It is believed that liquids differ from gases by possessing a limited but definite degree of structure. This concept is introduced into the theory with correlation functions that represent the extent to which the distributions of molecules are not completely random; that is, the relative positions of molecules are correlated. For example, the pair correlation function is related to the probability of finding molecules simultaneously at two given points separated by a given distance in a spatial manifold. Because fluids (but not liquid crystals) have spherical symmetry, the pair correlation function is related to the radial distribution function, which can be determined by X-ray or neutron diffraction experiments. Clearly, higher order correlation functions impose more structure on the liquid model.

In dealing with transport phenomena, the molecular theory introduces time-dependent distribution functions. Thus, by a spontaneous fluctuation or by the action of an external force, the phase space distribution of an assembly of molecules is disturbed from the equilibrium to which it will return in the course of time. It is assumed that the fluctuations decay, on average, according to the same laws that govern transport phenomena on the macroscopic scale. In this way the molecular and continuum theories are linked. In general, the fluctuations are taken to be small and the decay to be exponential. The continuum equations are generally restricted to the equation of the compressible viscous liquid (Navier-Stokes), and the molecular statistical model is thus used to calculate constant viscosity coefficients. More complicated rheological behavior has not been treated successfully.

Other molecular models are less rigorous.

Ree and Eyring (ref. 66) extend the Eyring (ref. 67) theory of viscosity to include non-Newtonian viscosity in solutions and suspensions. The basis of the original theory is too well known to require repetition; the basis of the Ree-Eyring theory is that in a shearing plane the material is composed of areas, n in number, of different types of structure, each contributing to the stress in proportion to the fractional area x_n. Then the total shear stress is a summation of n terms, thus leading to a general expression for viscosity

$$\eta(D) = \sum_{1}^{n} \frac{x_n \beta_n}{\alpha_n} \frac{\sinh^{-1} \beta_n D}{\beta_n D} \tag{83}$$

The variable β_n is a sort of relaxation time that is temperature dependent according to the well-known exponential equation, and α_n is related to the molecular size. It has been pointed out by Naylor (ref. 68) and others that the relationships between the parameters and molecular properties have never been clearly expressed, thus putting the equation into the category of a power law with disposable parameters. Furthermore, the theory is linear because no large-strain effects have been introduced explicitly and it is one dimensional because normal stress effects are not included.

An interesting new development carried out in the author's laboratory by Phillips (ref. 45) is founded on a model for dielectric relaxation introduced by Glarum (ref. 69). In this model a molecular-sized region of stress in a liquid is relaxed instantaneously when an element of free volume, or a defect, reaches it. Hence, the macroscopic relaxation function, which, incidentally, can be shown to be equal to a time-dependent correlation function of the statistical theories, is related to the probability that a defect does not reach a given region and, in turn, on the rate of diffusion of defects. The analysis is carried out for the one-dimensional case, that is, for diffusion along a line, and approximations are necessary to account for viscoelastic relaxation. Of course, the theory is linear as well as one dimensional. One of a series of stress relaxation functions obtainable is identical with that for the BEL model, equation (19). In a more recent development,[5] a defect diffusion model of greater plausibility has resulted in a stress relaxation function that is identical with the BEL model at short times but which deviates from it at longer times to give an exponential decay. This new function therefore has the advantages of the BEL model in representing the results of high-frequency shear measurements without its disadvantage of predicting an infinite normal stress coefficient.

The defect diffusion models have a sounder physical basis than the Ree-Eyring model, but they also suffer from rather ill-defined molecular parameters.

Polymeric Liquids

Bead-Spring Models

Molecular theories of polymer melts and solutions have achieved considerable success through a judicious combination of continuum mechanics and statistical mechanics. Thus, a polymer molecule, which is only larger than typical solvent molecules along its contour length, is considered to be embedded in a continuum that acts on it through a friction factor ζ according to the linear Stokesian equation

$$F_j^f = \zeta(\dot{r}_j - v'_j) \tag{84}$$

where F_j^f is the frictional force on the molecular element at position j, represented by the vector $\mathbf{r}_j$, $\dot{r}_j$ is the velocity of the element, and v'_j is the effective velocity of the continuum at j in the absence of the molecular element. The force opposing the fluid friction is an entropic-elastic force arising from the distortion of the molecule from its statistically preferred configuration. Clearly, such a model gives elasticoviscous properties.

The so-called bead-spring models, of which there are many (ref. 70), consider the sites of fluid friction to be represented by small spheres (beads) that are connected by a length of the polymer chain molecule. This chain is represented by a frictionless Hookean spring. Two cases have been considered: the dumbbell models, in which the beads are at the extremities of the chain, and the necklace models (fig. 5), in which they are uniformly distributed along the chain. The necklace models have received the greater attention since the publication of important papers by Rouse (ref. 71), Bueche (ref. 72), and Zimm (ref. 73). In all these treatments, the polymer molecule is considered in isolation. Hence they apply to dilute solutions. On the other hand, Bueche argues that the isolated molecule is a valid concept also for polymer melts, provided that the molecular weight is not

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[5] Phillips, M. C.: Personal communication.

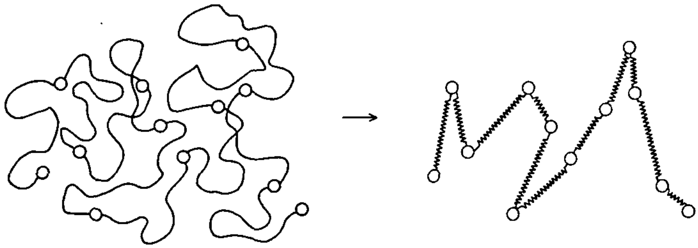

FIGURE 5.—Diagram representing the necklace type of bead-spring molecular model. The beads are equally spaced along the molecule and each segment of molecule between beads behaves as an elastic spring.

too high. Each submolecule length between beads is assumed long enough and flexible enough that its configuration can be represented by Gaussian statistics. Then the statistical theory of rubber elasticity (ref. 74) can be applied to give the elastic restoring force in terms of the gradient of the thermodynamic potential μ_j of the system disturbed by a shear field

$$F_j^e = -\nabla \mu_j \tag{85}$$

in which μ is given by the change in the distribution function of the coordinates r of the beads from its perturbed value Ψ to its unperturbed value Φ, namely,

$$\mu = kT\left(1 + \ln \frac{\Psi}{\Phi}\right) \tag{86}$$

where k is Boltzmann's constant and T is the absolute temperature.

The models assume the existence of N Gaussian submolecules and $(N+1)$ beads. Equation (84) is used to express the frictional force on the jth bead. The theories of Rouse and Zimm differ in the approximations made for v'_j. The Rouse model is a free-draining model, which means that the value and direction of v'_j are determined by the macroscopic velocity gradient and the distance from the boundary. It is the same as if the molecules did not exist. The Zimm model is non-free-draining, and v'_j is put equal to the Rouse value plus a term giving the influence of all the other beads on the hydrodynamic velocity at the jth bead. Thus,

$$v'_j = v_j + \sum_{j \neq k} T_{jk} F_k^f \tag{87}$$

where F_k^f is the frictional force on the kth bead and T_{jk} is an

$$(N+1) \times (N+1)$$

matrix known as an interaction tensor. In the Rouse theory, T_{jk} is zero; in the Zimm theory, T_{jk} is replaced by an approximation due to Kirkwood and Riseman (ref. 75), and in more recent developments of the model by Tschoegl (ref. 76), Fixman (ref. 77), and Pyun and Fixman (ref. 78), the interaction tensor is given different treatments.

A set of equations of motion is set up, ignoring inertial forces, to give

$$F^f + F^e = 0 \tag{88}$$

This is combined with a continuity equation for the distribution Ψ to give $3(N+1)$ equations for the time-varying distribution function Ψ in terms of a general velocity gradient in Cartesian coordinates. It is also assumed that Ψ is a linear function of the velocity gradient. The procedure leads to a set of coupled equations, and the contribution of Rouse and Bueche was to recognize that by a coordinate transformation to normal coordinates, these equations could be decoupled to give $(N+1)$ equations having $(N+1)$ real eigenvalues λ_p. In physical terms this means that the cooperative motions of all the segment junctions in a shear field can be represented by the summation of a series of $(N+1)$ individual normal modes which have decay times, or relaxation times, related to the λ_p. For $N=0$ $(p=0)$, the motion is a translation of the molecule as a whole; for $N=1$ $(p=1)$, the first normal mode is a coordinated damped motion of the molecule as a whole with the ends fixed; and so on up to $N=N$ $(p=N)$, which corresponds to the rapid damped motion of individual submolecules uncoordinated with the other submolecules.

The further development of the basic theories for oscillatory simple shear leads to the following general result for the real and imaginary parts of the complex shear modulus:

$$G'(\omega) = nkT \sum_{p=1}^{N} \frac{\omega^2 \tau_p{}^2}{1+\omega^2 \tau_p{}^2} \tag{89}$$

$$G''(\omega) = \omega \eta_s + nkT \sum_{p=1}^{N} \frac{\omega \tau_p}{1+\omega^2 \tau_p{}^2} \tag{90}$$

in which η_s is the viscosity of the solvent, n is the number of polymer molecules per unit volume, and τ_p is the relaxation time of the pth mode. For the Rouse free-draining model,

$$\tau_p = \frac{\sigma^2 \zeta}{6kT\, \lambda_p} \tag{91}$$

$$\lambda_p = 4 \sin^2 \frac{p\pi}{2(N+1)} \xrightarrow[5p<N]{} \frac{\pi^2 p^2}{N^2} \tag{92}$$

and for the Zimm non-free-draining model,

$$\tau_p = \frac{\sigma^2 \zeta N^2}{24kT\, h\lambda_p'} \tag{93}$$

in which σ^2 is the mean square end-to-end distance of the submolecule, h is a hydrodynamic shielding factor, and λ_p' is a set of numbers that form the solutions of an eigenvalue equation (75). It is a straightforward matter to express the relaxation times in terms of zero shear viscosity, to eliminate the unknown parameters ζ, σ, N, and h.

The other components of the stress tensor have been evaluated by Williams (ref. 79) for this model in oscillatory simple shear.

By comparing the results of equations (89) and (90) with equations (6), it is seen that the Rouse-Zimm models are equivalent to distributed Maxwell models. The relaxation spectra are line spectra, which are slightly different for the two models, and which can be approximated by continuous spectra $H(\tau)$ as pointed out by Ferry (ref. 70). By use of equation (14), the response of the models can also be expressed as stress relaxation functions.

The limiting values of shear modulus, viscosity, and normal stress coefficient for the molecular models are

$$G(\infty)=nkT \tag{94}$$

$$\eta(0)-\eta_s=nkT\sum_{p=1}^{N}\tau_p \tag{95}$$

$$\xrightarrow[5p<N]{}\frac{\pi^2 n\sigma^2\zeta}{36} \qquad \text{(Rouse)} \tag{96}$$

$$N_1(0)\equiv -2\alpha_2=nkT\sum_{p=1}^{N}{\tau_p}^2 \tag{97}$$

$$\xrightarrow[5p<N]{}\frac{\pi^2 n\sigma^4\zeta}{3340kT} \qquad \text{(Rouse)} \tag{98}$$

$$=\frac{2[\eta(0)-\eta_s]^2}{5\,G(\infty)} \tag{99}$$

It has already been mentioned that more recent developments of the bead-spring models have dealt with the hydrodynamic shielding term. Other developments have considered the effects of a polymer with a distribution of molecular weights; of a solvent-polymer interaction that causes a deviation from Gaussian statistics; of a polymer-polymer interaction, known as the excluded volume effect, that arises from the impossibility of more than one bead occupying a given position in space; of polymer molecules with branched chains; and, finally, of polymer chain entanglement that occurs at moderately high concentrations. All of these effects are described in surveys by Ferry (ref. 70) and Janeschitz-Kriegl (ref. 80). The latter paper is a comprehensive review of the theory of polymeric systems from the standpoint of optical properties. However, if it is assumed that the refractive index ellipsoid is coaxial with the principal stress ellipsoid, then the study of a system by optical means is exactly analogous to a study of the stresses.

A treatment of the properties of a bead-spring model in continuous shear was carried out by Bueche (ref. 81), who followed up a proof by Debye (ref. 82) that in a shear field D, a flexible polymer molecule rotates at angular velocity $\omega = D/2$. This is exactly analogous to the continuum treatment of shear in which, from equations (35) and (36), the velocity gradient D in simple shear defined by velocity components $(Dx^2, 0, 0)$ is the sum of a rate of shear $D/2$ and a vorticity of $D/2$. It is scarcely ever made clear in the molecular treatments that while the segments of a molecule rotate, the ellipsoidal envelope of the molecule maintains its orientation with the shear direction (fig. 6). The orientation is generally a function of the rate of shear and is conveniently studied by the refractive index properties (flow birefringence) mentioned in the previous paragraph (ref. 80). It should not be a surprise, following the discussion of the rheological analogy in an earlier section, that the Bueche theory shows that the frequency ω in an oscillatory experiment is replaced by D in a continuous shear experiment. The viscosity at rate of shear D, $\eta(D)$ is given by

$$\frac{\eta(D)-\eta_s}{\eta(0)-\eta_s} = 1 - \frac{6}{\pi^2}\sum_{p=1}^{N}\frac{D^2\tau_p^2}{p^2(1+D^2\tau_p^2)}\left(2-\frac{D^2\tau_p^2}{1+D^2\tau_p^2}\right) \tag{100}$$

in which the symbols have the same meaning as given above and τ_p is the same as the Rouse relaxation times in the approximate form (eqs. (91) and (92)). Equation (100) is for the free-draining case; for a non-free-draining model, the result is

$$\frac{\eta(D)-\eta_s}{\eta(0)-\eta_s} = 1 - (\tau_0 D)^{\frac{1}{2}} \tag{101}$$

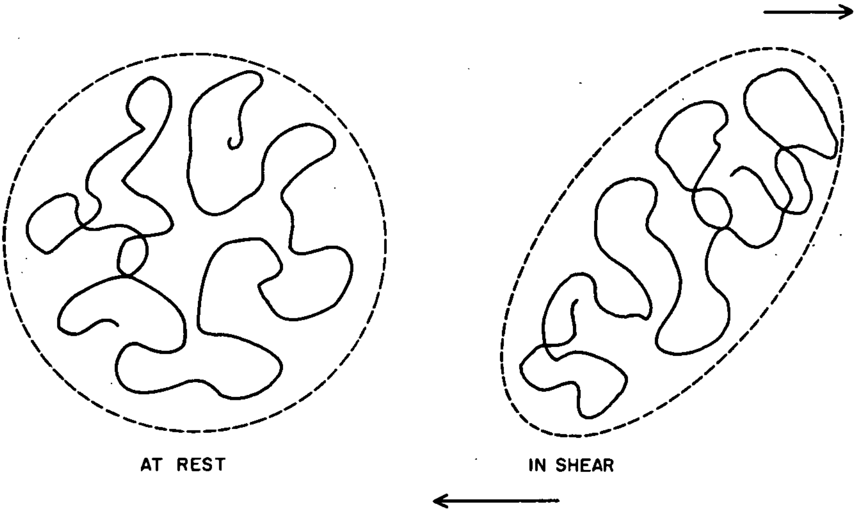

FIGURE 6.—At rest the polymer molecule chain is contained in a sphere. In steady shear the spherical envelope distorts to an ellipsoid whose orientation with respect to the direction of shear stays constant while the molecule rotates inside as it moves forward.

$$\tau_0 = 1.98\,\frac{r}{b}\,\frac{[\eta(0)-\eta_s]\,(M\ M_0)^{\frac{1}{2}}}{N_0 kTc} \tag{102}$$

where M is the polymer molecular weight, M_0 is the molecular weight associated with each chain link and for a vinyl polymer is equal to one-half the monomeric molecular weight, N_0 is Avogadro's number, r is the radius of a bead ($\zeta = 6\pi\eta_s r$), and b is the length of a chain unit. The parameters r and b are not well defined, but it is stated (ref. 81) that the ratio should be independent of the polymer and should have a value of about 2.

The largest (or terminal) relaxation time τ_1 is a useful ordering parameter. It determines when relaxation effects will first become apparent, and it can be used for normalizing. Thus, in applying Rouse-Zimm-type models, the frequency scale is normalized by plotting $\omega\tau_1$. It is found that the effect of elasticity becomes marked in the vicinity of $\omega\tau_1 = 1$. Similarly, for the non-Newtonian viscosity, equation (100) can be rearranged by making the substitution (compare eqs. (91) and (92))

$$\tau_p = \frac{\tau_1}{p^2} \tag{103}$$

An equation is then found expressing the relative change in viscosity as a function of $D\tau_1$ and independent of temperature and concentration of polymer. The viscosity is markedly different from $\eta(0)$ when $D\tau_1 = 1$. The dimensionless group $D\tau_1$ can also be written $6D[\eta(0)-\eta_s]/\pi^2$, following a substitution from equation (96), and if $\eta(0)$ is not considerably different from $\eta(D)$, this can be put equal to $AD\eta(D)$, where A is a numerical factor, and hence to Ap_{21}. This explains why the results of Horowitz (ref. 9) normalize to a curve independent of temperature and polymer concentration when the relative change in viscosity is plotted against the logarithm of the shear stress.

Entanglement Models

It has already been stated that one of the developments of bead-spring models has been the inclusion of entanglement coupling. This concept of the entwining of neighboring molecules with the given molecule was used by Bueche (ref. 83) to explain why, up to a certain critical molecular weight, the viscosity of a polymer melt increases linearly with molecular weight and thereafter increases as molecular weight to the power 3.5. Incidentally, the concept as applied in this way has often been applied too literally, being applied even to log η/log M relationships that are smooth curves rather than two intersecting straight lines. It has also given rise to the view that intermolecular entanglement does not occur below the critical molecular weight. The nature of entanglements has not been specified exactly, but they have the effect of requiring the coordination of normal modes in more than one molecule and thus add to the relaxation time spectrum relaxation times longer than τ_1 of the Rouse-Zimm theories.

The required modification of the Rouse theory was carried out by Chompff, Duiser, and Prins (refs. 84 and 85). They reduced the problem of chain interaction to one of adding to the normal modes of an isolated Rouse molecule of N submolecules the normal modes of an additional isolated Rouse molecule of m "giant submolecules," where $(m-1)$ is the number of entanglement linkages along the molecule. Figure 7 illustrates the procedure that is justifiable on the grounds of the normal mode analysis that the contributions of each mode are additive. The friction factors of all but the two giant submolecules at the ends of the chain are higher by a factor $1/\delta$ than the normal friction factor ζ because of the influence of the other molecules. The additional relaxation times are then given by (compare eqs. (91) and (92))

$$\tau_{pe}=\frac{\sigma_e{}^2\zeta}{6kT\ \lambda_p}\xrightarrow[5p<N]{}\frac{\sigma_e{}^2\zeta(m-1)^2}{6\pi^2kT\ \delta p^2} \tag{104}$$

where $\sigma_e{}^2$ is the mean square end-to-end distance of the giant submolecules between entanglement (or slow) points and

$$m\sigma_e{}^2=N\sigma^2 \tag{105}$$

A unit volume containing n entangled molecules constitutes a network, and, for the purpose of summing the effects of an individual molecule over the n molecules, a particular type of network must be assumed to avoid counting the contribution of a given entanglement more than once. The theory assumes a tetrafunctional network in which $n/4$ molecules have $(m-1)$ entanglements and the remaining $3n/4$ molecules have one-half with $(m-1)/2$ entanglements, one-quarter with $(m-1)/4$ entanglements, and so on. Relaxation spectra have been computed and compared with experimental results. Figure 8 shows the type of curve obtained for the variation of G' with ω which, qualitatively at least, compares very well with a general form of this curve (fig. 1). It contrasts with the Rouse-Zimm

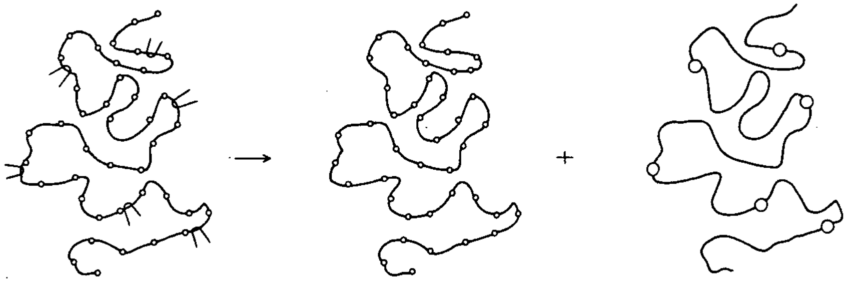

FIGURE 7.—In the Chompff-Duiser-Prins entanglement theory an $(m-1)$-entangled bead-spring molecule having $(N+1)$ beads is treated as the sum of an unentangled molecule having $(N+1)$ beads and an unentangled molecule having $(m-1)$ high-friction beads.

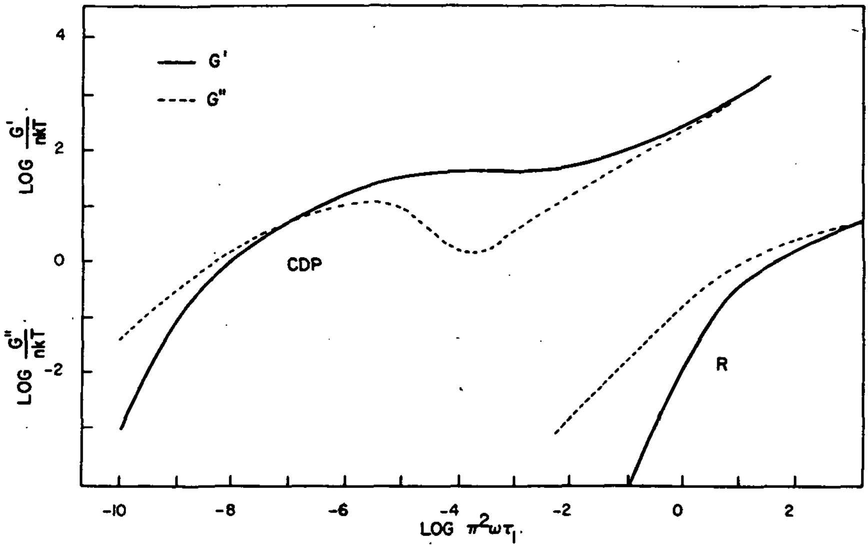

FIGURE 8.—Curves of reduced shear moduli against reduced frequency for the Chompff-Duiser-Prins (CDP) model and the Rouse model. The CDP model has been fitted to data for molten poly(*n*-octylmethacrylate) and is reporduced from reference 85. The Rouse model is included to show the absence of a plateau region; it was never intended to apply to molten polymers.

models, which do not give a well-defined plateau region. By making detailed comparisons between theory and experiment, values for δ and m can be determined. It is unfortunate that these parameters cannot be derived a priori from molecular considerations.

Network Models

There is a degree of similarity between entanglement models and network models, and, happily, recent research is in the direction of unifying these approaches. The network model is older than the entanglement model and derives from the theory of vulcanized rubber (ref. 74). This states that permanent cross-links exist between polymer molecule chains and that during a deformation their positions move in a regular way parallel to the boundaries causing the deformation. This deformation is called an affine deformation. It is also assumed that the length of chain between cross-links is Gaussian. Then by use of the kinetic theory, the stress tensor in Cartesian coordinates becomes

$$p^{ij} = -p\delta^{ij} + p'^{ij} \tag{106}$$

$$p'^{ij} = sn_0kTB^{ij} = sn_0kT\,\frac{\partial x^i}{\partial x'^m}\,\frac{\partial x^j}{\partial x'^m} \tag{107}$$

in which summation over m is implied (eq. (28)). In equation (107), k is

Boltzmann's constant, T is the absolute temperature, n_0 is the concentration of cross-link junctions, and s is a numerical factor (approximately 2) such that the product sn_0 is equal to the concentration of chain segments terminated by cross-links. Like N and m defined in the bead-spring models, s and n_0 are not a priori determinable. The variables x^i and x'^i denote the Cartesian coordinates of any junction (the affine deformation approximation requires no distinction to be made between junctions) at current time t and an earlier time t', respectively.

The above network model is of a solid. Green and Tobolsky (ref. 86) considered the junctions to be temporary to obtain a model that predicted stress relaxation and creep, and Lodge (ref. 87) applied this concept in constructing his famous theory of elastic liquids. A similar theory was developed at about the same time by Yamamoto (ref. 88). Hydrodynamic resistance is neglected, so for solutions the stresses from the solvent are simply added to the stress contributed by the network. The network formed by the polymer molecules is assumed to arise from temporary junctions with finite lifetimes, during which they support stress in the same way as the permanently cross-linked rubber. In steady flow there is an equilibrium concentration of junctions, with the rate of formation being equal to the rate of disappearance. This concentration is assumed in the original theories to be independent of the shear. The junctions formed in a time interval $(t', t'+dt')$ act independently of others, and the stress contributed by them is proportional to their lifetime $(t-t')$, where t is current time. Then the extra stress tensor is

$$p'^{ij} = skT \int_{-\infty}^{t} \mu \frac{\partial x^i}{\partial x'^m} \frac{\partial x^j}{\partial x'^m}\, dt' \tag{108}$$

where $\mu\, dt'$ is the concentration of junctions that formed in the interval dt' and are still in existence at time t. The function $\mu = \mu\ (t-t', T, c)$, with c = concentration of polymer in the case of a solution, is a junction-age distribution. Lodge assumed a logarithmic form:

$$\mu = \sum_q \mu_q\, e^{-(t-t')/\tau_q} \tag{109}$$

in which μ_q and τ_q are positive constants and q indicates different types of junction.

In oscillatory simple shear the model behaves like a distributed Maxwell model with the τ_q as relaxation times and with

$$G(\infty) = skT \sum_q \mu_q \tau_q \tag{110}$$

From equation (107), for a permanent network the shear modulus is given by

$$G = \frac{p'^{ij}}{B^{ij}} = sn_0kT \tag{111}$$

At infinite frequency the temporary network becomes indistinguishable from a permanent network because in this limit the junctions have no time to make or break. Hence, we can equate the moduli in equations (110) and (111) to give the parameters of the junction-age distribution function in terms of the concentration n_0 of junctions taking part in the network:

$$n_0 = \sum_q \mu_q \tau_q \tag{112}$$

Hence the concentration of junctions of the type q is

$$n_{0_q} = \mu_q \tau_q$$

whence

$$G(\infty) = skT \sum_q n_{0_q} \tag{113}$$

Since equation (107) is written in the large-strain formulation, an oscillatory normal stress difference $(p_{11} - p_{22})$ is predicted. This is made up of an oscillatory part with a frequency equal to twice the applied shear frequency and a steady part. In a steady simple shear (eq. (52)), a shear-rate-independent viscosity is predicted:

$$\eta - \eta_s = skT \sum_q \mu_q \tau_q^2 = skT \sum_q n_{0_q} \tau_q \tag{114}$$

and shear-rate-independent normal stress coefficients are

$$\left.\begin{aligned} N_1 &\equiv \frac{p_{11} - p_{22}}{D^2} = 2skT \sum_q \mu_q \tau_q^3 = 2skT \sum_q n_{0_q} \tau_q^2 \\ N_2 &\equiv \frac{p_{22} - p_{33}}{D^2} = 0 \end{aligned}\right\} \tag{115}$$

There is a considerable degree of similarity in the predictions of the Lodge network model and the Rouse-Zimm bead-spring models (compare eqs. (113) and (114) with (95) and (97)), but the models themselves are quite different. The Lodge model is not as specific as Rouse-Zimm models; for example, the junction concentration n_0 is not as readily determined by nonrheological methods as the polymer molecule concentration n and, further, the relaxation time distribution function is arbitrary in the Lodge model but a specific function in the Rouse-Zimm formulation. The Chompff-Duiser-Prins entanglement model is an intermediate case. Lodge (ref. 89) has recently discussed the relative merits of network and bead-spring models.

EFFECTS OF SHEAR ON RELAXATION SPECTRA: NONLINEAR THEORY

Generally, the polymeric models mentioned above are linear models, and, consequently, they do not conform in detail with experimental results (ref. 70). With the exception of the Bueche model, they do not predict a variation of viscosity with rate of shear; the Bueche model predicts a too rapid variation of viscosity. They predict a first normal stress coefficient that is independent of rate of shear and a second normal stress coefficient that is 0.

The models have been modified in recent years to include nonlinear effects and to give among other things a more realistic variation of viscosity with shear rate. A big step forward was made following the publication in 1963 by Osaki, Tamura, Kurata, and Kotaka (ref. 90) of the results of experiments in which polymer solutions were sheared unidirectionally. Simultaneously the relaxation functions were determined by superimposed, small-amplitude oscillatory shear. This type of work has been repeated a number of times, notably by Booij (ref. 91), and Tanner and Simmons (refs. 92 and 93). Vinogradov and coworkers (ref. 94) have carried out a related study using large-amplitude oscillatory shear alone.

The results are amenable to treatment by either continuum or molecular models, but care has to be taken in this because of the possibility of cross-terms appearing (ref. 87) and the appearance of higher order effects that cannot be ignored even in a simple theory (ref. 95). It is not proposed to discuss the details of the experimental results, but merely to point out that they strongly support the conclusion that in a steady unidirectional shear, the long-time end of the relaxation time spectrum is destroyed. In terms of a molecular model, such a finding can only add support to the entanglement-network type of model.

A number of theories have been put forward. That of Yamamoto (ref. 88), which preceded the experimental work, introduced a chain-breaking function. This theory predicts shear thinning if a step function such that no chains longer than a critical value can take part in the network is used. The Leonov-Vinogradov model (ref. 96), recently summarized by Leonov,[6] is based on the continuum model of Walters (eqs. (62), (63), and (64)) and uses as its main assumption the idea that the elements of structure that give rise to the relaxation spectrum $N(\tau)$, called relaxators, will be destroyed if the elastic energy in a relaxator exceeds a critical value. The process is reversible. In terms of a network model, an alternative picture of the Leonov concept is that a given junction will survive only as long as the strain energy associated with it (and in a steady shear this is increasing with elapsed time $(t-t')$) is less than a critical value. Other authors have expressed the survival of a junction as depending on the stress (ref. 97) or on the strain (refs. 98 and 99). Tanner (ref. 99) has pointed out that the Kaye approach is inconvenient because the stress tensor cannot be written explicitly. The entanglement model initiated by Bueche has been developed by Graessley (refs. 100 and 101) on the hypothesis that entangle-

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[6] Leonov, A. I.: Thixotropic Effects in Viscoelastic Media. Vol. 5 of Progress in Heat and Mass Transfer, in press. (Paper presented at an int. sem. (Herceg-Novi), Sept. 1970.)

ments in a flowing polymer solution will have a lower concentration than in the solution at rest; a molecule will be prevented from joining an entanglement network if the adjacent liquid flows past in a time shorter than the time required for the molecule to execute its possible configurations. This configuration time, which is close to the longest relaxation time τ_1 of the Rouse-Zimm models, is necessary for entanglement to occur. In yet another treatment, Booij (ref. 102) has generalized the Chompff-Duiser-Prins model after the manner of Leonov to account for the destruction of entanglement modes of motion when the free energy of the mode reaches a critical value.

It is rather too early to make an assessment of the nonlinear models mentioned, as well as of others of a more empirical nature (refs. 103 and 104). The most promising seem to be those of Leonov and Booij, because the theories have more secure foundations and the results conform more closely to the rather limited experimental data available. The most important conclusion derived, as far as the present review is concerned, is that the relaxation spectrum is truncated at a value τ_m. Consequently the stress tensor of Walters, written in equations (62), (63), and (64), must be modified so that the upper limit of integration in equation (64) is now τ_m

$$\phi(t-t',\,D)=\int_0^{\tau_m}\frac{N(\tau)}{\tau}\,e^{-(t-t')/\tau}\,d\tau$$

The related extra stress tensor of the Lodge network theory (eqs. (108) and (109)) must be modified so that the age distribution function becomes

$$\mu(t-t',\,D)=\sum_{q=1}^{q=m}\mu_q e^{-(t-t')/\tau_q}$$

By experiment, the relationship between τ_m and rate of shear D is found to be of the form

$$\tau_m=\frac{b}{D}$$

where b is a constant of about 2.5 (between 2 and 3) that has been found to be the same for different polymer systems [7] (refs. 91 and 105).

A highly simplified way of appreciating the consequences of the truncated relaxation spectrum is to use the approximation, illustrated in figure 9, that a truncated spectrum is equal to a complete spectrum multiplied by a unit step function. This procedure is similar to that described by Vinogradov et al. (ref. 106). Now, the Lorentzian term appearing in linear viscoelasticity theory and with the form

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[7] Vinogradov, G. V.: Flow, High Elasticity and Relaxation Characteristics of Polymer Systems. Vol. 5 of Progress in Heat and Mass Transfer, in press. (Paper presented at an int. sem. (Herceg-Novi), Sept. 1970.)

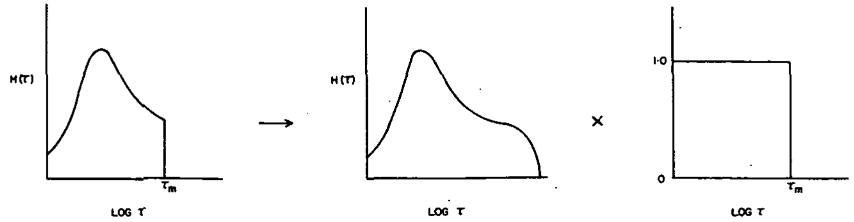

FIGURE 9.—A diagrammatic representation of the relationship: a truncated spectrum is replaceable by the complete spectrum multiplied by a unit step function.

$$\frac{1}{1+(\tau/\tau_m)^2}\ \tau_m=\text{constant}$$

is a good approximation to a step down from unity at low values of τ to 0 as τ passes through τ_m. Then, a relaxation spectrum $H(\tau)$ which gives a viscosity at zero frequency and zero rate of shear of

$$\eta'(0,\,0)=\int_0^\infty \tau H(\tau)\,d\tau$$

will give, at zero frequency and rate of shear D,

$$\eta'(0,\,D)\doteq\int_0^\infty \frac{\tau H(\tau)\,d\tau}{1+(\tau/\tau_m)^2} \tag{116}$$

Now the dynamic viscosity at frequency ω and zero rate of shear is obtained from equation (6) by putting η' equal to G''/ω and is

$$\eta'(\omega,\,0)=\int_0^\infty \frac{\tau H(\tau)\,d\tau}{1+\omega^2\tau^2} \tag{117}$$

Therefore, the analogy, discussed earlier, between continuous shear and oscillatory shear also applies with the model if ω is replaced by $1/\tau_m$. The difference now is that $1/\tau_m$ need not be a linear function of D and, in the substitution $\omega=KD$, K need not be independent of the rate of shear. In the limited number of experiments reported above, it was found that $\tau_m\doteq 2.5/D$, which means that in the experiment K was constant and equal to 0.4.

LIQUID FAILURE

All the linear theories discussed above presuppose no change in the material during shear, and the nonlinear theories presuppose only the structural changes specifically mentioned. No account is taken of the known fact that in a polymer solution the molecules themselves will degrade permanently. No account is taken either of other instabilities that we lump together as liquid failure. Failure is not built into the theories, and a specific failure concept must be added. What is well known is that elastic solids can be made to fracture either in a ductile way or in a brittle way, depending on the rate of strain. Glasses are also breakable. Generally, fracture occurs when the elastic energy, the stress, or the strain exceeds a critical value. There may well be an analogous phenomenon with elastic liquids. Indeed, there is a growing amount of evidence that elastic liquids, hence most liquids, will fracture, not only in an isotropic tension but also in linear extension and shear flows.

The study of the fracture of solids is very difficult because of the presence of structural heterogeneities and microcracks and of the large amount of plastic work necessary at the root of an opening crack. The liquid should be relatively free of these difficulties. Reiner (refs. 107 and 108) has given accounts of the critical elastic strain energy concept as applied to the Maxwell liquid and the Kelvin solid. The author (ref. 109) has attempted to apply a similar theory to explain an instability observed in the flow of elastic silicone fluids in cone-and-plate and parallel-plate rheometers. In this instability a free surface forms in the liquid parallel to the shearing surfaces, and the observed forces, both shear and normal components, fall rapidly. Had the reduced shearing area not been observed, the results would have been interpreted in terms of structural breakdown, whereas there is in fact no structural breakdown, in the sense of a change in microstructure, but a macroscopic breakdown in the sense of a fracture. The effect occurs also with polymer solutions. Work done in the author's laboratory agrees with observations reported by Cox (ref. 110) that a like effect occurs with lubricating greases. In fact, many so-called structural studies on materials in which rheometers were used are exceedingly suspect because of the possible nonrecognition of the effect mentioned. The effect is dependent on shearing geometry and on the elastic properties of the material.

Similar instabilities have been observed in the flow of polymers in tubes. They are grouped under the name "melt fracture," which is a name coined by Tordella (ref. 111) who was one of the first to study the phenomena systematically. The term "elastic turbulence" has also been used. This particular series of instabilities is of great importance in extrusion forming of plastics because the extrudates may have a rough or wavy surface or be fragmented. Hence, production rates are limited. Although the name "elastic turbulence" has been used, the effects have nothing to do with turbulence. Indeed, depending on material and tube size, they have been observed[8] between Reynolds' numbers of 10 and 10^{-15}. A recent discussion on mechanisms of melt fracture has been published by den Otter (ref. 112).

One of the effects has been ascribed by Metzner and White (refs. 113 and 114) to extensional failure in the inlet to a tube. As it passes the narrowing zone of the apparatus, an element of the liquid, which upstream was a cube, extends to a rectangular parallelepiped. If the rate of extension is

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[8] Tordella, J. P.: Personal communication.

sufficiently rapid, the element will fail. There are other examples in plastics processing of these rapid extensional flows that have interesting consequences and are being widely studied. Their importance in lubrication seems to be uncertain (refs. 115 and 116).

The view taken by Metzner and his coworkers (refs. 113, 114, and 117) is that a completely general constitutive equation such as equation (72) can be written in two limits. The steady flow, or slow flow, limit is exemplified by equations (73), (74), and (75) in which the memory functions M_i are allowed to decay to long times. At the other extreme, in a rapidly accelerating flow, these can be replaced by initial constant values of material parameters to give

$$p'_{ij}=M_1(0)\;C_{ij}(s)\Delta s + [M_2(0)\;C_{im}(s_1)\;C_{mj}(s_2)+N_2(0)\;C_{mm}(s_1)\;C_{ij}(s_2)\Delta s_1\;\Delta s_2] + O(\|C_{ij}\|^3) \qquad (118)$$

Such an equation relates stress to the strain accumulated in a short time interval Δs from the start of the motion. It is characteristic of a solidlike behavior and will apply when Δs is short compared with the relaxation time of the material.

In a number of cases in which liquid failure has been suspected, there have also occurred secondary flows, and the relative roles of the two classes of mechanism cannot always be assessed. Secondary flows in Newtonian liquids are well known and are due to inertia forces (ref. 118). Thus, spiraling flow in a curved tube and Taylor vortices in a concentric cylinder flow are familiar examples. The presence of elasticity in the liquid may influence the secondary flow characteristic (ref. 119). The influence is sometimes considerable; sometimes it enhances the secondary flow, and sometimes it opposes. A new class of rheological test method for the measurement of elastic properties of liquids has been studied based on secondary flows [9] (refs. 120 and 121). As regards the problem of failure being a secondary flow process, it is unlikely that this is the complete answer because failures in Newtonian liquids do not occur in similar conditions in which secondary flows are present.

DIMENSIONLESS GROUPS FOR ELASTIC LIQUIDS

Rheology theory is still not sufficiently advanced to explain more than small isolated ranges of material behavior. Therefore, it is useful to make an experimental attack on a problem and correlate the data by using dimensionless groups. With elastic liquids we have available all the usual

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[9] Hayes, J. W.; and Hutton, J. F.: The Effect of Very Dilute Polymer Solutions on the Formation of Taylor Vortices. Vol. 5 of Progress in Heat and Mass Transfer, in press. (Paper presented at an int. sem. (Herceg-Novi), Sept. 1970.)

groups, and in addition we have others by which elasticity may be taken into account.

It has already been mentioned that the group $\omega\tau_1$, where τ_1 is the longest Rouse relaxation time and ω is the frequency of shear, is a useful normalizing parameter for oscillatory shear experiments. For continuous shear experiments, the product $D\tau_1$, where D is the rate of shear, is used. It is a special form of the Weissenberg number, which has been defined in a number of ways (ref. 122) but always as a product of a rate characteristic of the motion and a time characteristic of the material. A related group is the Deborah number, which is the ratio of a time characteristic of the material to a time characteristic of the motion (refs. 122 and 123). Astarita has discussed these groups with special reference to proper invariance, which will allow different types of shearing motions to be correlated. In a slow simple shear the Weissenberg number and the Deborah number are equal, but in other shears this is not necessarily true.

ACKNOWLEDGMENT

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DISCUSSIONS

J. Lamb (The University of Glasgow, Glasgow, Scotland)

This discussion is based mainly upon results presented in two papers that are to be published shortly in the *Proceedings of the Royal Society*.[10, 11] The work described in them has been carried out in the discusser's laboratory, and he is indebted to his colleagues and to the Royal Society for permission to quote a summary of this recent work in the following discussion.

Mr. Hutton has discussed the structure of the modern theory of rheology both from the standpoint of continuum mechanics and as a branch of chemical physics. Much of the work of the discusser and his colleagues is included in this excellent review. The aim of the present discussion is to present some results of more recent experiments that were not generally available to Mr. Hutton at the time he wrote his paper, but which extend the previous understanding of viscoelastic behavior of nonpolymeric liquids. The reader is also referred to the notable contribution that has been made by Dyson (refs. 39, 124, and 125) and more recently by Harri-

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[10] Barlow, A. J.; and Erginsav, A.: Viscoelastic Retardation of Supercooled Liquids. Proc. Roy. Soc., to be published.

[11] Barlow, A. J.; Harrison, G.; Irving, J. B.; Kim, M. G.; Lamb, J.; and Pursley, W. C.: The Effect of Pressure on the Viscoelastic Properties of Liquids, Proc. Roy, Soc., to be published.

son and Trachman [12] in using the measurements which have been made of the linear viscoelastic properties of liquids under cyclic shear and compression in an attempt to analyze the complex situation encountered in EHD lubrication.

In his contribution to the discussion of Naylor's paper presented at the 1969 NASA symposium on the lubrication of concentrated contacts, Dyson (ref. 125) has shown that an analysis based upon the BEL model of a viscoelastic liquid (refs. 17, 18, and 126) can provide a satisfactory representation of the frictional traction exerted in EHD contacts. The present purpose is to elaborate on a previously known deficiency of this model that is now resolved and to present new results carried out under high hydrostatic pressures in the hope that this may stimulate further analysis of the contact lubrication problem. The BEL model as described by Mr. Hutton in his paper for an angular frequency $\omega(=2\pi f)$ of alternating shear gives the expression for the complex shear compliance of a pure liquid

$$J^*(j\omega)=J'-jJ''=J_\infty+\frac{1}{j\omega\eta}+\frac{2J_\infty}{(j\omega\tau_m)^{\frac{1}{2}}} \tag{119}$$

where $J_\infty(=1/G_\infty)$ is the limiting high-frequency shear compliance, η is the steady-flow viscosity, and τ_m is the characteristic Maxwell relaxation time $\tau_m=\eta J_\infty$. Separating real and imaginary parts of both sides of this equation gives equations (12) and (13) of Mr. Hutton's paper:

$$J'(\omega)=J_\infty+\frac{J_\infty}{(\omega\tau_m/2)^{\frac{1}{2}}}=J_\infty+J_1(\omega) \tag{120}$$

$$J''(\omega)=\frac{1}{\omega\eta}+\frac{J_\infty}{(\omega\tau_m/2)^{\frac{1}{2}}}=\frac{1}{\omega\eta}+J_2(\omega) \tag{121}$$

The quantities $J'(\omega)$ and $J''(\omega)$ are obtained from the measured values of density ρ and the components of the shear mechanical impedance of the liquid $Z_L=R_L+jX_L$:

$$J'(\omega)=\rho\frac{R_L{}^2-X_L{}^2}{(R_L{}^2+X_L{}^2)^2} \tag{122}$$

$$J''(\omega)=\frac{2\rho R_L X_L}{(R_L{}^2+X_L{}^2)^2} \tag{123}$$

where

$$J^*(j\omega)=\frac{\rho}{Z_L{}^2}$$

Inspection of equations (120) and (121) shows that for the BEL model, $J_1(\omega)=J_2(\omega)=J_\infty/(\omega\tau_m/2)^{\frac{1}{2}}$, so a plot of $J2(\omega)$ versus $J_1(\omega)$ would give a straight line of slope 45°. Since both $J_1(\omega)$ and $J_2(\omega)$ are proportional to

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[12] Harrison, G.; and Trachman, E. G.: The Role of Compressional Viscoelasticity in the Lubrication of Rolling Contacts. J. Lubric. Technol., to be published.

$\omega^{-\frac{1}{2}}$, each tends to infinity as $\omega \rightarrow 0$. However, the effect on $J^*(j\omega)$ is swamped by the term $1/\omega\eta$ in $J''(\omega)$, which represents the viscous flow term and predominates at low frequencies.

As indicated by Mr. Hutton, this model gives a satisfactory representation of the available experimental data obtained from measurements using cyclic shear over the viscoelastic relaxation region. Nevertheless, the limitation of the model was realized and pointed out in 1969 (ref. 18). When the equations of the BEL model are transformed to calculate the (linear) creep behavior, this gives rise to the prediction of unlimited creep strain, which is physically unacceptable. The predicted deformation in creep as a function of time t increases as $t^{\frac{1}{2}}$ in consequence of the dependence of $J_1(\omega)$ and $J_2(\omega)$ on $\omega^{-\frac{1}{2}}$, as mentioned above. The inadequacy of the model clearly arises at low frequencies or long times corresponding to the experimentally ill-defined region between truly Newtonian behavior and the onset of viscoelastic relaxation. In this region the components R_L and X_L of the shear mechanical impedance tend to equality with decreasing frequency. Measured values of $J''(\omega)$, as obtained from equation (123), are here predominately governed by the viscous term $1/\omega\eta$ of equation (121); and $J'(\omega)$ obtained from equation (122) is subject to considerable error as a result of the term $(R_L^2 - X_L^2)$ in the numerator. This explains why this inadequacy of the model was not revealed by the earlier measurements of the viscoelastic response under alternating shear. This effect would have a pronounced influence on creep or stress relaxation, but, with a single exception, such measurements have not been carried out on nonpolymeric liquids.

More recently, Barlow has developed a new experimental system designed to give results at a frequency of cyclic shear of 30 MHz of an order of magnitude greater in accuracy than previous techniques. This has been used in the work of Barlow and Erginsav to determine the viscoelastic properties of a number of organic liquids in the supercooled state.[13] The results obtained can best be described in the context of the general expressions set forth by Gross (ref. 25), who shows that in oscillatory shear the complex compliance of a liquid can be described by

$$\begin{aligned} J^*(j\omega) &= J_\infty + \frac{1}{j\omega\eta} + J_r^*(j\omega) \\ &= J_\infty + \frac{1}{j\omega\eta} + J_r \int_0^\infty \frac{N(\tau)\,d\tau}{1+j\omega\tau} \qquad (124) \end{aligned}$$

where $N(\tau)$ is the spectrum of retardation times defined so that the integral of $N(\tau)\,d\tau$ is unity. The variable J_r is the retardational compliance, and at low frequencies the real part of $J^*(j\omega)$ tends to the value $J_\infty + J_r$.

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[13] See footnote 10.

For a Maxwell liquid characterized by a single retardation time $\tau_m = \eta J_\infty$, the retardation process is absent and J_r is zero.

In creep experiments the time variation of the shear strain $\epsilon(t)$ in response to a constant stress γ_0 imposed at $t=0$ is given (ref. 25) by

$$\frac{\epsilon(t)}{\gamma_0} = J(t) = J_\infty + \frac{t}{\eta} + J_r \int_0^\infty N(\tau)\ (1 - e^{-t/\tau})\ d\tau \tag{125}$$

and J_r is therefore the recoverable delayed compliance.

The new results obtained by Barlow and Erginsav[14] show that the complex retardational compliance $J_r^*(j\omega)$ of equation (124) can be described by an empirical equation used by Davidson and Cole (ref. 127):

$$J_r^*(j\omega) = \frac{J_r}{(1 + j\omega\tau_r)^\beta} \tag{126}$$

where τ_r is a characteristic retardation time that marks the termination of the spectrum at long times and β is a constant found to be close to 0.5 for the liquids investigated.

A comparison between the new measurements of improved accuracy and the predictions of the BEL model is shown in figure 10 for tri(*o*-tolyl) phosphate: the deviations in the region below $\omega\tau_m = 1$ are small but significant and were obscured within the experimental scatter of the earlier measurements. The plot of $J_2(\omega)/J_\infty$ versus $J_1(\omega)/J_\infty$ is shown in figure 11 for two of the liquids, tri(*m*-tolyl)phosphate and tri(*o*-tolyl)phosphate, for each of which the value of β is found to be 0.5. The points obtained at the highest and lowest temperatures of measurement are indicated on figure 11 for each liquid, and the frequency of measurement was 30 MHz throughout. All measurements were confined to the supercooled region where the variation of viscosity with temperature is described by the modified free-volume equation (ref. 128):

$$\ln \eta = \frac{A + B}{T - T_0} \tag{127}$$

Results of a similar nature have been obtained for a number of other liquids with values of β ranging from 0.4 for tri(β-chloroethyl)phosphate to 0.6 for squalane. Measured values of J_r ranged from 4.0 J_∞ for di(isobutyl) phthalate ($\beta = 0.5$) to 26.0 J_∞ for tri(β-chloroethyl)phosphate.

The skewed arc plots of figure 11 are drawn as the best fit to the experimental points, following the Davidson-Cole equation. The temperature dependence of the term $\omega\tau_r$ is not apparent in the plot of figure 11, but is demonstrated in figure 12 where $J_1(\omega)/J_\infty$ and $J_2(\omega)/J_\infty$ are plotted versus $\log \omega\eta J_\infty$ [$= \log \omega\tau_m$]. The variation for tri(*m*-tolyl)phosphate described by the BEL equation, namely, $J_1(\omega)/J_\infty = J_2(\omega)/J_\infty = (2/\omega\eta J_\infty)^{\frac{1}{2}} = (2/\omega\tau_m)^{\frac{1}{2}}$ is shown by the broken line in figure 12. The measured values converge to

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[14] See footnote 10.

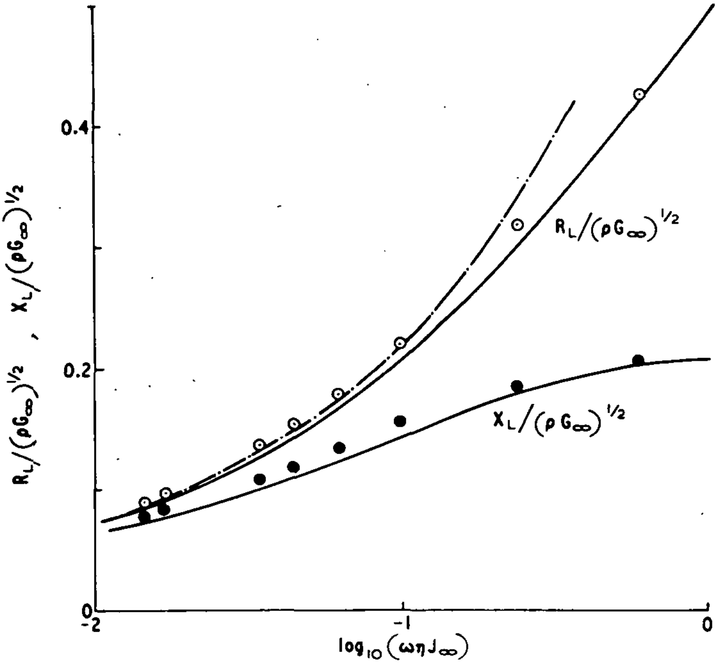

FIGURE 10.—Measured values of the normalized shear impedance components for tri(*o*-tolyl)phosphate compared with the prediction of the Barlow-Erginsav-Lamb model equation (119) (solid lines). The broken line represents Newtonian behavior:

$$\frac{R_L}{(\rho G_\infty)^{\frac{1}{2}}}=\frac{X_L}{(\rho G_\infty)^{\frac{1}{2}}}=\left(\pi f\frac{\eta}{G_\infty}\right)^{\frac{1}{2}}$$

(By permission of the Royal Society.)

this curve as $\omega\tau_m$ increases toward unity so that for $\omega\tau_m>1$ it is not possible to distinguish between the form of variation given by the BEL equation and that of the Davidson-Cole expression. In the latter case (eq. (126)), τ_r is always found to be greater or much greater than τ_m. Thus for $\omega\tau_m>1$, $\omega\tau_r>>1$, and in this range equation (126) reduces to

$$J_r^*(j\omega)\simeq\frac{J_r}{(j\omega\tau_r)^\beta}$$

which for $\beta=0.5$ gives

$$J_r^*(j\omega)\simeq\frac{J_r}{(j\omega\tau_r)^{\frac{1}{2}}} \tag{128}$$

Now the BEL equation gives

$$J_r^*(j\omega)=\frac{2J_\infty}{(j\omega\tau_m)^{\frac{1}{2}}}$$

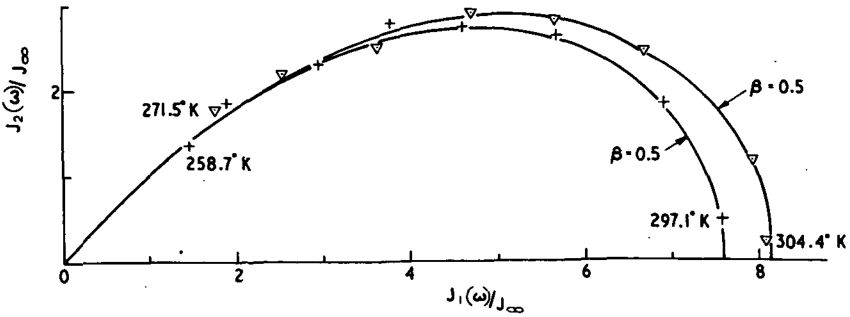

FIGURE 11.—Davidson-Cole skewed arc plots of $J_2(\omega)/J_\infty$ versus $J_1(\omega)/J_\infty$ in accordance with equation (126):

$J_r^*(j\omega) = J_r/(1 + j\omega\tau_r)^\beta$
+: tri(*m*-tolyl)phosphate
▽: tri(*o*-tolyl)phosphate
$\beta = 0.5$ for each liquid
$f = 30$ MHz

(By permission of the Royal Society.)

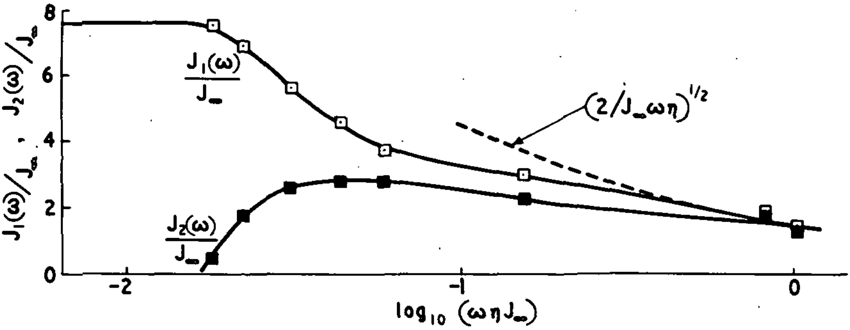

FIGURE 12.—Measured values of $J_1(\omega)/J_\infty$ and $J_2(\omega)/J_\infty$ for tri(*m*-tolyl)phosphate plotted versus log $(\omega\tau_m)$, where $\tau_m = \eta J_\infty$. (By permission of the Royal Society.)

Thus for $\omega\tau_r >> 1$, we find by comparing these equations that

$$\frac{\tau_r}{\tau_m} = \left(\frac{J_r}{2J_\infty}\right)^2 \tag{129}$$

The variable J_r has been assumed in this work to have the same temperature variation as J_∞ so that in the lower temperature range τ_r/τ_m becomes constant independent of temperature, as is found to be the case. The numerical value for this ratio predicted by equation (129) is also found to apply.

Assuming that equation (126) is valid, τ_r may be calculated at any given

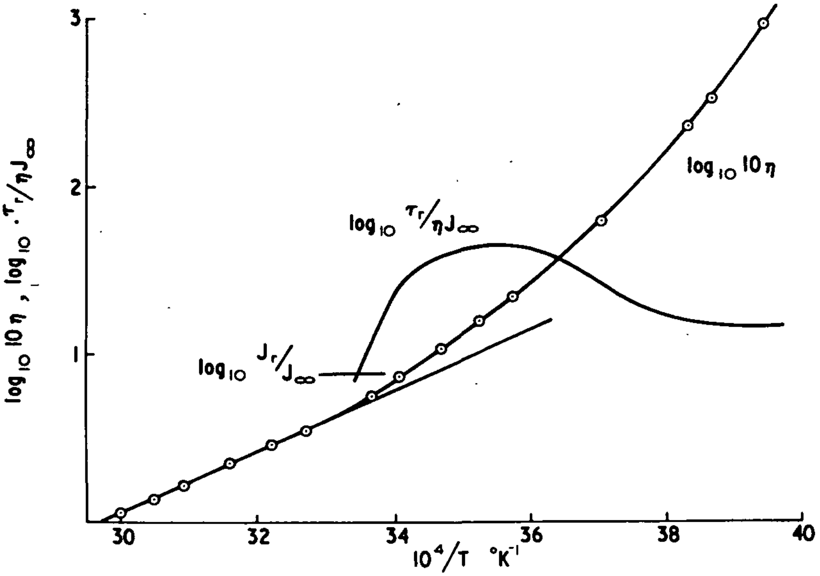

FIGURE 13.—The variation of $\log_{10} \tau_r/\tau_m$ and $\log_{10} \eta$ with $1/T$ for tri(*m*-tolyl)phosphate. (By permission of the Royal Society.)

temperature in the retardation region and plotted, as in figure 13, as $\log (\tau_r/\tau_m)$ versus $1/T$. The constant value of this ratio at low temperatures, in accordance with equation (129), is here demonstrated. Clearly at higher temperatures τ_r has a markedly different dependence upon temperature than does τ_m. Also shown in figure 13 is the plot of $\log \eta$ versus $1/T$ showing the transition from the free-volume limited viscosity region (eq. (127)) to the Arrhenius region around the Arrhenius temperature T_A. A general finding is that at this temperature $\tau_r/\tau_m = J_r/J_\infty$, indicating that the retardation viscosity $\eta_r = \tau_r/J_r$ is the same as the viscosity η. Unfortunately, it was not possible to extend these measurements to temperatures above T_A.

Direct comparison of the above results with data obtained in creep is not yet possible for any given liquid. The only nonpolymeric liquid on which creep results are available is 1,3,5-tri(α-naphthyl)benzene for which the recoverable compliance has been measured by Plazek and Magill at temperatures close to the glass transition temperature (refs. 129 and 130). They find that their data obtained over a wide range of temperatures reduces to a single curve. Their curve for this liquid is reproduced in figure 14 for a reference temperature of 64.2° C. At short times the curve tends to a value corresponding to $J_\infty = 0.81 \times 10^{-10}$ cm^2/dyne and to $J_r + J_\infty = 2.58 \times 10^{-10}$ cm^2/dyne at long times. Hence $J_r = 1.77 \times 10^{-10}$ cm^2/dyne. Substitution in Davidson-Cole equation (126) with $\beta = 0.3$ and $\tau_r = 3.55$

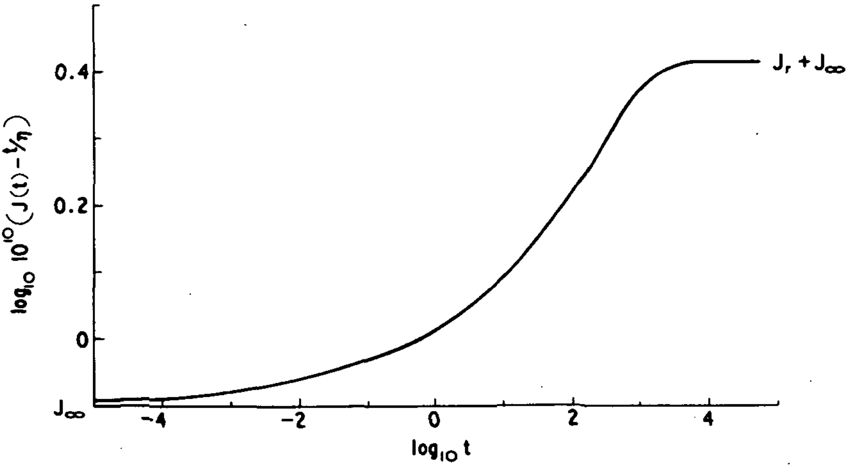

FIGURE 14.—Recoverable compliance $[J(t) - t/\eta]$ of 1,3,5-tri(α-naphthyl)benzene at 64.2° C plotted against log t. The curve shown is the temperature-reduced curve of Plazek and Magill (refs. 129 and 130). This agrees with the transformed calculation of the total recoverable compliance using the equation

$$J^*(j\omega) = J_\infty + 1/j\omega\eta + J_r/(1 + j\omega\tau_r)$$

where $J_\infty = 0.081 \times 10^{-10}$ cm²/dyne, $J_r = 1.77 \times 10^{-10}$ cm²/dyne, $\beta = 0.3$, and $\tau_r = \eta_r J_r$, where $\eta_r = 3.55\eta = 3.55 \times 10^{12.35}$ P. (By permission of the Royal Society.)

$J_r\eta$, where η is the measured viscosity of $10^{12.35}$ poise at 64.2° C, leads to a transformed calculation of the total recoverable compliance as a function of time, which is indistinguishable from the results of figure 14.

To conclude this part of the discussion, it would appear that the use of equation (126) gives predictions that are compatible with known experimental results in the linear viscoelastic region including alternating shear and creep. It remains, however, for the parameters τ_r, β, and J_r to be determined for each liquid in addition to J_∞, η, and ρ. Nevertheless, to a good approximation, except at long times ($>> \tau_m$), the BEL model can be used with confidence. It should perhaps be emphasized that in all cases J_∞ has been found to vary linearly with temperature and this has been confirmed for many liquids and mixtures of liquids.

Attention is now given to the measurement of viscoelastic behavior at high pressures, the results of which are of importance to the lubrication engineer, as has been shown [15] (refs. 124 and 125). The essential point here is that it is possible to make measurements under alternating stress in a liquid at high pressure because this method of measurement results in negligible energy dissipation. Hence the temperature and pressure of the

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[15] See footnote 12.

liquid are unaffected during the course of the experiments in contrast to measurements in steady rotation under high rates of shear. Again, truly characteristic parameters of the liquid are obtained in cyclic shear, which are amplitude independent.

Although some initial measurements of the viscoelastic properties of a lubricating oil at high pressures were made by Barlow and Lamb in 1959 (ref. 12), this high-pressure work has only recently been extended to cover measurements in other liquids.[16] To date, two liquids *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether and di(2-ethylhexyl)phthalate have been investigated at pressures up to 1400 MN/m^2 and for frequencies of 10 and 30 MHz. These two liquids were chosen from the many that have been studied as a function of temperature and frequency at atmospheric pressure. The complexities involved in measurements at high pressures are such that it is not feasible to measure the reactive part X_L of the shear mechanical impedance and only the resistive part R_L can be determined. On this account the existence of the retardational process, described in the paper by Barlow and Erginsav,[17] cannot be confirmed in the high-pressure measurements.

Separate measurements have been made of the density ρ and steady-flow viscosity η as a function of pressure. The apparatus used for measurements of density is described in detail by Yazgan (ref. 131) and is based on a method given by Shakhovskoi, Lavrov, Pushkinskii, and Gonikberg (ref. 132). The technique employs a bellows and a differential transformer enclosed within the pressure vessel. Measurements of the steady-flow viscosity as a function of pressure have been made using the automatic recording high-pressure viscometer developed in this laboratory by Irving and Barlow (ref. 133). Recordings are made electrically of the time of fall of a sinker in a vertical cylindrical tube.

Measured values of $R_L{}^2/\rho$ as a function of hydrostatic pressure at a temperature of 30° C are shown in figure 15 for *bis*(*m*-(*m*-phenoxyphenoxy)-phenyl)ether and in figure 16 for di(2-ethylhexyl)phthalate. At sufficiently high pressures the recorded values of $R_L{}^2/\rho$ at frequencies of 10 and 30 MHz are indistinguishable within experimental error. This is taken as evidence that in this high-pressure region, the liquid is behaving elastically and hence that $R_L{}^2/\rho = G_\infty$. This is also supported by previous experience from the variable frequency and temperature measurements at atmospheric pressure where the elastic region is known to be reached for these frequencies when conditions are such that the steady-flow viscosity exceeds 10^6 poise (10^5 Nsec/m^2). The value of G_∞ at atmospheric pressure is also known from previous work, and the appropriate value is marked on the ordinate axes of figures 15 and 16. The results of the pressure measurements show that G_∞ is a linear function of pressure and this is particularly

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[16] See footnote 11.

[17] See footnote 10.

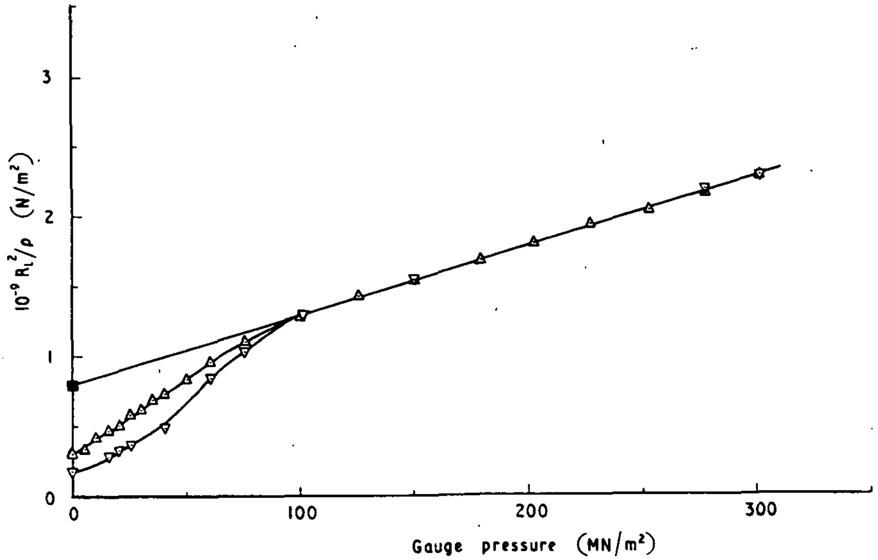

FIGURE 15.—Measured values of $R_L{}^2/\rho$ as a function of hydrostatic pressure for *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether at 30° C. ▽: 10 MHz; △: 30 MHz; ■: extrapolated value obtained by variation of temperature at atmospheric pressure. (By permission of the Royal Society.)

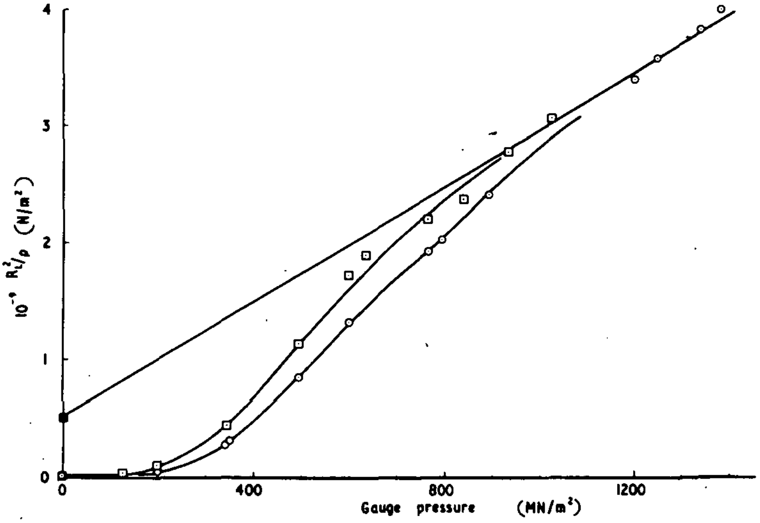

FIGURE 16.—Measured values of $R_L{}^2/\rho$ as a function of hydrostatic pressure for di(2-ethylhexyl)phthalate at 30° C. ⊙: 10 MHz; ⊡: 30 Mhz; ■: extrapolated value obtained by variation of temperature at atmospheric pressure. (By permission of the Royal Society.)

well established for *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether (fig. 15). The accuracy is sufficient to establish that J_∞ ($=1/G_\infty$) is not linearly dependent upon pressure. The variation of G_∞ with pressure is described by the following equations.

For *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether

$$G_\infty = 790 + 4.97p \ \mathrm{MN/m^2}$$

for di(2-ethylhexyl)phthalate

$$G_\infty = (500 + 2.45p) \ \mathrm{MN/m^2}$$

where p is in $\mathrm{MN/m^2}$.

The data obtained over the relaxation region are plotted in normalized form in figure 17 together with results obtained at atmospheric pressure by variation of temperature. The solid curve represents the behavior according to the BEL equation (119).

The results shown in figure 17 demonstrate that within experimental error the viscoelastic relaxation in these liquids conforms to the predictions of the BEL equation if due account is taken of the variation of viscosity and density with pressure. We have no reason to doubt the general validity of this conclusion, but supporting measurements on other liquids are in progress. Dyson has incorporated these findings in his most recent analysis of the problems encountered in EHD lubrication (ref. 39). The use that can be made of such information as can be obtained from measurements using oscillatory shear would now seem to be established. In this connection, my colleagues and I have greatly benefited from regular discussions which we have had with Mr. Dyson and Mr. Hutton. I hope that these remarks may serve to amplify some of the analysis that Mr. Hutton has given in his excellent review paper.

H. Markovitz (Carnegie-Mellon University, Pittsburgh, Pa.)

Mr. Hutton has prepared a remarkable statement on the theory of rheology. He is to be congratulated. It is not that I agree with everything he says, but, in many cases, my points of disagreement are technical points that might better be discussed elsewhere. My comments here will be limited to relatively minor matters: suggestions for rearrangements, changes of emphasis, and additions. One can hope that this somewhat different point of view might be helpful in rounding out the subject. It would be tiresome to bring up every such difference of viewpoint; only a few have been selected for discussion.

The Boltzmann Equation.—For example, in the section on small-strain linear viscoelasticity, more emphasis could be placed on Boltzmann's equation

$$\sigma(t) = \int_{-\infty}^{t} \phi(t-t') \, \frac{d\gamma(t')}{dt'} \, dt'$$

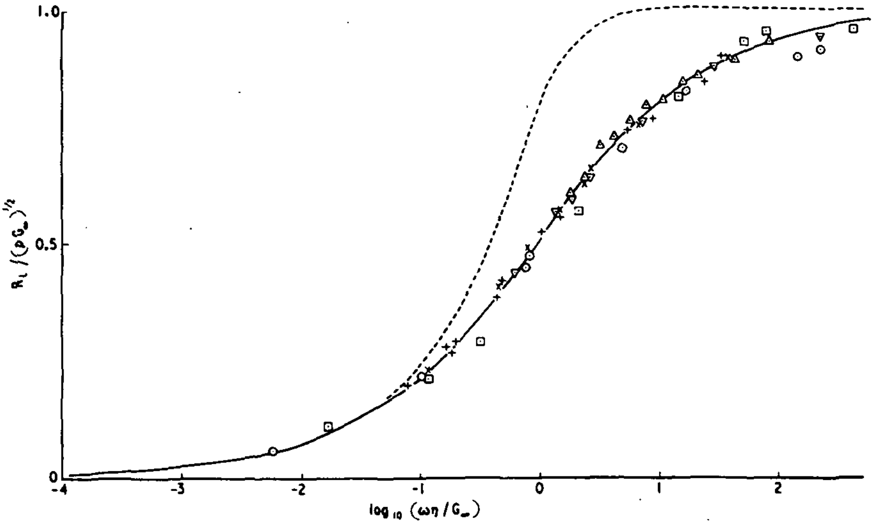

FIGURE 17.—Normalized values of the resistive component of the shear mechanical impedance with pressure, temperature, and frequency as experimental variables. Measurements at atmospheric pressure as a function of temperature at frequencies *from 6 to 450 MHz:*

+: *bis*(*m*-(*m*-phenoxyphenoxy)phenyl) ether
×: di(2-ethylhexyl)phthalate

Measurements at 30° C as a function of pressure:

▽: *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether, 10 MHz
△: *bis*(*m*-(*m*-phenoxyphenoxy)phenyl)ether, 30 MHz
⊙: di(2-ethylhexyl)phthalate, 10 MHz
⊡: di(2-ethylhexyl)phthalate, 30 MHz

The solid curve represents the behavior described by the BEL equation The broken curve represents the theoretical variation for a single relaxation process. (By permission of the Royal Society.)

which, as the author recognizes, is the most general expression of linear viscoelasticity for simple shearing deformation. The other models, Maxwell, BEL, and distributed Maxwell, are special cases, as indicated. It is not difficult to give a motivation, some may loosely call it a derivation, for this equation of viscoelasticity in terms of the physical phenomenon of stress relaxation coupled with the assumption of linearity or superposition.

The Boltzmann equation also clearly shows the basic idea of viscoelasticity: that the stress σ in a deformed viscoelastic body is not determined by the deformation (or rate of deformation) at that instant t, but depends on states of strain γ the material particle has undergone during all previous terms t' or, as stated in more anthropomorphic terms, the material has a memory. Actually, the stress depends more on recent strains than on earlier ones, as reflected mathematically in the fact that the relaxation function $\phi(t)$ is a monotonically decreasing function of time. Thus, it is often said that the material has a fading memory.

It must be admitted that introducing viscoelasticity as a combination of viscous and elastic components has pedagogical virtue. However, it seems to me that this approach is frequently misunderstood and leads to the obliteration of the basic distinction between viscoelasticity and the more classical models of elasticity, where the stress is determined by the strain at that instant of time, and viscosity, where the rate of deformation determines the present value of the stress.

Emphasizing the Boltzmann equation is also helpful because of its relation to nonlinear theories of viscoelasticity, for example, to Noll's theory of the simple fluid. (See eq. (70).) If the deformation history is such that the strain has been small in the recent past, then the theory of the simple fluid reduces to the Boltzmann equation.

Let me hasten to add that I am not advocating that all mention of the special cases, such as the Maxwell and BEL models, should be eliminated. They serve very useful purposes. For example, some calculations can be carried out for these models that cannot be for the more general formulation. However, one must always keep in mind the limitations of the special models. One should expect that the results of such calculations frequently bear only a qualitative resemblance to the behavior of actual materials.

Miscellaneous Comments.—In a similar fashion to the discussion of linear viscoelasticity, my personal preference would have been to introduce finite-strain viscoelasticity through the Coleman-Noll simple fluid model (or the essentially equivalent theories of Rivlin and Green) rather than through the modification of small-strain models. Generalizing equations of linear viscoelasticity by techniques such as Oldroyd's do not lead to unique nonlinear relations. Qualitatively different behavior is predicted by the various nonlinear theories arising from the same linear theory. A sufficiently good simple nonlinear theory is still a matter of earnest pursuit and debate.

It seems to me that the theories of viscoelasticity, both linear and nonlinear, should find use in discussing some lubrication problems. In many applications, an element of fluid is taken from an essentially stationary state to a highly deformed state in a matter of 10 or 100 μsec. The time-dependent, i.e., the viscoelastic, properties are likely to be of importance. There is a good probability that the steady-state properties, such as the shear-dependent viscosity $\eta(\dot{\gamma})$ and the usual normal stress functions, cannot characterize the material in such cases. The importance of viscoelasticity in a given problem depends on the time scale of the experiment and the nature of the lubricant. Polymer-containing lubricants are more likely to require a viscoelastic analysis.

The solution of many theoretical problems frequently involves some assumption about the nature of the flow field. In dealing with fluids exhibiting nonlinear viscoelastic behavior, this calls for special caution, because qualitatively different flow patterns have been found with these fluids from those observed for Newtonian fluids.

Nonlinearity also introduces unexpected time-dependent behavior that differs from linear viscoelastic behavior. For example, if a fluid is brought to a state of steady simple shear from a rest state, the shear stress monotonically goes from 0 to its steady-state value if it exhibits linear viscoelastic behavior; however, with nonlinear characteristics, the stresses (shear and normal) go through a maximum in some cases. It seems that such effects could be of importance in some lubrication problems.

From Hutton's text, one might conclude that viscoelasticity in isotropic expansion or contraction is not theoretically treated. Actually in linear viscoelasticity the relation between the isotropic pressure and volume changes follows an integral relationship similar to that between shear stress and shear cited above. In fact, Boltzmann proposed the full three-dimensional equations of linear viscoelasticity about 100 years ago (1874). However, it is true that only limited data are available on the viscoelastic properties of polymers in isotropic deformations.

Although it is implicit in the text and is generally known, it should be explicitly stated that, in the actual solution of a problem, the constitutive equations must be supplemented with the force balance equation and by the boundary and initial conditions.

Development of appropriate applicable molecular theories is a difficult task. Fairly rigorous theories can be made for dilute polymer solutions where the individual molecules do not interact, but even here it has been found necessary to base the calculation on a fictitious model, such as the bead-spring chain rather than a more realistic model. When interactions between molecules are to be taken into account, further assumptions covering the model must be made. I do not find believable Bueche's argument that "the isolated molecule is a valid concept also for polymer melts." These assumptions may be fairly readily acceptable, such as the δ factor of Chompff, Duiser, and Prins. On the other hand, the temporary network model appears to require ad hoc assumptions, such as the assumption of equation (109) for μ and then leads to oversimplified results.

Perhaps, when we remember that there is still not a completely acceptable molecular theory of the viscosity of liquids consisting of small molecules, we should not be too impatient over the lack of a rigorous theory for concentrated polymer systems.

G. H. Kinner (Royal Aircraft Establishment, Farnborough, England)

Mr. Hutton says his paper is not concerned with applications to lubrication theory, past or future. He does admit, however, that the theory of rheology requires further advancement and that there is a need to correlate theory with experimental data.

Accepting these last remarks, I thought you would be interested in a brief statement regarding some work we are sponsoring on EHD lubrication under conditions of lubricant starvation in the entry region to a rolling contact.

The objective is an improved understanding of the lubrication of gyroscope bearings where the sole supply of lubricant is a few milligrams of oil impregnated into a porous cage. Previously, the EHD lubrication problem has been solved by assuming the inlet space is so completely filled with lubricant that the pressure rise commences at a considerable distance from the effective load-carrying region. If the contact operates under partially starved conditions, the thin layers of lubricant on the approaching surfaces will not merge until they reach a point closer to the Hertzian contact zone. The extreme case is when the contact is completely dry, whereby the point of pressure buildup is on the leading edge of the Hertzian contact zone.

Using this concept, the theoretical analysis of line contacts operating under EHD lubrication conditions has now been appropriately modified. The variations of film thickness, film shape, pressure distribution, and rolling friction for limited lubricant quantities have been computed for a given speed and load.

Denoting in the x-direction the limits of the Hertzian zone as being ± 1000, the negative side indicates the inlet region. A zero pressure starting at $-\infty$ represents the fully flooded condition and one at -1000 denotes dry contact. For the load and speed selected, solutions were obtained for zero pressures at values of -5000, -4000, -3000, -1500, -1400, -1300, and -1200. The theoretical film shapes, thicknesses, and pressure distributions were computed, and some of the data are shown in table 1.

TABLE 1.

x_{inlet}	$H_{\text{min}} \times 10^6$	x_{spike}	$P_{\text{spike}} \times 10^4$	$T_R \times 10^8$ [a]
$-\infty$	15.97	858	26.32	------------
-5000	15.86	858	26.39	1.38
-4000	15.85	859	26.18	1.31
-3000	15.70	860	26.02	1.17
-2000	14.99	864	25.48	.91
-1500	13.54	864	21.92	.57
-1400	12.77	891	20.76	.47
-1300	11.62	902	18.96	.35
-1200	9.93	921	16.30	.22

[a] T_R = dimensionless traction force $\frac{1}{2}\int P\,dH$.

It is predicted that, as the severity of starvation increases, the pressure profile tends more toward the Hertzian ellipse with a reduced pressure spike. Also, while the film thickness values do not drop markedly until there is a high degree of starvation, the traction forces are by then greatly reduced in comparison with those for the fully flooded case.

The operational and economic significances of these results may well be considerable. The results indicate that not only is a very small amount of lubricant sufficient to produce the full EHD film, but if such a quantity is used, the friction losses and hence the temperature of the conjunction are also appreciably lowered. In turn, this situation would give an enhanced film thickness due to a lower drop in lubricant viscosity.

We feel that this theoretical study, after being verified experimentally, should lead to a better understanding of and design modifications for components operating in the EHD regime. Rolling-element bearings are on top of the list of machine parts that could benefit from the results of this research.

We are grateful to Professor Dowson and his colleagues who are carrying out this work under contract to the Ministry of Defence. A more detailed description will be given at a conference on EHD lubrication at the Institution of Mechanical Engineers.[18]

P. M. Ku (Southwest Research Institute, San Antonio, Tex.)

Mr. Hutton has accomplished a superb feat of introducing the theory of rheology to lubrication engineers: giving them a physical exposition of the subject matter as well as tangible mathematical tools with which to work. Indeed, if a lubrication engineer, after having read this article, does not try to put some of the tantalizing ideas to use, it will not be Mr. Hutton's fault but his own. Having said this, and with due deference to Mr. Hutton, it must also be recognized that rheology is only one facet of the complete lubrication problem. There is the question of priorities.

As Mr. Hutton has observed, the assumption of Newtonian lubricant behavior has been found to be quite adequate in many lubrication problems, but not in others. The lubrication of machine elements with counterformal surfaces and operating at high loads and speeds is a prime example of the latter class. The fact that rigorous rheological theory has been slow in finding its way into such problems, those which may very well stand to benefit much, is regrettable but perhaps also understandable. First, the physical and chemical situations involved are so exceedingly complex that one hardly knows how to differentiate the individual trees in a vast forest. Indeed, one needs only to refer to the various lectures presented at this

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[18] See Castle, P.; and Dowson, D.: A Theoretical Analysis of the Starved Elastohydrodynamic Lubrication Problem for Cylinders in Line Contact. Elastohydrodyn. Lubric. Symp. (Leeds, England), Apr. 11–13, 1972. (Editor's note.)

symposium, and the discussions that they have provoked, to realize that many key aspects of the problems are not only not amenable to satisfactory treatment but also not really understood. Second, assuming that the other physical and chemical behaviors can be quantitatively described, the addition of a sophisticated rheological description for the lubricant only adds another dimension to an already difficult mathematical problem. The lubrication engineer needs help and, above all, inducement to seek help, and who but the rheologist can supply both?

Quite apart from the issues raised in their lectures presented at this symposium by Professor Cheng and Drs. Cameron and Gentle, as well as by their discussers, Mr. Kinner has now mentioned the phenomenon of the starvation of EHD conjunctions in the preceding discussion on this lecture. Inasmuch as the problem has been raised, one wonders if Mr. Hutton has any comments regarding the effect of the lubricant's rheological or other properties on the starvation of EHD conjunctions? How can it be controlled from the lubricant's point of view?

Another phenomenon of considerable rheological implications, at least in this discusser's opinion, is the "dimple" reported by Chiu and Sibley (ref. 134). Using polybutene and an optical ball-flat conjunction, these investigators noted that the EHD film profiles were different in pure rolling and pure sliding at the same load and entrainment velocity. In pure rolling, they observed the usual flat region in the center of the horseshoe. However, in pure sliding, they observed a local thickening of the film in the center, resulting in a dimple, at very low speeds. They attributed this phenomenon to the Weissenberg effect. Would Mr. Hutton care to comment on it from the rheological standpoint?

Finally, it appears to this discusser that a fundamental aspect of EHD lubrication, one which sorely requires attention and understanding, is the rheological behavior of the surface films. The conventional EHD computations assume that the bulk rheological properties of the lubricant applies. These surface films may be formed by physical adsorption, by chemical adsorption, or by some form of chemical reaction, and the presence of oxides and wear debris may cause further physical or chemical interactions. Can we assume that the rheological behavior of such surface films be the same as the bulk behavior of the lubricant, under typical EHD operating conditions at any rate? What do we know about the rheological behavior of the surface films with respect to temperature, pressure, stress and strain, and strain rate? How can we go about determining these?

R. J. Mannheimer (Southwest Research Institute, San Antonio, Tex.)

Mr. Ku has made a plea for more basic information on film rheology. While this phenomenon has not been precisely defined, I assume that we are referring to the film formed by the adsorption, either physical or chemical, of surface-active species at the metal-oil interface. While it is well known that the rheology of an interface can be altogether different from that of the bulk phases, the actual measurements of the properties have been confined to gas-liquid or liquid-liquid systems. Furthermore, the theory of measurement has been quite primitive; however, recent publications have described techniques that can provide quantitative information of complex surface rheological phenomena, including both shear-dependent and viscoelastic behavior (ref. 135).

The question that I want to pose is this: Since it has been shown by Mr. Groszek in his lecture at this symposium that the metal surface is normally contaminated with bound water, would it be possible to obtain information that is important to liquid lubrication technology by making rheological measurements of the oil-water interface? To answer this question, one must have information on the similarities, if any, between the state of the adsorbed film on a metal surface containing bound water in the presence of free oil as compared to the state of the film at an ordinary oil-water interface. If it can be shown that the film is in essentially the same physical state, then it may be possible to obtain the basic properties of the lubricating film that have been requested.

LECTURER'S CLOSURE

Professor Lamb's contribution does not call for a detailed reply. The limitations of the BEL model of linear viscoelasticity are now generally recognized. Nevertheless, as a simple two-parameter representation of a considerable amount of experimental data, it is an excellent model. (See figs. 2 and 17.) M. C. Phillips and I noticed some time ago (ref. 19) that there was a systematic deviation of experimental results from the predictions of the BEL model. The deviation was just outside experimental error. From our experience of the technique, I can confirm that experimental accuracy of a very high degree is necessary so that the results may be split into the various contributions of the new model.

Since Professor Lamb has introduced the topic of measurements of viscoelastic behavior at high isotropic pressures, I should like to add that at Thornton Research Center we have been involved in a similar project. We have conducted measurements of di(2-ethylhexyl)phthalate at a number of temperatures at pressures up to 700 MN/m^2 and at frequencies of 6, 18, 30, and 78 MHz. Our results point to a rather smaller variation of $G(\infty)$ with pressure than that quoted by Professor Lamb. We are also measuring volume viscosity by acoustic wave propagation in conjunction with the shear wave technique, over the same pressure, temperature, and frequency ranges.

I am grateful to Professor Markovitz for putting emphasis on a point that requires emphasis, namely, that the difference between viscoelasticity, on the one hand, and elasticity and viscosity, on the other, is that the stress in a viscoelastic material is determined by the history of strain, whereas the stress in the classical materials is determined solely by the current values of strain or rate of strain. His suggested approach is the one I should prefer, but in writing my paper I decided that an audience of nonspecialists would prefer an introduction via the simple models of linear viscoelasticity. (Incidentally, for the information of the reader of this document the verbal presentation of the paper "Theory of Rheology" was different from the written version.)

I regard the miscellaneous comments as supplementary to my paper and of great value in laying stress on points that I may not have dealt with sufficiently well. I can agree completely with the spirit of all but his first comment, in which there is an implied criticism of the Oldroyd technique of generalizing equations of state. Because the Oldroyd technique leads to results identical with that of Coleman and Noll (ref. 58) and in addition gives equations that are more immediately useful, the grounds for this criticism must be suspect.

The results reported by Mr. Kinner are clearly of great practical significance. I share his view that there is a need to corroborate theoretical predictions with experimental results and hope that his work will eventually lead to a better understanding of the role of lubricant rheology in EHD lubrication.

I thank Mr. Ku for his very kind remarks. Regarding his specific questions, there is very little that I can contribute. The "dimple" phenomenon he refers to appears to agree well with the analysis of Chiu (ref. 136) and it is reasonable to ascribe the dimple to the normal stress effect.[19] Where I would disagree with Chiu and Sibley (ref. 134) is in the matter of estimating the normal stress coefficient γ [20] at the pressure existing in the contact. Firstly, estimates of this nature will be true only in the limit of vanishingly small rates of shear. Second, the value of the limiting shear modulus $G(\infty)$ is probably overestimated by about three orders of magnitude. The linear variation of $G(\infty)$ with p follows the relationship

$$G(\infty, p) = G(\infty, 0) + Ap$$

where the slope A, for the few liquids tested in my own laboratory and by Professor Lamb (and referred to above), lies between 1 and 3. Hence if $G(\infty, 0)$ is about 10^4 atm and p is 10^4 atm (Chiu and Sibley's values, roughly), then $G(\infty, p)$ is only two to four times higher than $G(\infty, 0)$ and not 7000 times higher.

Both Mr. Ku and Dr. Mannheimer refer to the rheology of surface films. This is a subject that must be of great importance in EHD and boundary

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[19] Although the Weissenberg effect is due to normal stresses, not all normal stress effects can be called Weissenberg effects.

[20] Chiu and Sibley are not correct in using the expression "cross viscosity coefficient" for this.

lubrication, but one that I was unable to include in my paper. This is not the place to summarize the work done in this area, but it should be recognized that there is one view that the rheological properties of an interfacial layer differ greatly from those of the bulk material and another view that this difference is small and unimportant. I believe this is an area requiring careful experimental work. The latest contribution to this controversy is from Cambridge University (ref. 36), in which it is suggested that rheological behavior characteristic of bulk material exists down to one or two monolayers.

Dr. Mannheimer refers to a rather different branch of rheology, called interfacial rheology, which is probably of less importance in lubrication than the rheology of surface films mentioned in the previous paragraph. Interfacial rheology describes the processes of changes of area (interfacial tension) and of shears in the interface. If the Cartesian axes 1 and 2 lie in the interface and axis 3 is normal to it, interfacial rheology is concerned with shears carrying the suffixes 2, 1, while the shears of greater importance in lubrication of adjacent surfaces carry the suffixes 3, 1 or 3, 2. Interfacial rheology is more relevant to the stability of surface films than to the calculation of frictional forces.

NOMENCLATURE

b	length of unit of polymer chain in the Bueche theory
b	dimensionless coefficient
c	concentration of polymer in a solution
^{e}	(superscript) referring to elastic effects
$_e$	(subscript) referring to polymer chain entanglements
e_{ij}	i, jth component of the strain tensor in the space coordinate system
$e_{ij}^{(n)}$	i, jth component of the nth strain rate (nth time derivative of strain) tensor in the space coordinate system
^{f}	(superscript) referring to frictional effects
$g_{ij}, g_{ij}(x)$	i, jth component of the metric tensor as a function of space coordinate system x
h	dimensionless hydrodynamic shielding factor
$h(s)$	influence function in Coleman-Noll theory
i	$\sqrt{-1}$
$^i, _i$	(subscript and superscript) index referring to the x^ith coordinate with the values 1, 2, 3
$^j, _j$	(subscript and superscript) index referring to the x^jth coordinate with the values 1, 2, 3
$_j$	(subscript) index referring to the jth bead in the Rouse-Zimm models with values 1 to N
k	Boltzmann's constant

^{k}, $_{k}$	(subscript and superscript) index referring to the x^kth coordinate with the values 1, 2, 3
^{l}, $_{l}$	(subscript and superscript) dummy coordinate index with the values 1, 2, 3
^{m}, $_{m}$	(subscript and superscript) dummy coordinate index with the values 1, 2, 3
m	number of giant submolecules per polymer molecule
m	meter
$_{n}$	(subscript) index referring to the nth value with the values 1, 2 . . .
^{n} $_{n}$	(subscript and superscript) dummy coordinate index with the values 1, 2, 3
$n,(no)$	number of polymer molecules (cross-link junctions) per unit volume of solution
0	referring to a value at elapsed time $s=0$
$_{o}$	subscript referring to a reference value
p	component of isotropic pressure
p_{ij}	i, jth component of the total stress tensor in the space coordinate system
p'_{ij}	i, jth component of the extra stress (total less isotropic) tensor in the space coordinate system
$_{p}$	subscript referring to relaxation modes in the Rouse-Zimm theories with values 1 to N
p	$i\omega$
$_{q}$	subscript referring to types of junction in the Lodge theory
r	radius coordinate in a cylindrical coordinate system
r	radius of a bead in the Bueche theory
r, r_j	position vector of the jth bead in the Rouse-Zimm theories
s	elapsed time $(t-t')$
$_{s}$	subscript referring to solvent
s	dimensionless factor in network theory of rubber elasticity
sec	second
t	current time
t'	a time in the past
^{v}	(superscript) referring to viscous effects
v	solvent velocity unperturbed by polymer molecules
v'	solvent velocity perturbed by polymer molecules
v^i	ith component of velocity
x^i	ith coordinate in the x coordinate system
x'^i	ith coordinate in the x' coordinate system
A	dimensionless coefficient
$A_{ij}^{(n)}$	i, jth component of the nth Rivlin-Ericksen strain rate tensor

B_{ij}	i, jth component of the Finger deformation tensor
C_{ij}	i, jth component of the Cauchy deformation tensor
D	rate of shear
F	relaxation frequency
$F(D)$	a function of rate of shear defined in equation (58)
F_j	force acting on the jth bead in the Rouse-Zimm theories
G^*	complex shear (rigidity) modulus
$G'(\omega)$	real part of the complex shear modulus as function of ω
$G''(\omega)$	imaginary part of the complex shear modulus as function of ω
$G(\infty)$, G	the value of G' at infinite frequency
$H(\tau)$, $H(F)$	distribution of relaxation times τ or frequencies F
J^*	complex shear compliance
$J'(\omega)$	real part of the complex shear compliance as function of ω
$J''(\omega)$	imaginary part of complex shear compliance as function of ω
K	dimensionless coefficient
K_1, K_2	dimensionless coefficients
M	molecular weight
M_0	molecular weight of a polymer chain link in the Bueche theory
M_n	memory (hereditary) function of nth order in elapsed time
N	number of submolecules in a polymer molecule
N	Newton
N_0	Avogadro's number
N_1	first normal stress coefficient
N_2	second normal stress coefficient
N_n	memory (hereditary) function of nth order in elapsed time
$N(\tau)$	normalized distribution of relaxation times
$O(\ )$	a term of the order of the argument
P_{ij}	i, jth physical component of the stress tensor
R	real part of the complex shear impedance
S	distance
T	absolute temperature
T_{ij}	i, jth component of any tensor in space coordinates which has components τ_{ij} in material coordinates
$T_{ij,\ m}$	partial derivative of T_{ij} with respect to x^m
T_{jk}	j, kth component of polymer-solvent interaction tensor in the Zimm theory
V_i	ith physical component of velocity
X	imaginary part of the complex shear impedance
Y	complex shear admittance
α_n	material parameters in the Coleman-Noll equations
α_n	material parameters in the Ree-Eyring equation

β_n	material parameters in the Coleman-Noll equations
β_n	material parameters in the Ree-Eyring equations
γ	shear strain
$\gamma_{ij}(\xi)$	i, jth component of the metric tensor as a function of the material coordinate system
δ	dimensionless interaction coefficient of the Chompff-Duiser-Prins theory
$\delta(\ )$	Dirac delta function
δ_{ij}	i, jth component of the Kronecker delta: for $i=j$, $\delta=1$; for $i\neq j$, $\delta=0$
ϵ_{ij}	i, jth component of strain in the material coordinate system
ζ	friction factor in bead-spring theories
η	dynamic viscosity
$\eta(D)$	viscosity as a function of rate of shear
$\eta'(\omega)$	real part of the complex viscosity as a function of ω
$\eta(0)$	viscosity at zero frequency and rate of shear
$\eta'(\omega, D)$	real part of the complex viscosity as a function of ω and D
θ	angular coordinate in a cylindrical coordinate system
λ_1, λ_2	time constants in the Oldroyd models
λ_p	relaxation times in the Rouse-Zimm theories
μ_0, μ_1, μ_2	time constants in the Oldroyd models
μ_j	thermodynamic potential at the jth bead in the Rouse-Zimm theories
μ, μ_q	age distribution functions for network junctions
ν_1, ν_2	time constants in the Oldroyd models
ξ^i	ith coordinate in the ξ coordinate system
ξ'^i	ith coordinate in the ξ' coordinate system
π_{ij}	i, jth component of the total stress tensor in the material coordinate system
π'_{ij}	i, jth component of the extra stress (total less isotropic) in the material coordinate system
ρ	density
σ	shear stress
σ	mean square end-to-end distance of a polymer submolecule
σ_1, σ_2	functions of the time constants of the Oldroyd models
τ	relaxation time
τ_p	Rouse-Zimm relaxation time
τ_1	longest Rouse-Zimm relaxation time
τ_m	cutoff relaxation time in the Leonov theory
τ_q	time constant of the qth network in the Lodge theory
τ_{ij}	i, jth component of any tensor in material coordinates which has components T_{ij} in space coordinates
$\phi, \phi(t)$	stress relaxation function

Φ	unperturbed distribution function of bead coordinates
Ψ	perturbed distribution function of bead coordinates
ω	angular frequency
ω_{ij}	i, jth component of the vorticity tensor
d	ordinary derivative
∂	partial derivative
D	time derivative following the translational motion
$\mathfrak{D}$	Jaumann derivative
$\mathfrak{d}$	total derivative
∇	gradient
$\mathfrak{F}$	functional
II	second invariant of rate of shear

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Rheology in Lubrication

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The rheological effects on lubrication are discussed in two parts. The first part deals with thick-film hydrodynamic lubrication, and the second part with thin-film elastohydrodynamic (EHD) lubrication.

In the regime of hydrodynamic lubrication, a review is given of the temperature-viscosity, viscoelastic, shear-thinning, and normal stress effects on the lubrication of journal bearings.

In the regime of EHD lubrication, emphasis is given to three topics. First, the importance of the pressure-viscosity and temperature-viscosity dependence on the film-forming capability, the pressure redistribution, the maximum surfaces and the maximum film temperatures, as well as the total traction in the contact, is discussed in the light of recent EHD theories. Second, the inadequacies of considering pressure-temperature-viscosity dependence alone for high-speed and high-load cases will be shown by discrepancies between the EHD theories and recent experiments conducted under extreme conditions. Last, viscoelastic effects on traction and film-forming capability are examined with recent results of viscoelastohydrodynamic analyses.

IN HYDRODYNAMIC AND ELASTOHYDRODYNAMIC (EHD) LUBRICATION, the effectiveness of lubrication is largely measured by the ability of the lubricant to generate an adequate lubricant film to maintain separation between two moving surfaces, to yield a pressure distribution free from local pressure intensification, to produce a minimum temperature rise within the film, and to produce a minimum frictional force during sliding.

Earlier work on lubrication has only recognized the importance of bulk viscosity on hydrodynamic lubrication, and much of the effort has been confined to classical solutions of Reynolds equation with isoviscous, Newtonian fluids. It is only within the last two decades that major work has begun on the effect of the other rheological properties of the lubricant on the performance of hydrodynamic and EHD lubrication. The increase of interest in rheology on lubrication can be attributed to the need of knowing the precise effect of polymer-thickened oils on lubrication of journal bearings and the lack of agreement between the Newtonian, EHD

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theories and the measured friction and film thickness for high-speed, heavily loaded, concentrated contacts.

This presentation is not intended to give a complete review of the rheological effects on lubrication because there have been at least four preceding efforts (refs. 1 to 4) covering this area. Rather, it is aimed toward updating and filling the gaps of the state of the art on this subject. Discussions will be divided into two groups: the thick-film hydrodynamic lubrication and the thin-film EHD lubrication. The rheological effects of the lubricant considered will include pressure-viscosity effects, temperature-viscosity effects, shear-thinning effects, viscoelastic effects, normal stress effects, and transient pressure-viscosity effects or compressional viscoelastic effects.

THICK-FILM HYDRODYNAMIC LUBRICATION

The thick-film lubrication is in the regime where the lubricant film thickness is many times greater than the root-mean-square (rms) roughness of the surfaces, and the effect of the surface deformations is negligible in the mechanics of lubrication. With the exception of extremely slow speed, or highly loaded cases, the lubrication in journal or thrust bearing falls in this category. Because the pressure in thick-film hydrodynamic lubrication very seldom reaches a level where the viscosity is significantly altered by the pressure, both the static and transient pressure-viscosity effects are not considered in thick-film discussion.

Temperature-Viscosity Effects

The loss of viscosity due to heating in the lubricant film has always been recognized to be important in predicting journal bearing performance. In most cases, predictions based on the inlet temperature of the lubricant would definitely yield optimistic results, and current practice calls for the use of a constant viscosity based on an average film temperature in calculating the load capacity. More accurate accounts for the temperature-viscosity effects has been made by Hunter and Zienkiewicz (ref. 5), Dowson and Hudson (ref. 6), and Hahn and Kettleborough (ref. 7). Their results indicate that the use of an average temperature gives a significant improvement over the solution using the inlet temperature but still is inadequate if accuracies of the order of 10 to 25 percent are required. In terms of the basic understanding of the effects of temperature-viscosity dependence and the methods of predicting the influence, the state of the art is almost complete. Perhaps more efforts are needed in using these analytical tools to convert them into more accurate design data.

Viscoelastic Effects

For rapidly applied shear stresses, part of the deformation rate would be caused by the elasticity of the fluid and the rest by the viscous action.

Under this condition, the fluid is known to be viscoelastic, and a simple model that consists of a spring and dashpot was proposed by Maxwell (ref. 8). Milne (ref. 9), using the simple Maxwell model,

$$\frac{\partial u}{\partial y}=\frac{\tau}{\mu}+\frac{1}{G}\frac{\delta\tau}{\delta t} \tag{1}$$

completed an analysis for the slider lubrication. He found a reduction in load capacity due to the viscoelastic effects. Burton (ref. 10) later used the same model and reached the same conclusion for the case of lubrication in rolling contacts.

Tanner (ref. 11) showed that for continuous shear flow, such as that treated by Milne and Burton, the use of the Maxwell model in the form of equation (1) is inadequate because the derivative of the stress component with time must include the rotation of the fluid. Including this component, the final expression between the shear stress and shear rate becomes

$$\tau=\frac{\mu_0}{1+\lambda^2\left(\frac{\partial u}{\partial y}\right)^2}\frac{\partial u}{\partial y} \tag{2}$$

where $\lambda=\mu_0/G$ is the relaxation time. Based on equation (2), the Maxwell liquid in shear flow behaves like a shear-thinning fluid with an effective viscosity decreasing with shear rate. Tanner completed the analysis for the lubrication for rolling contacts, valid for $\lambda(\partial u/\partial y)<<1$, and also found a reduction in load capacity due to viscoelastic effects.

Shear-Thinning Effects

Lubricants containing long-chain linear polymers usually exhibit a nonlinear relation between shear stress and shear rate in shear flow. The apparent viscosity decreases with shear rate and finally approaches the viscosity of the base stock at high shear rates. The effects of shear thinning on the pressure distribution in hydrodynamic lubrication can be analyzed by assuming a certain stress-shear rate relation, such as a power law or the Ree-Eyring model (ref. 12) in the flow equation. The power relations between stress and shear rate have been employed by Ng and Saibel (ref. 13), expressing τ in terms of powers of $\partial u/\partial y$, and also by Hsu and Saibel (ref. 14), expressing $\partial u/\partial y$ in terms of powers of τ. In both cases, the shear-thinning effect would cause a reduction in pressure and frictional force, depending on the magnitude of the shear rate. Analytical results are available for predicting the pressure profile and friction, provided the constants in the power relation can be found from the viscometric data.

A numerical scheme was developed by Horowitz and Steidler (ref. 15) that can handle any arbitrary stress and shear rate relation taken from viscometry. This procedure was later used by Tao and Philipoff (ref. 16) in calculating the theoretical pressure profile in journal bearings to com-

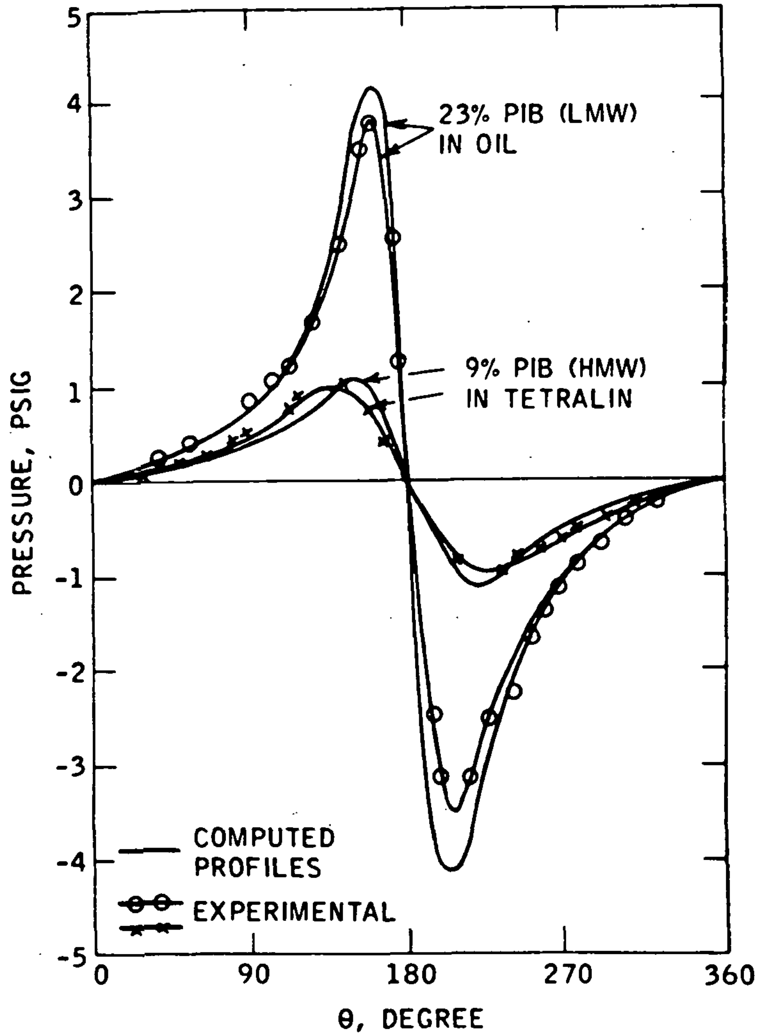

Figure 1.—Pressure distribution of viscoelastic liquids in journal bearings (ref. 16).

pare with the measured pressure profile. Figure 1 shows the close agreement between the calculated and measured data for a journal bearing lubricated with viscoelastic fluids. It is also of interest to note that the non-Newtonian effects appear to promote the occurrence of negative pressure in the diverging section. They also found considerable reduction in load capacity attributable to shear-thinning effect of the lubricant. Contrary to Tao and Philipoff's conclusion, Ocvirk, Dubois, and Wehe (ref. 17) have found that the load capacity of a journal bearing for a viscoelastic fluid is superior to that for a Newtonian lubricant with the same bulk viscosity.

Tao and Philipoff speculated that the results in reference 17 are conducted under very high shear rates at which there might be other beneficial viscoelastic effects overshadowing the detrimental shear-thinning effect. Actually, whenever the shear-thinning effect is significant, the heating effect also becomes important. It is quite possible that the superior load capacity found by Ocvirk et al. for the viscoelastic fluid is attributable to the thermal effect. The viscoelastic fluid, having a smaller temperature-viscosity coefficient than the Newtonian lubricant, can give a higher load capacity than a Newtonian lubricant. It appears that in any future correlations with experimental data for viscoelastic fluids, one must use theories that include the temperature-viscosity effects. Further efforts are certainly needed before the exact non-Newtonian effects of the lubricant in hydrodynamic lubrication are determined.

Normal Stress Effects

The significance of the normal stresses in the directions perpendicular to the flow remains controversial. Tanner (ref. 18) estimated that for the normal stress difference to have any significant influence on the load capacity in lubricated contacts, it must be of the order $\tau R/h$, where τ is the shear stress. Because $h/R \approx 10^{-3}$ for most journal bearings, normal stress difference must approach 10^3 times the shear stress for it to be significant. He considered this ratio to be very unlikely and therefore concluded that normal stresses are negligible in sliding bearings.[1] This conclusion was not fully accepted by Tao and Philipoff (ref. 16) on ground that the order-of-magnitude analysis may not be sufficient proof for the negligible importance of the normal stresses. It appears that an extremely careful experiment using a slider bearing and a viscoelastic lubricant may settle this controversy.

THIN-FILM EHD LUBRICATION

EHD lubrication is concerned with the lubrication process in which the deformation of the boundaries plays an important role in governing the performance. In the previous three conferences, EHD lubrication has been given much attention, and an excellent review of this subject was contributed by Dowson and Dyson (ref. 2). In most EHD contacts, load is usually supported over a very small conjunction region in which the local pressure becomes extremely high. Under this extreme condition, the change of viscosity with pressure and temperature has significant influence on the film thickness, pressure, temperature, and shear stress distribution in the conjunction region. Moreover, for very-high-speed rolling and sliding contacts, the lubricant is subjected to a high shear rate in the high-

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[1] The author wishes to thank J. F. Hutton for calling his attention to an oversight in interpreting Tanner's conclusion as appeared in the preprint of this paper. This oversight has now been corrected.

pressure region, and the assumption of a linear relation between the local shear stress and shear rate under these conditions ceases to be valid. For these cases, the viscoelastic effects of the lubricant must be included in the analysis. In addition to the viscoelastic effects, there is also strong evidence that the pressure-viscosity dependence is time dependent. For high-speed contacts, the lubricant in the high-pressure region would not reach the viscosity as predicted by the pressure-viscosity relation based on the static viscosity measurements. Effects of this kind are known as the transient pressure-viscosity effects. The ensuing sections will be devoted to the review of the past and current investigations on the performance of EHD lubrication as affected by four rheological effects of the lubricant: pressure-viscosity effects, temperature-viscosity effects, shear-thinning effects, and transient pressure-viscosity effects or compressional viscoelastic effects.

Film Thickness

Pressure-Viscosity Effects

The influence of pressure-viscosity dependence on the film-forming capability in an EHD contact was first considered in a classical paper by Grubin and Vinogradova (ref. 19). By assuming that the viscosity varies exponentially with the pressure and by assuming that the deformation profile in the inlet region is identical to the Hertzian profile, they solved the Reynolds equation and obtained the following formula for calculating the inlet film thickness as a function of speed, load, and pressure-viscosity coefficient parameters for a line contact.

$$\frac{h_0}{R}=1.95\,\frac{(\alpha E')^{8/11}\,(\mu_0 U/E'R)^{8/11}}{(W/E'R)^{1/11}} \tag{3}$$

Grubin's analysis established that the nominal film thickness is proportional to the 8/11th power of the pressure-viscosity coefficient. Further inlet solutions by Crook (ref. 20) and Archard and Cowking (ref. 21) have all confirmed this power relation.

A more detailed EHD analysis by Dowson and Higginson (ref. 22), considering the film distribution in the entire conjunction, showed that the power exponent for the pressure-viscosity coefficient is 0.6, which is slightly lower than Grubin's result. This exponent has been recently revised by Dowson (ref. 2) to 0.54 instead of 0.6.

Experimental confirmation on the pressure-viscosity influence is somewhat difficult to achieve because for most oils there does not exist a wide range of the pressure-viscosity coefficient. The capacity measurements by Dyson, Naylor, and Wilson (ref. 23) using lubricants covering a range of pressure-viscosity coefficient between 0.8×10^{-4} to 1.73×10^{-4} in^2/lb did not reveal any results significantly different from that calculated by the Dowson-Higginson film-thickness formula.

The power relation between the film thickness and pressure-viscosity coefficient α, according to Grubin or Dowson and Higginson, is only meaningful when the value of $e^{-\alpha p}$ Hz approaches 0. For moderate loads or lubricants having extremely low effective pressure-viscosity coefficient, the film thickness becomes gradually less dependent on α and finally approaches the isoviscous film thickness according to the theory developed by Herrebrugh (ref. 24).

The effect on film thickness over the entire range of α has been recently investigated by Cheng [2] by extending the full EHD solution in the first half of the Hertzian width. The inlet film thickness is plotted against G in figure 2. It is seen that the power relation of 0.6 between h_0/R and α only exists for very high values of G. For small G, the pressure-viscosity influence is absent. Archard and Cowking (ref. 21) demonstrated that the power relation between h_0/R and α is not affected when the side leakage effects are included for spherical contacts. In a refined numerical solution for elliptical contacts, Cheng (ref. 25) showed that the side leakage effect in elliptical contacts has a slight influence on this power, but the influence is negligibly small.

Temperature-Viscosity Effects

At high pressures, viscosity of lubricants in concentrated contacts is known to be highly dependent not only upon pressure but also upon the temperature in the film. In forming the lubricant film at the inlet, the beneficial pressure-viscosity effect can be compensated by the reduction in viscosity due to increase in temperature. Both Cheng and Sternlicht (ref. 26) and Dowson and Whittaker (ref. 27) have demonstrated that temperature rise of the lubricant in the contact region has little influence upon the nominal film thickness in the contact. Steel contacts up to 250 in./s have negligible heating effects on film-forming capability. For extremely-high-speed rolling and sliding contacts such as those used in jet engines, Cheng (ref. 28) in a recent report showed that the heating effect in the inlet region would cause a significant reduction in viscosity to affect the nominal film thickness.

The results in reference 28 are shown as the thermal reduction factors ϕ_T that are defined as the ratio of the actual film thickness with the thermal effects to the isothermal film thickness based on the Dowson-Higginson formula. Results cover the range of temperature-viscosity coefficients evaluated empirically from the ASME high pressure-viscosity report (ref. 29) by using the following pressure-temperature-viscosity relationship

$$\frac{\mu}{\mu_0}=\exp\left[\alpha p+(\beta+\gamma p)\left(\frac{1}{T}-\frac{1}{T_0}\right)\right] \tag{4}$$

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[2] Cheng, H. S.: Isothermal Elastohydrodynamic Theory for the Full Range of Pressure-Viscosity Coefficient. J. Lubric. Technol., to be published.

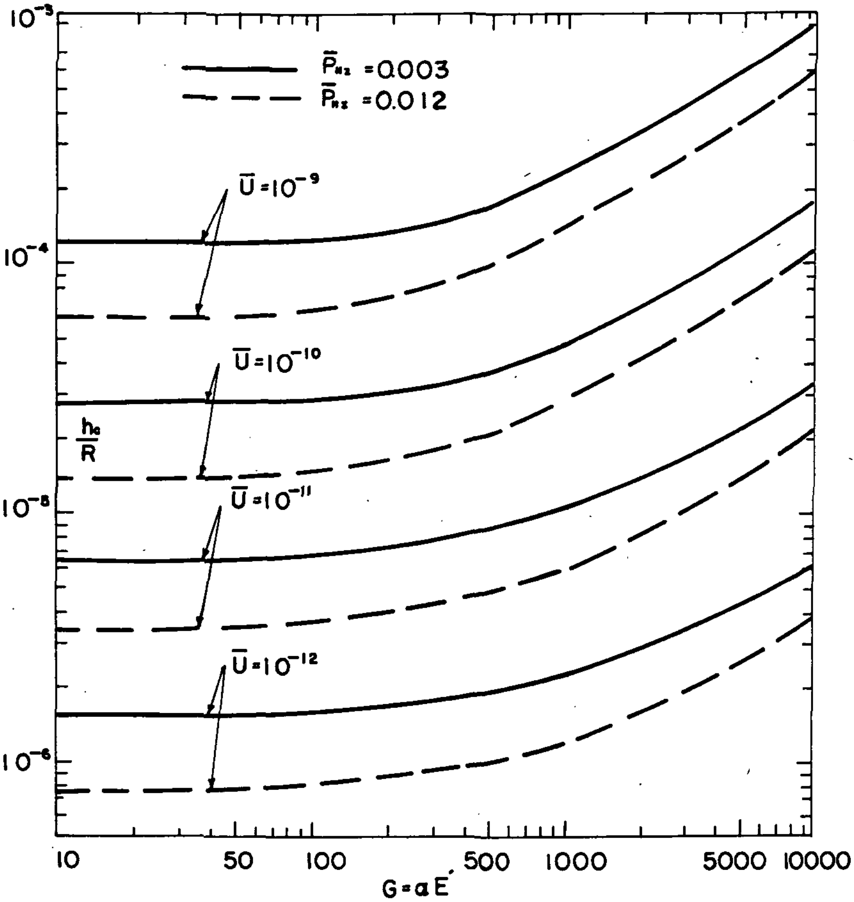

FIGURE 2.—Effect of pressure viscosity coefficient on h_c/R. (h_c = film thickness at the center, $x = 0$; R = equivalent radius; $\bar{U} = \mu_0 U/E'R$; $\bar{P}_{Hs} = P_{Hs}/E'$.)

The reduction in film thickness caused by the temperature-viscosity dependence can be shown in figure 3 of the plot of ϕ_T against a thermal parameter Q_m.

Inadequacy of Newtonian EHD Theory

Prediction of film thickness with the assumption of a Newtonian fluid but with a viscosity dependent on temperature and pressure proved to be successful only for loads within 100 000-psi maximum Hertz stress. Beyond this load, there is evidence that the actual film-thickness level is lower than that calculated from the present EHD theories even with the consideration of the heating effects at the inlet region. Recent measured film thicknesses by the X-ray techniques at loads up to 350 000 psi (ref. 30) were compared

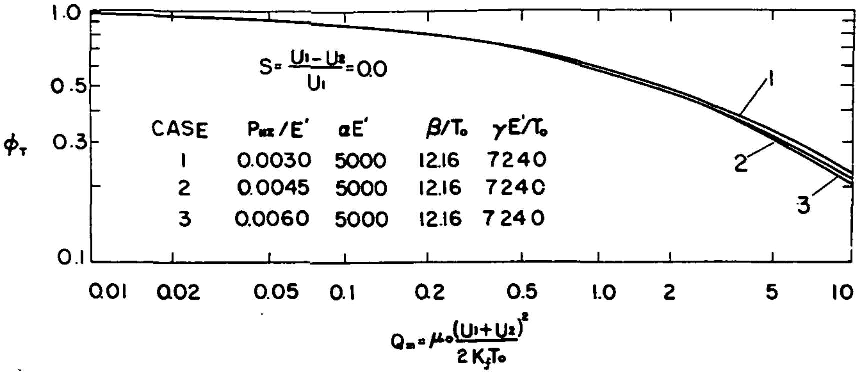

FIGURE 3.—Typical variation of thermal reduction factor ϕ_T. (Q_m = thermal parameter.)

with various EHD theories in figure 4 against the maximum Hertzian pressure. It is seen that the experimental data are much lower than the calculated film even with the thermal effects included in the theory. Considerable efforts were made in examining the accuracy of the X-ray techniques under these conditions, and it was concluded in reference 32 that the X-ray measurements are indeed valid. Since most rolling-element bearings operate in the load range between 100 000 and 350 000 psi, the explanation of this disagreement certainly appears to be one of the most challenging tasks in EHD lubrication.

It has been suggested by Bell (ref. 33) that the lubricant under these high loads ceases to be Newtonian, and the reduction of the film thickness may be due to the nonlinear shear stress and shear rate relation. Still another suggestion was put forth by Bell and Kannel (ref. 31) that the pressure-viscosity effect is dependent on time and the time delay of pressure-viscosity dependence could be the chief factor for the reduction of film-forming capability. The discussions of the non-Newtonian effects as well as the transient pressure-viscosity effects are given in the next section.

Shear-Thinning Effects

In examining the non-Newtonian effects, one must choose a rheological model governing the relations among stresses, strains, and strain rate. An excellent coverage of various non-Newtonian models used in EHD analysis was given by Naylor (ref. 4). These include the power-law model, the Ree-Eyring model, the Maxwell model, the Barlow and Lamb model, and the Smith plastic-shear model.

Each of the above models postulates a definite functional relation between the shear stress and shear rate in a shear flow. Figure 5 gives a qualitative picture of the differences among these models.

The power-law model was employed by Dyson and Wilson (ref. 34) in

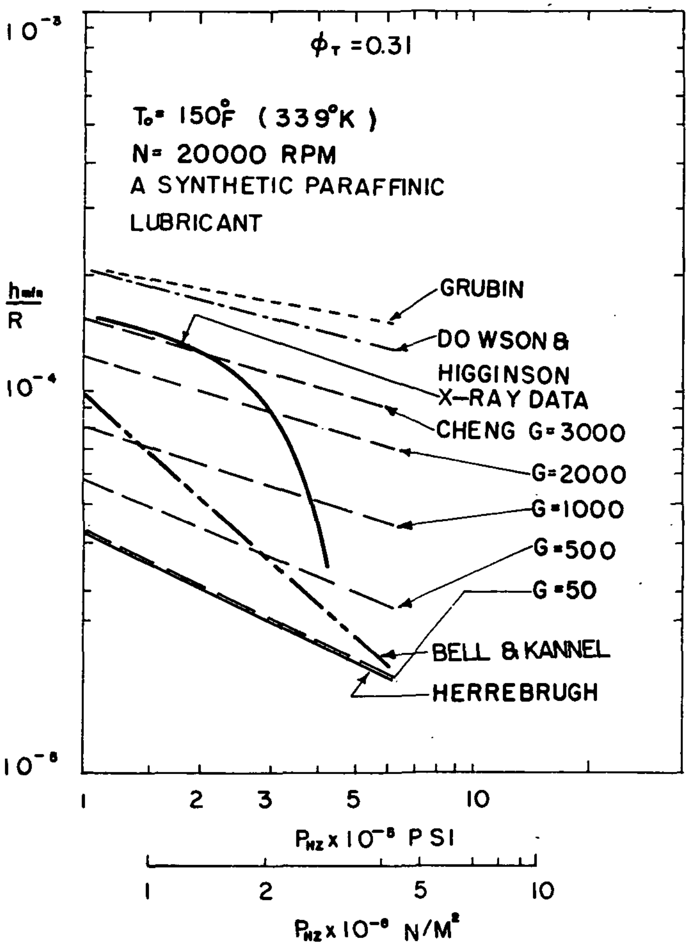

FIGURE 4.—Comparison between measured and calculated film thickness. T_0 = 150° F; N = 20 000 rpm (refs. 19, 22, 24, 30, and 31; Cheng data are from Cheng, H. S.: Isothermal Elastohydrodynamic Theory for the Full Range of Pressure-Viscosity Coefficient. J. Lubric. Technol., to be published.)

analyzing the film thickness in EHD contacts lubricated by silicone fluids. They assumed a power relation of the form

$$\tau=\left(\phi \frac{\partial u}{\partial y}\right)^n \tag{5}$$

where ϕ is a function of pressure and temperature. They also arrived at a value of 0.65 for the exponent n based on the measurement of the complex modulus taken by Barlow et al. (ref. 35) for six polydimethylsiloxane liquids. Figure 6 shows that the power-law model was able to predict the

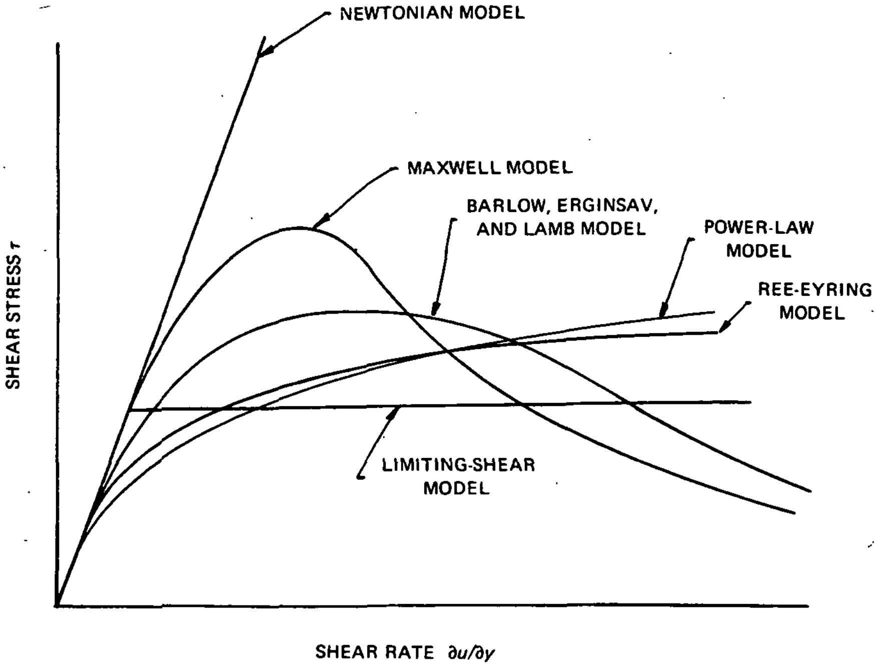

FIGURE 5.—Qualitative behavior of various shear-thinning models.

film thickness much more closely than the Dowson-Higginson theory for the Newtonian lubricant.

It is of particular interest to note that the power-law model predicts a film thickness to be proportional to

$$\left(\frac{W}{E'R}\right)^{-\left[0.13+\frac{0.7(1-n)}{2(3n+1)}\right]} \tag{6}$$

For fluids with shear-thinning viscosity, n would be less than one, which means the film would be dependent more upon the load. For the limiting case when n approaches zero, the film becomes proportional to the square root of the load or directly proportional to the maximum Hertzian stress for line contacts.

As early as 1961, Bell (ref. 33) envisioned the importance of non-Newtonian effects in EHD lubrication and developed a Grubin-type analysis using a Ree-Eyring fluid of the form

$$\tau=\frac{X}{\alpha}\sinh^{-1}\left(\beta\,\frac{\partial u}{\partial y}\right) \tag{7}$$

where $X=X_0e^{\gamma_1 p}$ and $\beta=\beta_0e^{\gamma_2 p}$. Five rheological constants are required to describe the behavior of this fluid: α, X_0, β_0, γ_1, and γ_2.

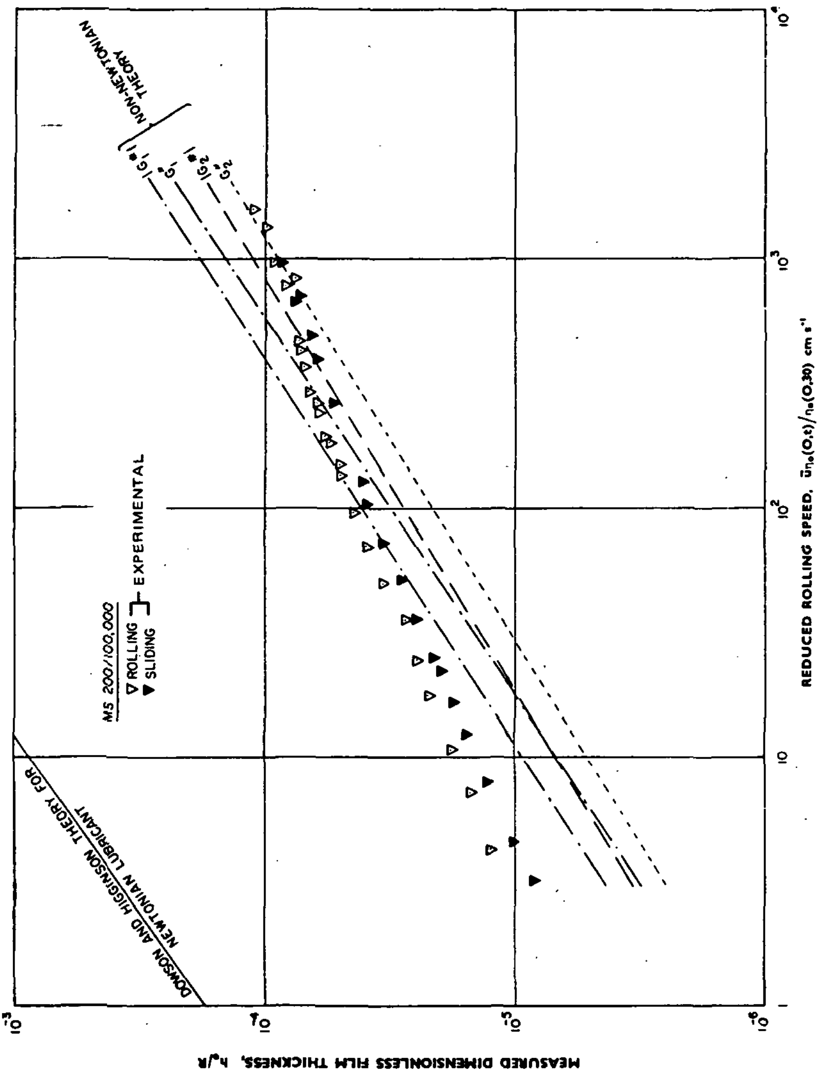

FIGURE 6.—Shear-thinning effects on EHD film thickness (ref. 34).

Early correlations with the film thickness measured at high speed and high load were somewhat inconclusive because of the uncertainty of the Ree-Eyring constants for the lubricants tested. Recently Bell and Kannel (ref. 31) have reexamined the film-thickness theory with a Ree-Eyring fluid by comparing it with some recent X-ray data. They concluded that while the Ree-Eyring model predicts a significant reduction from the Newtonian film thickness, the reduction is still not enough to agree with the measured film.

The Maxwell model has been recognized as the simplest model to account for the viscoelastic effect of the liquid. The constitutive equation for a Maxwell liquid is

$$e_{ij}=\frac{1}{\mu_0}\left(\sigma_{ij}+\lambda\,\frac{d\sigma_{ij}}{dt}\right) \tag{8}$$

where e_{ij} and σ_{ij} are the strain and stress components, μ_0 is the static viscosity, and λ is the relaxation time. The variable G is the shear modulus of the liquid. For continuous shear flow, Tanner (ref. 11) showed that the time derivative of the stress component must include the rotation of the fluid, and the final relation between the shear stress and shear rate takes the form of equation (2). The viscoelastic effect of the lubricant on the film-forming capability using a Maxwell model was recently investigated by Chow and Saibel (ref. 36). Following Tanner's analysis for cylinders, they developed a Grubin-type film-thickness formula for both the isoviscous case and cases of pressure-dependent viscosity. For the isoviscous case, the ratio of non-Newtonian thickness to Newtonian thickness is

$$\frac{h_{\text{non-New}}}{h_{\text{New}}}=1-0.736\left(\lambda\,\frac{U}{h_{\text{New}}}\right)^2 \tag{9}$$

For the case of pressure-dependent viscosity, this ratio takes a far more complex form involving integrals that are yet to be evaluated.

So far, there have been no attempts made in using either Barlow and Lamb's model or the Smith plastic-shear model to analyze the film thickness in EHD contacts. Analytically, Barlow and Lamb's model appears to be extremely complex to implement, if not intractable, even for Grubin-type analysis; however, the plastic-shear concept is extremely simple and should present fewer complexities in the non-Newtonian film-thickness analysis.

Transient Pressure-Viscosity Effects

In most rolling contacts, the transit time is usually less than 10^{-4} to 10^{-5} sec, and the rate of change in pressure becomes extremely large particularly under heavy loads at the inlet region. Under these conditions, the viscosity may not respond to the rapid pressure change according to the static, high-pressure viscosity data. Bell and Kannel (ref. 31) employed a time-delay constant in the pressure-viscosity effect and developed a

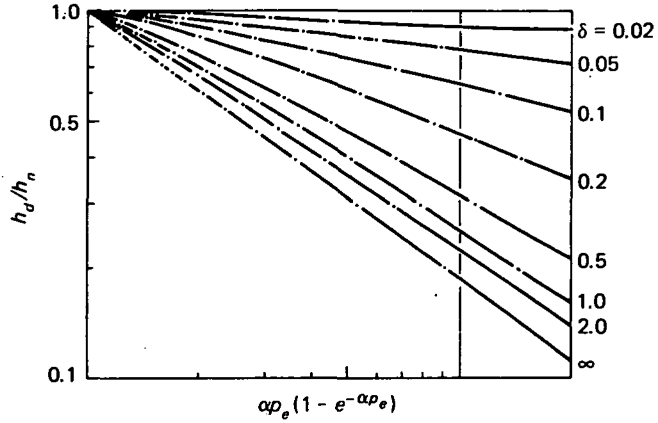

FIGURE 7.—Correlation of film thickness computed from the time-delay theory.

Grubin-type film-thickness theory. Figure 7 shows the reduction of the film due to time delay of pressure-viscosity effects as a function of $\alpha p_e^{(1-e^{\alpha p_e})}$ and δ, where α is the pressure-viscosity coefficient; p_e, the pressure at the entrance of the Hertzian region; and δ, a nondimensional time-delay constant. The film thickness calculated from the Bell and Kannel time-delay theory with $\delta = \infty$ for a typical EHD contact is compared with other theories and the measured X-ray data in figure 4.

Film Shape

In previous sections, discussions have been focused upon the rheological influence on the level of the film thickness, not on the film-thickness variation. Existing EHD theories so far can only predict the film-thickness variation in a line contact or the variation along the center strip of a point contact. Results in references 22, 24, 26, and 27 have indicated that the minimum film thickness at the exit protrusion is approximately 70 percent of the nominal film thickness at the inlet, and this percentage is unaffected by the speed, load, or pressure-temperature-viscosity dependence. However, the width of the exit protrusion is affected significantly by the pressure-viscosity coefficient. An empirical relation between the pressure-viscosity coefficient and the exit protrusion width can be found in reference 50.

The most accurate data on the film shape throughout the entire region of an elliptical contact, so far, have been obtained experimentally by optical techniques (refs. 38 to 41). The optical data revealed the very significant fact that the film thickness in the side lobes of the contact, in many cases, is considerably lower than the film thickness at the trailing edge along the center strip of the contact. Moreover, this minimum film in the side lobes is highly dependent upon load and, in all likelihood, also strongly dependent upon the rheological properties of the lubricant. Theoretically, the prediction of this film variation in the side lobes would require a three-dimensional EHD analysis, which appears to be an extremely difficult computational task.

In the absence of a three-dimensional EHD theory, one may offer some speculations about the nature of the film reduction in the side lobes. Effectively, the side strips of a point contact can be considered locally as a half portion of an elliptical contact with semimajor axis in the direction of rolling much greater than that perpendicular to rolling. As shown in reference 25, elliptical contacts of this kind have a very pronounced side leakage effect. The film at the entrance is only a small fraction of the nominal film thickness predicted by a line contact theory. The condition is further worsened at the edges inside the conjunction region because much of the lubricant dragged into the conjunction is leaked away through the edge. Thermal effects due to sliding in the conjunction would promote greater side leakage and hence would probably contribute to further reduction of film thickness in the side lobes. There is little doubt that the problem of full EHD analysis including side leakage effects is of considerable importance and should deserve immediate attention.

Pressure Profile

Pressure-Viscosity Effects

In 1959, Dowson and Higginson (ref. 22) showed that the inclusion of an exponential pressure-viscosity relation in EHD analysis introduces a sharp pressure spike at the exit of the conjunction region, as shown in figure 8. The formation of this pressure spike can be seen from the consideration of the Reynolds equation in the inverse form

$$\frac{e^{-\alpha p}}{12\mu_0 U}\frac{dp}{dx}h^3-h+h^*=0 \tag{10}$$

In this equation, the film-thickness distribution can be solved for a known pressure distribution. If one considers the assumed pressure profile to be Hertzian, then the resulting film distribution obtained from equation (10) would depend upon the pressure-viscosity exponent α. A large α would result in an abrupt corner from the Hertzian flat region to the exit protrusion as shown in figure 9. The subsequent pressure deviation required elastically to form this sharp corner produces a pressure spike just ahead of the protrusion. The larger the α, the more pronounced the spike, as shown by Dowson and Higginson in figure 8.

This striking influence of pressure-viscosity dependence upon pressure drew considerable attention. Other numerical solutions by Archard, Gair, and Hirst (ref. 42) and by Cheng and Sternlicht (ref. 26) all confirmed analytically the existence of the pressure spike and its dependence on α. Herrebrugh (ref. 24) showed that if the pressure-viscosity effects are

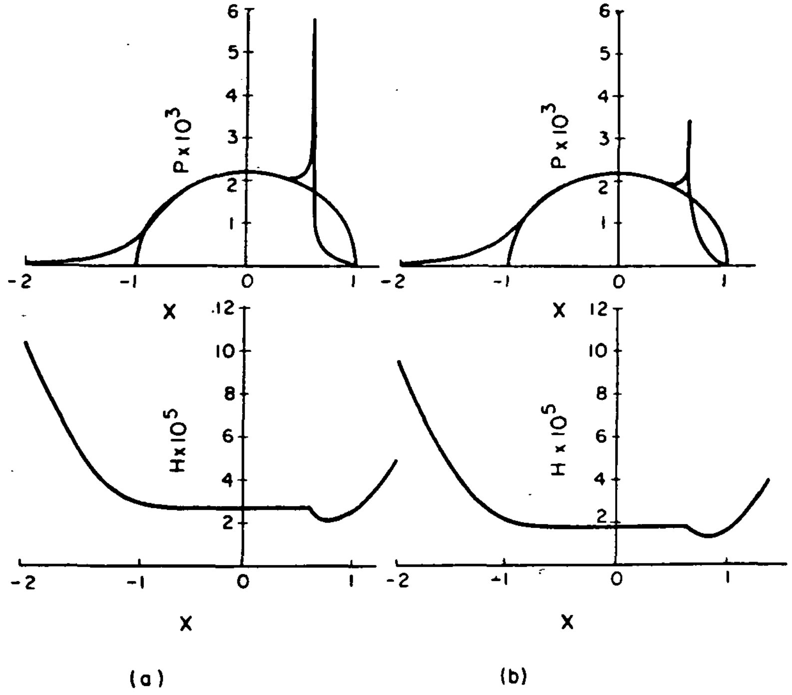

FIGURE 8.—Pressure distributions and film shapes. ($\bar{W} = W/E'R = 3 \times 10^{-5}$; and $\bar{U} = \mu_0 U/E'R = 10^{-11}$.) (*a*) $G = 5000$. (*b*) $G = 2500$.

absent ($\alpha = 0$), the pressure distribution contains no spike and only deviates slightly from the Hertzian distribution.

Temperature-Viscosity Effects

Because temperature and pressure have opposing effects on lubricant viscosity, it was believed earlier that the pressure spike predicted by the isothermal EHD theory might disappear if the temperature-viscosity dependence is included. It was this belief which motivated the developments in thermal EHD by Cheng and Sternlicht (ref. 26) and Dowson and Whittaker (ref. 27). Both solutions have shown that for oils with pressure-viscosity coefficients in the neighborhood of 10^{-4} in^2/lb, the pressure spike is not suppressed significantly by the temperature-viscosity effect, even for sliding contacts with 50 percent slide-to-roll ratio. Moreover, the inclusion of temperature-viscosity effects tends to shift the pressure spike toward the inlet side. In the case of a large pressure-viscosity coefficient,

$$\alpha = 1.7 \times 10^{-4} \text{ in}^2/\text{lb}$$

reference 26 showed the temperature effect tends to enhance the maximum pressure in the contact. However, for a more moderate pressure-viscosity coefficient,

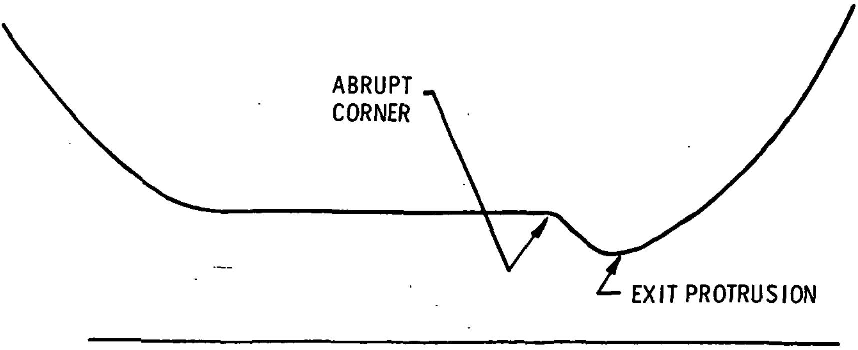

FIGURE 9.—Exit protrusion.

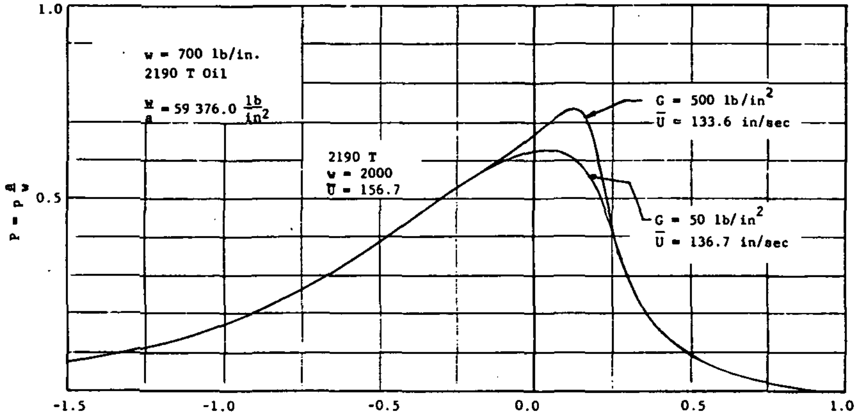

FIGURE 10.—Pressure profiles considering a viscoelastic lubricant.

$$\alpha=1.1\times10^{-4}\ \text{in}^2/\text{lb}$$

reference 27 showed the temperature-viscosity dependence for high-slip cases does indeed have a softening effect upon the pressure spike.

Viscoelastic Effects

Viscoelastic effects of the lubricants are likely to have a strong influence on the pressure spike in heavily loaded EHD lubrication because the local shear stress around the pressure peak is likely to exceed the critical shear stress proposed by Smith. A full account of the viscoelastic effect in full EHD analysis even assuming a simple Maxwell liquid appears to be extremely difficult. A partial account of the viscoelastic effect by ignoring the rotation of the fluid would make the analysis tractable, and this was investigated by Cheng (ref. 43). Results, as shown in figure 10, indicate that the value of shear modulus that would be required to suppress the pressure spike is in the neighborhood of 500 psi for $\alpha = 1.7 \times 10^{-4}$ in^2/lb.

Transient Pressure-Viscosity Effects

The transient pressure-viscosity effects in the vicinity of a pressure spike is obviously significant if the time-delay α model suggested by Bell and Kannel (ref. 31) in their film-thickness analysis is proven to be valid. Modifications of isothermal EHD theory including a time-delay α model should be an interesting problem in future EHD research.

Temperature and Friction

Thermal analysis in concentrated contacts by Crook (refs. 44 and 45), Cheng (ref. 46), Dyson (ref. 47), and Archard (ref. 48) have shown a strong mutual dependence between temperature and friction in EHD contact. Traction is directly governed by the viscosity, which, in the case of a sliding contact, depends strongly upon the temperature in the contact. The temperature field is in turn governed directly by the heating function, which is the product of the local shear rate and traction. For this reason, they are usually analyzed simultaneously. Before discussing the effects of lubricant rheology upon the temperature and friction, it is useful to clarify some of the symbols used in designating the temperature at various locations in the film. The equations used in determining the temperature field are the energy equation and the equation relating the shear stress and shear rate.

$$\frac{\partial}{\partial z}\left(K\frac{\partial T}{\partial z}\right) = \tau\,\frac{\partial u}{\partial z} \tag{11}$$

$$\tau = f\,\frac{\partial u}{\partial z} \tag{12}$$

In the above, the temperatures at the boundaries are T_0, the inlet temperature of the conjunction; $T_1(x)$, the surface temperature of the upper roller; and $T_2(x)$, the surface temperature of the lower roller.

The variable T_0 is approximately the same as the roller surface temperature at the inlet, and it is usually governed by the heat transfer between the roller and the environment; $T_1(x)$ and $T_2(x)$ are governed by how the heat is being conducted into the solids. The energy equation (eq. (11)) is based on the assumptions that heat convected by the fluid is neglected in comparison to the heat conducted into the solids, heat conduction in the direction of rolling is neglected, and heat due to compression is neglected.

Except for extremely high rolling speeds, these assumptions have been shown by Crook (ref. 44) and Ng (ref. 49) to be valid for most EHD contacts.

The effect of lubricant rheology depends on the relation used between the shear stress and shear rate. In the last decade, most treatments on temperature and friction have been restricted to a linear relation between τ and $\partial u/\partial y$, i.e., a Newtonian liquid, but with pressure- and temperature-dependent viscosity. Contribution in this area include Crook (ref. 44), Cheng (ref. 46), Dowson and Whittaker (ref. 27), and Johnson and Cameron (ref. 50). Johnson and Cameron also obtained extensive experimental friction data that showed that the Newtonian theory is only valid for very moderate loads. For loads encountered in most EHD contacts, the friction predicted from a Newtonian fluid is too high compared with the experimental friction. The influence of a nonlinear relation between τ and $\partial u/\partial y$, such as those shown in figure 5, is yet to be explored fully.

A review of the effects of pressure-temperature-viscosity dependence as well as the non-Newtonian effects on temperature and friction in EHD contacts is given in the following sections.

Pressure-Temperature-Viscosity Effects

Using an exponential model for the pressure and temperature dependence on viscosity, Crook (ref. 44) developed an analysis to predict the temperature and friction in an EHD contact according to equations (11) and (12) with a linear relation between τ and $\partial u/\partial y$. His results were recently expressed in a more explicit manner by Dyson (ref. 47) as

$$T_c - T_1 = \frac{\tau(U_1 - U_2)h_0}{4k_0} \tag{13}$$

$$\tau_{\max} = \frac{0.66}{h_0}\left(\frac{8k_0\mu_1}{\beta}\right)^{\frac{1}{2}} \tag{14}$$

$$f_{\max} = \frac{0.66\ \alpha}{h_0}\left(\frac{8k_0\mu_0}{\beta}\right)^{\frac{1}{2}} \frac{e^{[(\alpha/2)p]}}{\alpha p} \tag{15}$$

According to the above results, both the center-film temperature rise and the maximum obtainable friction $f_{\max}$ vary exponentially with the α and are directly proportional to $1/\sqrt{\beta}$. Thus, the influence of α is likely to be much stronger on friction than on the film thickness or pressure. For this reason, it has been believed strongly that the traction experiments in rolling and sliding disks can be used as an effective viscometer for measuring α. However, the use of traction data to deduce α based on the Newtonian theory for friction has not been fully feasible because, so far, there is still serious lack of agreement between the friction data and the values calculated from equations (11) and (12). For example, Crook (ref. 44) calculated the Newtonian frictional coefficient in terms of the effective viscosity, and plotted them against the sliding speed in figure 11 along with the experimental data. There are three calculated curves representing three different values of the ratio of the thermal conductivity of the lubricant to the temperature-viscosity coefficient. It is seen that even if this ratio is increased by almost one order of magnitude, it is still not possible to obtain close agreement with experiments. Crook's experimental data were also

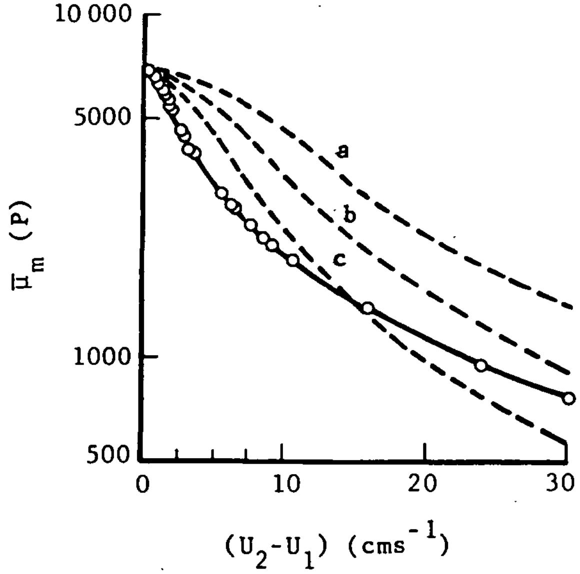

FIGURE 11.—Variation of μ_m with sliding speed. Load = 1.2 × 10^3 dyne-cm^{-1}; U = 400 cm-sec^{-1}; μ_0 = 1.4 P; ——O——: from experiment; ——: calculated; (a) K_f/β_1 = 1.5 × 10^5 dyne-sec^{-1}. (b) K_f/β_1 = 7.5 × 10^4 dyne-sec^{-1}. (c) K_f/β_1 = 3.75 × 10^4 dyne-sec^{-1} (ref. 45).

compared with the frictional coefficient calculated from the full thermal EHD theory provided by Cheng (ref. 46). Even for a moderate load of 715 lb/in. or maximum Hertzian pressure of 70 000 psi, the disagreement between the theoretical and experimental maximum frictional coefficients is clearly seen in figure 12.

The inadequacy of a Newtonian model in predicting friction becomes more pronounced at higher loads. Johnson and Cameron (ref. 50) obtained a series of experimental frictional coefficients using a conventional two-disk machine for loads up to 250 000-psi maximum Hertzian stress and rolling speed up to 260 in./sec. Their data show that there exists a ceiling to all the experimental traction coefficients that cannot be exceeded regardless of the rolling speed or load. Figure 13 shows two sets of friction curves calculated by using equations (11) and (12). It is evident that the calculated traction assuming a Newtonian lubricant is too high in comparison to the experimental ceiling curve.

Shear-Thinning Effects

Based on Johnson and Cameron's data, it is clear that the consideration of the effects of temperature-viscosity dependence alone in the friction theory is not sufficient for accurate prediction of frictional coefficient. Other effects such as shear-thinning, viscoelastic, and transient-viscosity effects may also play important roles in governing friction.

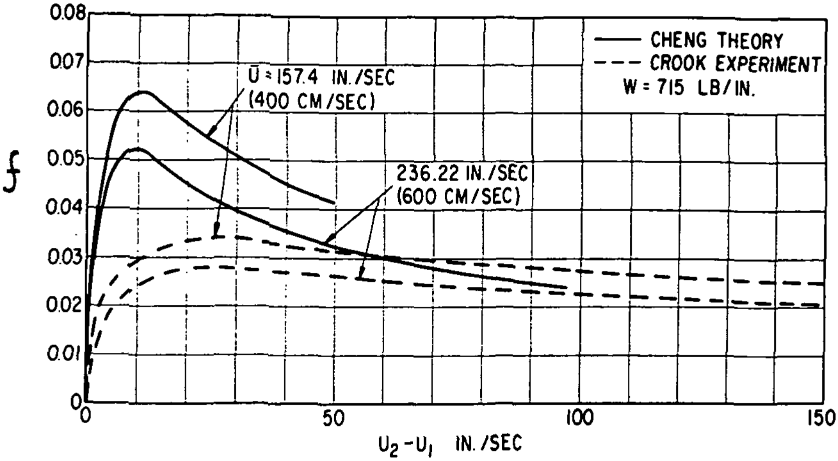

FIGURE 12.—Comparison between theoretical and experimental sliding friction coefficient (ref. 46).

The shear-thinning and viscoelastic effects were recently explored by Dyson (ref. 47) and also reviewed by Naylor (ref. 4). Dyson postulated that the variation of friction with sliding speed can be explained by three separate effects depending upon the amount of slip.

In the region of extremely small slip, the deviation of friction from Newtonian theory could be due to viscoelastic effects without the inclusion of the rotation of the fluid in the stress-strain-rate derivation. He employed the recently developed Barlow-Lamb viscoelastic model (ref. 35) and the Maxwell model (ref. 8) to calculate the apparent viscosity as a function of the rolling speed. If the viscoelastic effect is absent, then the apparent viscosity should be constant with respect to the rolling speed. His calculation shows that the apparent viscosity decreases with the rolling speed, and the rate of decrease is dependent on the static viscosity evaluated at the contact pressure. The higher the static viscosity, the faster the apparent viscosity decreased with the rolling speed. However, this dependence upon the static viscosity has not been observed experimentally by Johnson and Cameron. More recently, Harrison and Trachman [3] have attempted to explain the loss of the apparent viscosity at high rolling speeds in terms of compressional viscoelastic effects and obtained satisfactory correlation with Johnson and Cameron's data.

In the region of high slip, Dyson adopted Smith's limiting shear concept and obtained a good correlation between the measured mean shear stress and the limiting shear stress predicted from the shear modulus measured by oscillatory shear experiment (ref. 35). However, he had to use a shifting

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[3] Harrison, G.; and Trachman, E. G.: The Role of Compressional Viscoelasticity in the Lubrication of Rolling Contacts, to be published.

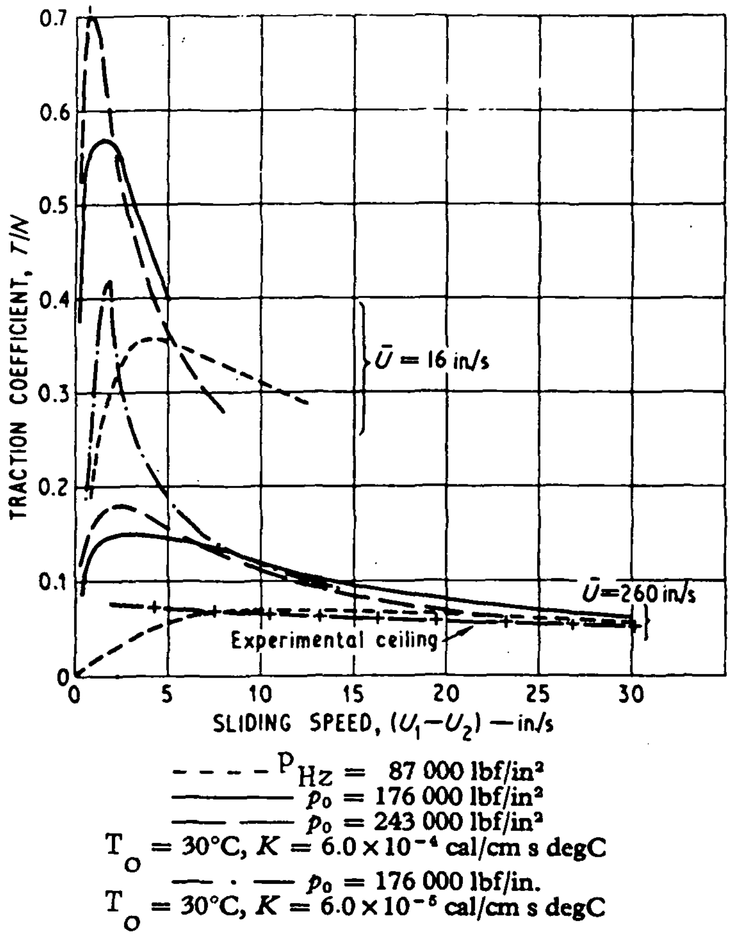

FIGURE 13.—Comparison of Crook's theoretical friction with Johnson and Cameron's experiments.

factor to scale down the limiting shear stress to obtain good agreement. The shifting constant was found to be independent of pressure or temperature. When the friction is governed by limiting shear, the frictional coefficient always decreases with an increasing slip. Dyson also designates the transition between the high-slip and low-slip region as the nonlinear region where the slope of the friction curve changes from positive to negative with respect to sliding speed.

To analyze the friction as a continuous function of the sliding speed, Trachman and Cheng[4] recently used a portion of a hyperbola to represent

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[4] Trachman, E. G.; and Cheng, H. S.: Thermal Analysis of Traction in EHD Contacts. Submitted for publication.

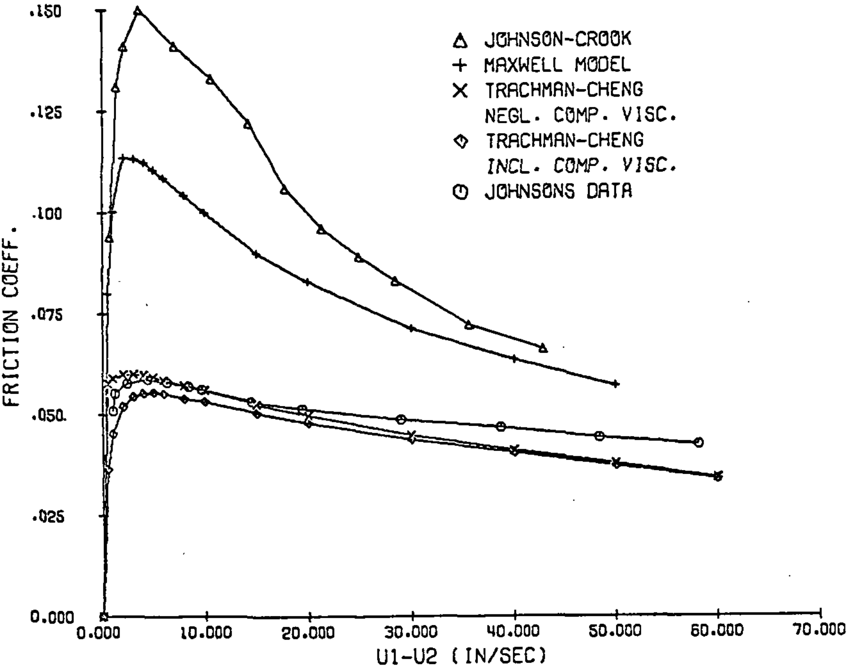

FIGURE 14.—Comparison of experimental friction with thermal friction theory based on a hyperbolic shear-thinning model.

the shear-stress–shear-rate relation. This model has the following advantages: The shear stress approaches a constant value as the shear rate becomes infinity, and the initial slope of the curve is the bulk viscosity of the fluid.

Using this shear-thinning model, they developed a numerical solution of the coupled fluid flow and energy equation for the shear stress, temperature, and friction. The shear modulus is assumed to vary with respect to pressure and temperature according to Dyson (ref. 47). Figure 14 shows a comparison between the thermal theories and Johnson's experimental data. The friction predicted from thermal effects alone according to Johnson-Crook is apparently too high. Incorporating the shear-thinning effect based on a Maxwell liquid still shows little improvement. The shear-thinning effects approximated by a hyperbola for the limiting shear apparently gives the best correlation with the experimental data for this particular condition. There are two friction curves associated with the Trachman-Cheng hyperbola model. The upper curve neglects the effect due to compressional viscoelasticity, also known as transient pressure-viscosity effect, and this upper curve takes a steeper rise and peaks a little earlier than the lower curve, which includes the compressional viscoelasticity effect. It is obvious that this transient effect is very important in the low-slip region, and it is discussed more fully in the next section.

Effect of Compressional Viscoelasticity

It was suggested earlier that in most heavily loaded rolling contacts, the fluid viscosity does not respond to the pressure rise instantly, and the effective viscosity in the high-pressure region is much smaller than the true viscosity measured statically. To estimate the reduction in the viscosity during a short transient, Harrison and Trachman[5] recently used Dolittle's relation between the free volume and viscosity (ref. 51) and derived a method for predicting the ratio of the effective viscosity and the true viscosity. In determining the volume change, a simple model consisting of two springs and a dashpot as shown in figure 15 has been used. Using this method, Harrison and Trachman calculated the effective viscosity as a function of rolling speed and contact pressure using the lubricant and contact dimensions in Johnson and Cameron's experiment (ref. 50). The large reduction of viscosity at high rolling speed and high loads is clearly visible in figure 16. To correlate with the experimental data in reference 50, they also included a shear-thinning effect at a small sliding speed of 0.02 in./sec and calculated the effective viscosity from 50 in./sec to 500 in./sec. Using the same extrapolation procedure used by Johnson and Cameron at small rolling speeds, they obtained the static viscosity at zero rolling speed. The comparison of the zero rolling speed viscosity between theory and experiment is shown in figure 17, and the agreement is indeed close.

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[5] See footnote 3.

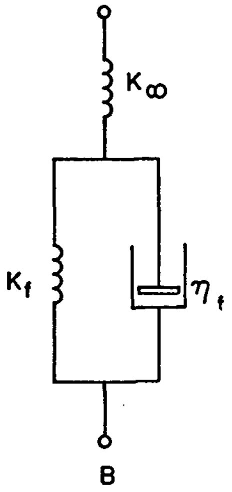


FIGURE 15.—Model for compressional viscoelasticity.

K_∞ = bulk modulus associated with the instant elastic compression of the liquid "lattice"

K_f = bulk modulus associated with the molecular rearrangements

η_f = viscosity associated with the changes in the free volume

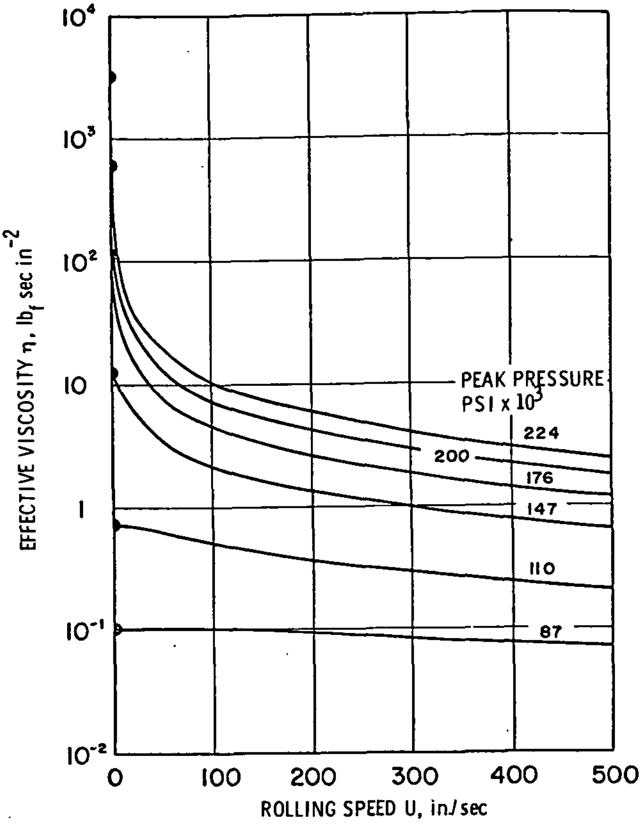


FIGURE 16.—Effect of rolling speed on effective viscosity.

CONCLUSIONS

In thick-film hydrodynamic lubrication, such as journal bearings, the temperature-viscosity effects and shear-thinning effects seem to have the same degree of influence on load capacity and friction. Lubricants containing additives to improve the temperature-viscosity characteristics are usually accompanied by undesirable shear-thinning effects. Methods are available to predict the above influence separately but not simultaneously. Analysis to study the combined effects is needed. Other rheological effects, such as pressure-viscosity, normal stress, and transient viscosity effects seem to have secondary importance in hydrodynamic lubrication.

In thin-film lubrication of concentrated contacts, present knowledge of the rheological effects on lubrication is far from complete. Developments in EHD lubrication so far indicate that—

(1) Pressure-viscosity effects on EHD film thickness are well understood analytically throughout the full range of pressure-viscosity

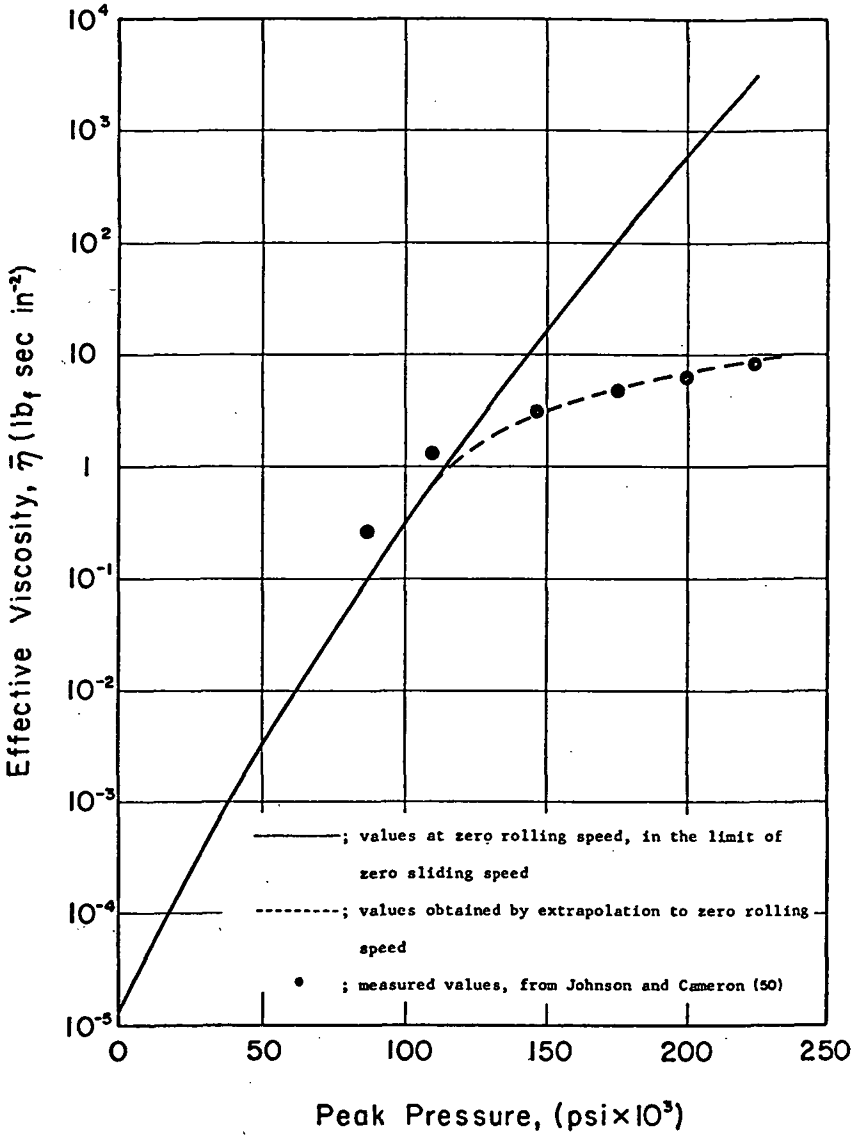


FIGURE 17.—Effective viscosity versus peak Hertzian pressure.

coefficients. Optical and capacitance film-thickness measurements have substantiated the pressure-viscosity effect on the film thickness for contacts of moderate speeds and loads. For very high loads (>200 000-psi maximum Hertzian stress) or high speeds (>250 in./sec), recent X-ray film-thickness data suggest the viscosity has a delayed response to the rapid pressure rise in the contact.

(2) EHD theories predict a pressure spike at the exit of the contact, and this spike is attributable to the pressure-viscosity effects. The severity of this pressure peak is not affected significantly by the temperature-viscosity effects. The viscoelastic and the transient viscosity effects would soften the spike, but quantitative understanding of these effects must await the full viscoelastic EHD theory.

(3) All traction measurements in EHD lubrication indicate that behavior of the lubricant in the contact region under extreme pressure is definitely non-Newtonian. Pressure-viscosity and temperature-viscosity effects are not the only major factors governing traction. A temperature-dependent shear-thinning model, with shear stress approaching an asymptote at high shear rates, predicts friction data correlating very closely with experimental traction.

(4) A recent theory on high-pressure, transient viscosity based on the concept of free volume predicts some low-slip traction data correlating remarkably well with traction experiments. This correlation strongly suggests that the response of viscosity to a rapid pressure rise is not immediate but time dependent. The transient viscosity is predictable from the concept of compressional viscoelasticity.

ACKNOWLEDGMENT

The efforts of this review paper have been partially covered by the support received under research grant NGR–14–007–084, currently being conducted at Northwestern University for NASA Lewis Research Center.

DISCUSSIONS

D. Dowson (The University of Leeds, Leeds, England)

Dr. Cheng is in a good position to present an account of the role of rheology in lubrication since he has considered important rheological features in a number of theoretical studies of EHD lubrication. Furthermore, he has a breadth of understanding of the subject that is essential to the preparation of a review paper.

There is a danger that those about to study lubrication might, if they first read the proceedings of this symposium, be inclined to the view that the materials they are concerned with behave in a most unconventional manner. A Newtonian lubricant might appear to be a rarity and a viscoelastic lubricant with time-dependent pressure-viscosity characteristics commonplace. It is not at all surprising that Dr. Cheng and others should devote space to the current problem areas that is disproportionate to the frequency, if not the importance, of these areas in the whole range of lubrication problems. It is as well to be aware of limitations in a subject, but on this occasion there is probably room for someone to point out that a great many successful bearings have been designed on the assumption that the lubricant was not only Newtonian but also isoviscous.

A general comment, not restricted to the present paper, is that the presentation would have been improved if a glossary of terms and definitions had been included. It is all too easy to misinterpret technical discussion when there is no common understanding of the terminology. Perhaps it is not too late to make this suggestion to the authors and organizers.

Many of Dr. Cheng's observations could have been related to recognized regimes of lubrication like fluid-film and EHD, rather than specific machine elements like journal bearings and rollers. I believe that many of his statements have a wider application than the subject headings suggest. For example, his general discussion of temperature-viscosity effects appears under the heading of thick-film hydrodynamic lubrication, but the views expressed are equally relevant to other forms of self-acting and even externally pressurized fluid-film lubricated bearings. I endorse the view expressed at the end of this section on the need to bridge the gap between procedures for the analysis of fluid-film bearings and the requirement for more accurate design data. The research worker generally leaps ahead to new problems and leaves behind a job of interpretation and preparation of design data that the general designer cannot readily undertake.

In his discussion of shear-thinning action, the author refers to the observation that "non-Newtonian effects appear to promote the occurrence of negative pressure in the diverging section." I am sorry that Dr. Cheng uses the unfortunate phrase "negative pressure" in this context, although it has been perpetuated by numerous writers on cavitation. Subambient pressures in the divergent regions of lubricating films have been recorded on many occasions, although values are usually in the range of 1 to 2 lbf/in^2 rather than the 3 to 4 lbf/in^2 recorded in figure 1. The discusser first encountered this effect some 20 years ago, and it would be interesting to know if the saturation pressure was recorded for the lubricant employed in the tests reported in figure 1. It is well known that if dissolved gas is drawn off or if the ambient pressure is raised considerably above the saturation pressure, appreciable subambient pressures can be recorded. A section dealing with gas release, boiling at reduced pressure, and the rheological implications of oil-film rupture under the heading "cavitation" would have been a welcome addition to the review. Another topic relevant to the present discussion is the behavior of liquids in tension. It is well known that liquids can withstand tensile stresses under quasi-static conditions, but can they do this in shear-flow situations? The author's views on this point would be appreciated.

The difficulties facing experimenters in this field are neatly introduced by Dr. Cheng's comment on the double effect of shear rate, first through non-Newtonian and second through thermal effects.

One of the more spectacular non-Newtonian lubricants is the fluid found in synovial joints. A typical plot of viscosity against rate of shear for synovial fluid is shown in figure 18.

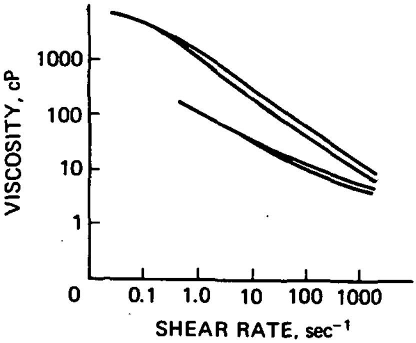


FIGURE 18.—Variation of the viscosity of synovial fluid with shear rate.

(a) $-CH_2-CH_2-O-$

(b)

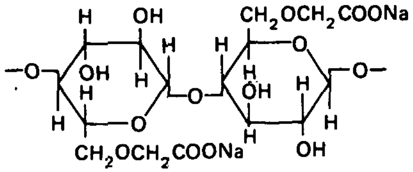


FIGURE 19.—(a) Polyethylene oxide. (b) Sodium carboxymethyl cellulose.

A further effect that may be encountered with shear-thinning lubricants containing long-chain polymers is that of mechanical or thermal degradation. Degradation has been demonstrated for the two lubricants shown in figure 19 in a simple experiment (ref. 52). Each lubricant was stirred for a period of 8 hr by a flat-bladed stirrer rotating at 700 rpm, and the viscosity before and after agitation was measured on a Ferranti-Shirley cone-on-plate viscometer at 37° C. The results are shown in figures 20 and 21. It can be seen that the degradation of polyethylene oxide is greater than that of sodium carboxymethyl cellulose and that recovery of initial viscosity is slight.

The discussion of rheological behavior in EHD lubrication achieves the high standard that one associates with Dr. Cheng's work. Perhaps the most exciting and rewarding concept to enter the arena in recent times is that of a transient viscosity. The analysis based upon a relationship between free volume and viscosity looks promising. If an omission can be detected in Dr. Cheng's survey of EHD conditions, it is to be found in the apparent difference between high-pressure, low-shear-rate viscometry and the behavior of fluids in pure rolling EHD contacts. Does the fluid solidify at high pressure, or is there once again a time effect that prevents the effect in conventional EHD contacts? An exploratory theoretical study, which has apparently enjoyed a good measure of experimental support, in which point contacts have been analyzed in terms of the applicability of viscometry evidence for solidification has been presented by Jacobson (ref.

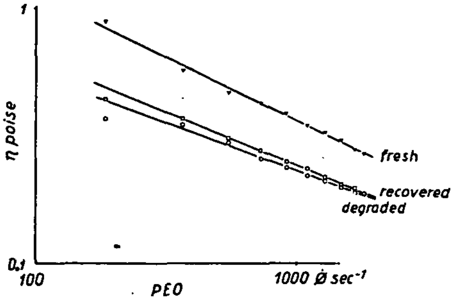
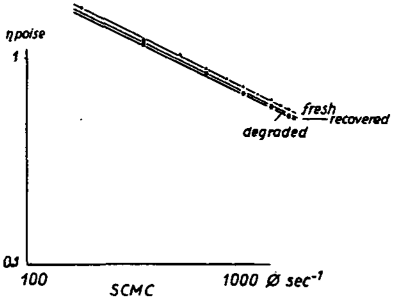


FIGURE 20.—Effect of mechanical degradation on the viscosity of polyethylene oxide and its subsequent recovery.

FIGURE 21.—Effect of mechanical degradation on the viscosity of sodium carboxymethyl cellulose and its subsequent recovery.



53). The author's comments on this aspect of rheology in EHD lubrication would be appreciated.

Dr. Cheng's most able survey of this wide and complex field of study is a welcome addition to the literature. It is clear that, although our appreciation of the subject is increasing rapidly, there is a continuing call for careful rheological studies of lubricants under high values and rates of change of pressure, temperature, and shear.

K. L. Johnson (University of Cambridge, Cambridge, England)

Professor Cheng is to be congratulated both on his review of rheological behavior in lubrication generally and also on his recent contributions to understanding the rheological properties of EHD oil films.

It is in the observation of traction in combined rolling and sliding at high contact pressures that the rheological properties of the lubricant are most apparent, and it is to this aspect of the paper that my contribution refers.

Since it became apparent that the observed traction in EHD lubrication could not be explained by thermal effects alone, two rheological hypotheses have been put forward: shear-thinning and compressional viscoelasticity. These hypotheses have been used by the author, with apparent success, to predict the results of traction measurements (fig. 14).[6]

First, may I ask a simple question about these calculations? The hyperbolic shear-thinning equation used by the author [6] includes a constant C, which may be interpreted as a measure of the limiting traction reached at

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[6] See footnote 4.

very large shear rates. How was the value of C chosen in computing the results [7] shown in figure 14? Was it chosen to obtain a good fit with experiment, or was it based on independent experimental evidence?

Second, a more general comment on shear-thinning relationships might not be out of place. The reduction of apparent viscosity with shear rate that is observed in simple continuous shear between large flat plates or concentric cylinders is usually attributed to viscoelasticity or some form of memory of the fluid of its past history of deformation. If this is indeed the case, then it is not strictly correct to apply the relationships derived in steady uniform shear to conditions of nonuniform or unsteady shear. The entry region of an EHD lubrication contact is clearly a region of nonuniform shear rate. In the parallel section of the contact, on the other hand, the shear is uniform, but the rapid rise in pressure and viscosity at entry corresponds approximately to a step change in conditions at entry, which will give rise to a transient response from a viscoelastic fluid within the parallel section. For these reasons, calculations of shear stress in EHD lubrication based upon the simple shear-thinning relationships of steady shear should be interpreted with caution.

Attempting, like Professor Cheng, to interpret traction measurements in terms of alternative rheological hypotheses about the fluid properties at high pressure has led me to the conclusion that disk machine data by themselves are insufficient to discriminate between the different hypotheses. For example, very similar traction curves would be obtained from a film of elastic-plastic solid between the disk to those obtained from a viscous temperature-dependent fluid. It appears that some different kinds of experiments are called for to throw a different light on the problem. I should like to report briefly on an attempt we are making in Cambridge toward this end.

Instead of superimposing sliding motion on rolling, as in the conventional disk machine experiment, we are superimposing a spin of one surface (about an axis normal to the contact) upon the pure rolling motion of a point contact. The slip between the surfaces, which produces shear in the lubricant film, in this case comprises a simple rotation about the center of the contact area.

The apparatus consists of three equispaced balls rolling between two parallel concentric disks, which are driven at equal speeds in opposite directions as in a simple thrust bearing (fig. 22). The balls rotate about horizontal radial axes. They are constrained against any tendency to creep radially by stops that are spring mounted so that any radial force exerted on the ball by the oil film can be measured. This radial force, which acts at right angles to the direction of rolling, is the significant observation made in these experiments.

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[7] See footnote 4.

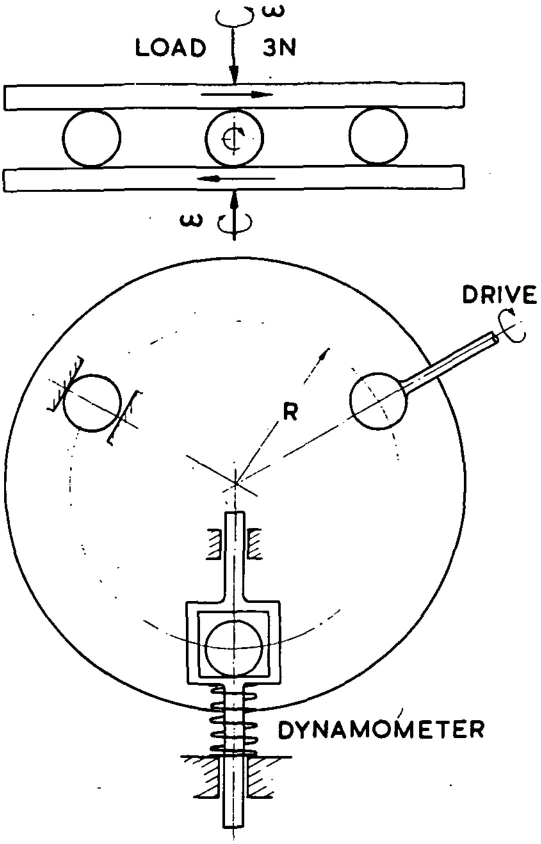

FIGURE 22.—Disk machine with radial force measurement.

The underlying principle of the experiment can best be understood from the diagrams of the contact area between the test ball and the upper plate shown in figure 23. Because of the rolling motion, the fluid flows through the contact along parallel streamlines from left to right with a steady velocity U. The relative velocity vectors **S** between the plate and the ball, due to the spin motion, are shown in figure 23(*b*). They are small compared with U because the radius of the contact circle a is small compared with the radius of the track R. If we follow an element of fluid along one of the streamlines and assume, in the first instance, that the film is of uniform thickness, the sequence of $\dot{\mathbf{S}}$ vectors indicates the variation in shear rate sustained by the element.

Suppose now that the fluid is Newtonian and further that its viscosity is either constant or symmetrical about the center because of the approximate symmetry of the pressure distribution. The shear stress distribution will then be similar to shear rate distribution as given by the $\dot{\mathbf{S}}$ vectors.

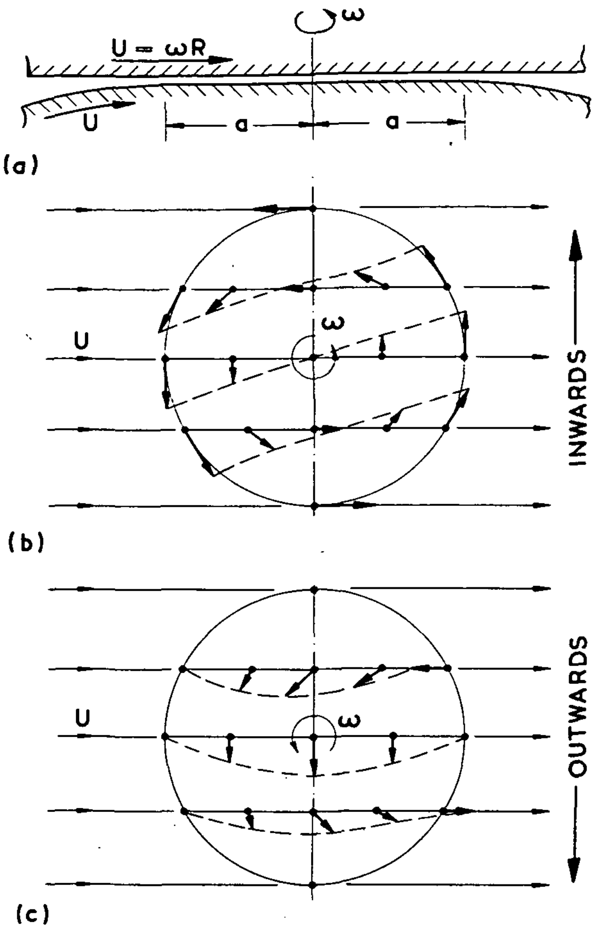

FIGURE 23.—(*a*) $U = \omega R$. (*b*) Slip velocities. (*c*) Slip displacements.

This symmetrical distribution of shear stress will add up to a couple opposing the spin motion, but there will be zero resultant force in either the radial or circumferential directions.

Let us now suppose, following the hypothesis of compressional viscoelasticity, that there is a delay in the buildup in viscosity with pressure. It is then likely that the viscosity in the trailing half of the contact area will be higher than that in the leading half so the shear stresses will be correspondingly higher in the rear half. It is immediately apparent that this effect will lead to a resultant inward radial force on the ball.

Transverse forces arising from a motion of rolling with spin were first observed under lubricated conditions by Poon and Haines (ref. 54) using a different apparatus. They found that the force, in the terminology of figure 23, acted outward. Experiments on our own apparatus carried out by Dr. A. D. Roberts (ref. 55) have confirmed that, over a wide range of rolling speed, at high contact pressure, an outward force is indeed exerted by the film. The order of magnitude of this force rises to about 0.02 N, where N is the normal load. This is a large force when it is remembered that the maximum traction forces in complete sliding only rise to about 0.06 N. (See, for example, fig. 14.) It is difficult to imagine how a delay in the rise in viscosity with pressure can, of itself, be reconciled with the observation of a resultant force acting in the outward direction.

It is interesting to add that some measurements have been made under isoviscous conditions at very low contact pressure using rubber balls. In this case the transverse force was observed to act inward. Its magnitude was found to be consistent with the increased traction at the rear of the contact due to the nonuniformity of film thickness, which has been revealed by optical methods (ref. 56).

We turn now to viscoelastic effects. The relative tangential displacement between points on the surfaces of the plate and ball that first make contact at the leading edge is denoted by the vector $\mathbf{S}$. The variation in $\mathbf{S}$ along three typical streamlines is shown in figure 23(*c*). (For the calculation of the field of $\mathbf{S}$ from the field of $\dot{\mathbf{S}}$, see ref. 57.) If now we imagine the lubricant film to be replaced by a thin uniform sheet of perfectly elastic material like rubber, it will give rise to shear stresses which are distributed in proportion to the shear displacement vectors $\mathbf{S}$. It is clear from figure 23(*c*) that such a stress distribution will produce a resultant radial force acting outward. In dry contact, such an outward force arises from the elasticity of the solids themselves (ref. 56).

The distinction between the field of $\mathbf{S}$ shown in figure 23(*c*) and that of $\dot{\mathbf{S}}$ shown in figure 23(*b*) indicates that the observation of transverse tangential forces during rolling with spin offers a possible method of separating elastic from viscous effects in the rheological properties of EHD films. Preliminary observations of an outward force are consistent with the hypothesis that the fluid exhibits some elasticity and does not respond instantaneously to its current strain rate.

In conclusion, it must be emphasized that our experiments are at an early stage in their development and that a quantitative evaluation of the results is not straightforward, so the conclusions should be regarded as tentative for the time being. It is hoped that a more complete report can be presented during next year.

J. F. Archard (University of Leicester, Leicester, England)

I would like to add a footnote to Dr. Johnson's contribution, but first I must add my congratulations to Professor Cheng for his contributions to the subject, both in this review and in his recent publications.

I strongly support Dr. Johnson's view that we require supplementary information that cannot be provided by the conventional torque-versus-slip type of disk machine experiment. In addition, the type of experiment that we plan should be designed to bridge the gap between the broad field of rheology that is reviewed in Mr. Hutton's lecture and the special conditions that occur in EHD. I therefore outline a technique that is under development in my laboratory. Although I cannot yet claim any meaningful results from this technique, its description here may encourage others to consider alternative types of experiment that could provide the new type of evidence which is needed.

Our experiments are based upon the well-known four-disk machine in which the central disk is restrained by its lubricated contacts with the three outer disks. As shown in figure 24, we plan to examine the rheology of the lubricant in these three contacts by applying axial oscillatory forces to the central disk and by measurements of its displacement with respect to the outer disks. There are problems in the development of this technique, and modifications to the simple arrangement shown in the figure have been necessary, but the essential principle of the experiment remains unchanged.

While our experiment lacks the elegant simplicity of Dr. Johnson's, it may yet provide more detailed information. In principle, it should be possible to use the machine both in the conventional torque-versus-slip mode

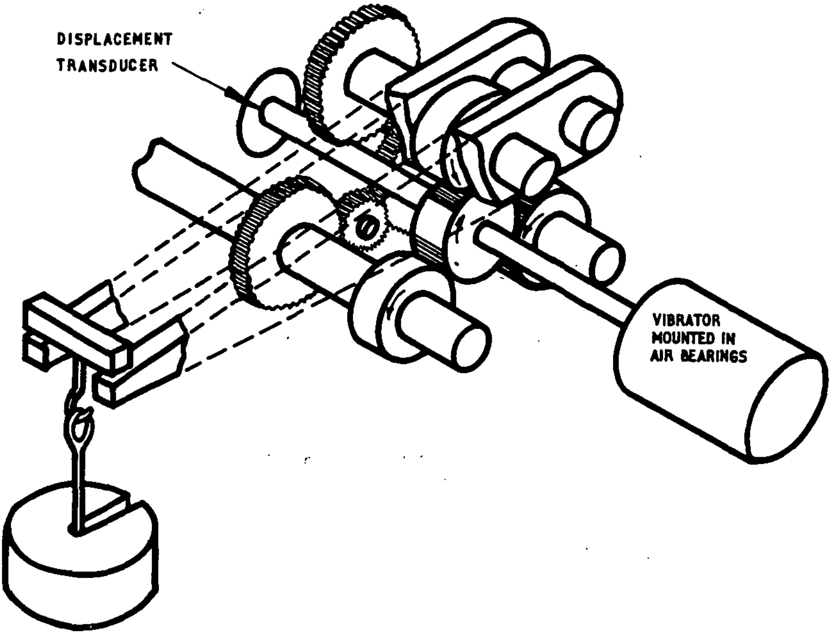

FIGURE 24.—Four-disk machine with axial oscillation.

and also in this modified form. From these experiments it may be possible to compare results from continuous shear (torque/slip results) with those from small-displacement oscillatory shear (hopefully, in the linear range).

W. O. Winer (Georgia Institute of Technology, Atlanta, Ga.)

The author has undertaken a difficult task in trying to review this field, which has a rapidly growing literature. In the field of thick-film hydrodynamic lubrication, there is relatively little disagreement and a much smaller literature than in the EHD field. We tend to agree with the author in the conclusion that for thick-film lubrication the major rheological considerations are those of shear-thinning and temperature-dependent viscosity. It is correct that there has been very little work on the combined effects of these.

In the area of EHD lubrication, however, the situation is not so clear. We suspect that the number of special phenomena attributed to lubricants in EHD contacts, and speculated about in the literature, exceeds the number of researchers interested in this field and certainly exceeds the number of independent experimental investigations into the same. In the final analysis, we hope that the dominant rheological characteristics of lubricants in EHD contacts will be independently confirmed by several experimental investigations and will be part of a unified theory explaining the full range of EHD phenomena. We agree with Professor Cheng's second conclusion: "In thin-film lubrication of concentrated contacts, present knowledge of the rheological effects on lubrication is far from complete."

At the risk of adding more confusion to a difficult area, we would like to make a few comments about some of the work discussed by the author and add still another possible explanation to the long list of mechanisms already proposed. It appears that except for the Battelle X-ray data, there is little disagreement about the effect of load (or maximum pressure) on EHD film thickness. These X-ray data are the motivating force behind several of the non-Newtonian rheological theories put forth in the review. The Battelle people say that their data are at higher pressure than any of the other data and therefore cannot be compared with other data in the literature. In their most recent defense of these data (refs. 31 and 58), they only mention data from 80 000- to 225 000-psi Hertz pressure (unlike that shown by the author in fig. 4). Some of the Battelle data (ref. 58) show a film-thickness-pressure slope of about −1.4. It is not clear why they chose not to use their earlier data from 225 000 to 350 000 psi, which show the precipitous drop in film thickness indicated in figure. 4. In our laboratory we have taken film-thickness data for point contacts by the optical interference method (ref. 40) at pressures up to 175 000 psi and have found that the centerline film thickness with load (or pressures) are very similar to those predicted by the classical analysis. The slope of the log (film thickness) against log (pressure) was typically less than −0.6. Data taken on a variety of fluids at pressures from 75 000 to 175 000 psi (fig. 10 of ref. 40) show a film-thickness-load dependence consistent with theory. Surely the behavior of lubricants in point and line contact are not so different as to readily dismiss these data. This brings us back to the question of why the X-ray data disagree with the analytical solutions in this respect. It is no longer obvious that the rheological behavior of the lubricant is the reason. Similar lubricants have been used in each laboratory. This is not the place to get into a discussion about the pros and cons of the X-ray technique, but since much of the rheological discussion is based on those data it is important to point out that the data are not verified by independent experiments. In fact, the available independent experiments under similar conditions contradict it.

A number of investigations of shear relaxation have been covered. None of them, however, have accounted for the observed behavior reported in the rheology literature that shows that the relaxation spectrum is strongly dependent on the steady shear rate the fluid is experiencing (ref. 30). It has been shown that steady shear effectively eliminates all relaxation phenomena with relaxation times greater than the reciprocal of the steady shear rate. In EHD contacts this means that the maximum relaxation times the fluid has available are 10^{-6} to 10^{-7} sec or less. These relaxation times may not be large enough to have any real influence on the lubricant behavior in an EHD contact.

Last, it is worth noting that there are indications in the rheology literature that suggest that the limiting shear concept may have some experimental justification. The work of Porter and colleagues (ref. 59) into the mechanical shear degradation of fluids shows that for some materials, similar to those used as lubricants, molecular degradation occurs under conditions of shear stress and energy dissipation density much less than those in an EHD contact. These observations of molecular degradation have been well documented and may have important implications in our understanding of EHD traction. The phenomena should be investigated for its possible role in EHD. If that role is found to be important, it may greatly change our thinking about lubricant behavior. The availability of free chemical bonds resulting from mechanical degradation may provide a long-awaited link between EHD and boundary lubrication.

W. J. Anderson (NASA Lewis Research Center, Cleveland, Ohio)

I would like to make a plea for more intensive experimental investigations of lubricant rheology. This is the information required before any further development of EHD lubrication as a useful technology can be achieved. Specifically, we need a better characterization of lubricant non-Newtonian and viscoelastic behavior, and the development of quantitative methods for treating short-time transient effects.

My plea is for an experimental approach because lubricants are extremely complex fluids. All fluids are viscoelastic to some degree. Rheological models, no matter how elegant, consider viscosity and elasticity separately, and a complete mathematical treatment of the situation quickly becomes intractable. This is not to say that the experimental approach will be easy. On the contrary, it will be very difficult, but it should be possible to develop lubricant characterizations that are more meaningful than those we are now using.

First, why should viscoelasticity be of concern? Most petroleum oils contain some paraffinic wax that tends to come out of solution at low temperatures or high pressures. High shear rates superimposed on high pressures will probably tend to promote fluidity, but little or no data on the behavior of oils at high pressures and shear rates are available.

There is some evidence to indicate that, at temperatures below their pour points, waxy petroleum products exhibit a finite yield stress (ref. 3). If they behave similarly at Hertzian pressures, the effect on high-speed ball bearing dynamics could be significant. Present ball bearing dynamics programs (ref. 60) use Archard and Cowking's point contact film-thickness formulation (ref. 21) and assume an exponential pressure-viscosity relationship and Newtonian behavior to calculate shear stress. Physically, this means that a gyroscopic moment about a given axis will produce ball spin about that axis. If the oil exhibits a finite yield stress, then ball motion could be significantly different. We plan to support a program to determine experimentally ball motions in high-speed ball bearings. Optical observations will be made and motion pictures taken of a uniquely coded ball in a thrust-loaded ball bearing.

The potential importance of short-time transient effects in EHD con-

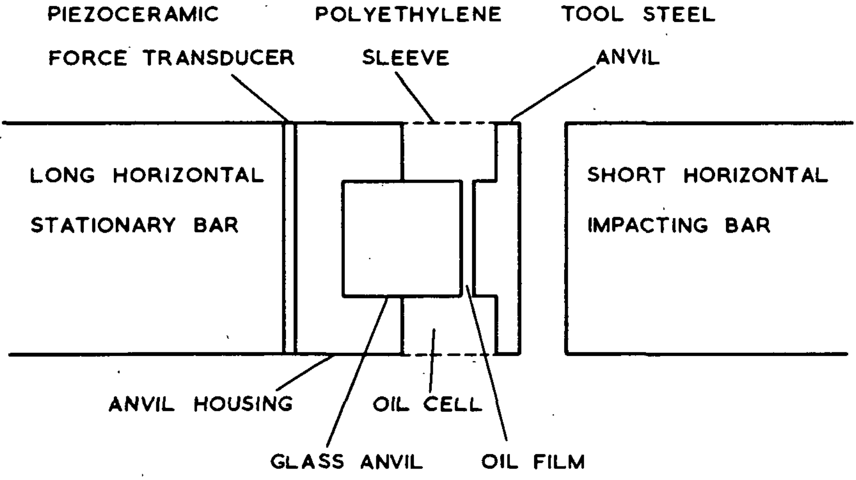

Figure 25.—Hopkinson bar apparatus for studying oil squeeze films.

tacts is well recognized (refs. 3 and 61). In a typical EHD contact, the deformation rate and the Deborah number (the ratio of relaxation time to time in transit) are so great as to make any assumptions of conventional fluidlike behavior not only quantitatively but qualitatively incorrect for lubricants possessing relaxation times greater than approximately 1 μsec (author's closure to discussion of ref. 61).

An analytical description of longtime steady-state lubricant behavior in an EHD contact is difficult enough, as is well known. A similar treatment for short-time transients seems hopelessly complex. The job therefore falls to the experimentalist, but this approach also appears to be a formidable task. The development of techniques for applying very brief pressure pulses (on the order of 1 to 10 μsec) even without superimposing high shear rates is difficult. We are presently funding a program to determine experimentally the viscous response of lubricants to short-time pressure pulses.

G. H. Kinner (Royal Aircraft Establishment, Farnborough, England)

Having listened to Dr. Cheng's paper, I get the impression that as far as EHD lubrication is concerned, most of the studies have dealt with behavior in sliding or rolling contacts.

You may therefore be interested in the following short summary of some work that Professor Hirst and his colleagues have been carrying out at the University of Reading under contract to the Ministry of Defence. It concerns the behavior of oil films located between flats subjected to impact loading.

A Hopkinson bar technique was used. This is shown schematically in figure 25. A piezoceramic element was incorporated to measure the force of impact. The rate of approach of the faces of the oil cell was measured by rate of change of electrical capacitance. To provide the necessary electrical resistance, the rear anvil was made of glass and an electrode evaporated onto it.

It was found that, despite the high pressures developed under impact conditions, mineral oils and silicone fluids exhibited a measured viscosity lower than the initial viscosity. In other words, the rate of approach of the oil cell faces was greater than would be predicted by Stefan's theory and greater still than would be predicted by current EHD theory taking the pressure coefficient of viscosity into account. The observed behavior could be explained by a full analysis of the heating effects involved.

On the other hand, the thermal theory did not predict the behavior of a concentrated polymer solution in oil, of a high-viscosity aromatic extract, or of a polyphenyl ether. These fluids gave an elastic response to impact. There was a very low effective viscosity as the force built up during impact, and the plates recoiled when the force was removed. The elastic modulus was very high, being $\simeq 10^{10}$ dyne/cm^2, in contrast to $\simeq 10^6$ dyne/cm^2 for polymer solutions at atmospheric pressure.

The magnitude of the elastic effect depended on the initial film thickness, being greater when the film was thin. On increasing the film thickness severalfold, the degree of elasticity changed to such an extent that the aromatic extract and polyphenyl ether ceased to appear elastic. The behavior of both these fluids then agreed with the thermal theory. The polymer solution remained elastic, but the elastic modulus fell to a value typical of the shear modulus for a normal polymer solution.

It was also found that the magnitude of observed elastic effects was dependent on fluid viscosity. For the same film thickness, more viscous fluids appeared more elastic. This suggests that elastic flow always occurs but can only be detected when it is large in comparison with the viscous flow. When the film was thin, the elastic effects were shown to be due to the bulk compressibility of the fluid.

Thus, bulk elastic effects occur in the thin-film, high-viscosity region and normal viscous behavior occurs in the thick-film, low-viscosity region. The position of the dividing line between the regions depends on the radius of the plates (9 mm in the work described). A similar pattern would be expected for a smaller radius but with the dividing line set at a lower film thickness. Quantitative evaluation of the change in position of the dividing line is not yet available.

Even when elastic rebound occurs, a meaningful viscosity value may be deduced from the part of the impact where the force is constant and no elastic strain is being recorded. For the strong polymer solution the viscosity is found to be lower than the initial viscosity by a factor of about 10. This is the well-known temporary loss of viscosity that polymer solutions suffer at high shear stresses.

In contrast, the aromatic extract and polyphenyl ether exhibit a considerably enhanced viscosity. This implies a domain in which normal EHD theory is applicable. In these conditions of high viscosity and thin films, not only is less heat generated, but it is more readily conducted through the film into the plates. Thus, the assumption in thermal squeeze-film theory that all the heat remains in the fluid and leaves the system by convection is probably no longer valid.

In summary, we have seen two types of behavior in squeeze films. When the film is thick, the thermal theory applies. When the film is thin, normal EHD theory applies. The critical film thickness at which one regime gives way to the other is $\simeq 25$ μm (0.001 in.) when the viscosity of the lubricant is 1 poise and the radius of the plates 9 mm.

From the practical point of view, one can recognize that there will be significant squeeze-film action in the inlet zone of gear teeth and roller bearings. In this zone the film will be appreciably thicker than at the center of contact, and there is a likelihood of thermal squeeze-film action and its attendant fall in viscosity. We conclude that the initial thickness of this film and the degree of filling of the inlet zone must be considered in the light of the present work if satisfactory EHD lubrication is ever to be achieved.

A. Dyson (Shell Research Ltd., Thornton Research Centre, Chester, England)

I am very impressed by the measure of agreement between theoretical and experimental traction results as given in figures 14 and 17 of the paper. I have tried to do something like this several times myself, and I have never obtained such good agreement.

Apparently it is necessary to include both shear-thinning and compressional viscoelasticity effects, and I ask Professor Cheng to give some more details about the nature of the assumptions made in the calculations. For example, what considerations govern the choice of the values adopted for the three parameters of the compressional viscoelasticity model shown in figure 15 and also for the parameters of the hyperbolic shear-thinning model?

If we consider film thickness in EHD lubrication, the situation is very satisfactory. We have a number of theories, all of which contain only quantities that can be evaluated independently; e.g., by conventional viscometry. In contrast, traction in EHD lubrication seems to be enclosed within a tight circle. The conditions are so unusual that it is difficult to obtain all the information from other fields, and it is necessary to incorporate parameters that have to be adjusted to fit the observations.

Has Professor Cheng succeeded in breaking out of this closed circle? How many of his parameters are disposable, and how many are fixed by considerations outside EHD lubrication?

W. J. Derner (FMC Corp., Link-Belt Bearing Division, Indianapolis, Ind.)

The author's review of the rheological effects on lubrication is worthy of careful consideration by the serious student in the field. His effort is most welcome and timely.

Of significant interest and importance to the rolling-element bearing field is the indicated response of lubricants in the high-load, high-speed, thin-film regime. In this model, where the lubricant properties are assumed to be elastic, it is important that we consider the elastic properties of the rest of the bearing-lubricant system. Likewise it is important that we consider the time constants involved for both the structural materials and the lubricants. Should these be such that the response of the structural materials is significantly out of phase to the response of the lubricant films, there is reasonable doubt as to the authenticity of the rheological model described.

Would the author please describe and compare the elastic properties and the time constants of the system considered in his analysis?

P. M. Ku (Southwest Research Institute, San Antonio, Tex.)

The preceding discussers have responded well to Professor Cheng's comprehensive and scholarly lecture by presenting complementary information or techniques and by posing interesting questions. My purpose is, to quote two Chinese expressions, not "to add embroidery to a tapestry," but "to borrow illumination from a lantern."

Among other matters, Professor Dowson called attention to cavitation. Mr. Kinner referred to the squeeze film. In their discussions on Mr. Hutton's lecture, Mr. Kinner also mentioned the starvation of EHD conjunctions, and this discusser asked about the normal stress effect and the rheology of surface films. Comments from Professor Cheng regarding the relevance of these phenomena or effect on hydrodynamic and EHD lubrication and how lubricant properties enter into these problems will be greatly appreciated.

Professor Winer's comments on the EHD film thickness strike a rather sympathetic chord in this discusser, but examination from another point of view may be in order. The lubricant film thickness of paramount interest is the minimum film thickness, which, for the general case of an elliptic conjunction, takes the approximate shape of a banana. It is now quite clear that the minimum film thickness is controlled basically by the inlet conditions and not by what happens after the inlet. However, the magnitude of the minimum film thickness for the circular or elliptic conjunctions is somewhat uncertain because there are no full analytical solutions yet, and the experimental data still need careful evaluation and reconciliation. Nevertheless, the increasing volume of experimental data appearing in recent years, generally with circular conjunctions, might provide a tangible start. Similar experimental work with elliptic conjunctions of varying aspect ratios are still needed. All of these, however, do not negate the need for full analytical solutions.

Along the same line, Professor Cheng's side leakage and thermal corrections represent what might be considered as interim solutions to two important and intriguing problems for which no full analytical solutions are yet available. My own concern is that these correction factors are derived from a Grubin-type treatment that ignores the presence of a banana-shaped constriction. How validily these correction factors can be applied to the minimum film thickness is a matter that requires some scrutiny.

Anyone who has examined the traction behavior in EHD conjunctions, from Crook's classical studies to many recent ones, cannot but be frustrated by a sense of helplessness. Though the problem appears simple at first glance, accurate experimental determination of traction is by no means easy, and truly plausible theoretical understanding is immensely difficult to achieve. In traction behavior, what happens inside the conjunction becomes important. Perhaps some way of looking into the conjunction such as suggested by Drs. Johnson and Archard, will be helpful.

Finally, Professor Cheng has dealt basically with situations where a full, intact lubricant film prevails. The analytical solution assumes perfectly smooth surfaces and the key confirmatory experiments generally employ extremely smooth surfaces. In practical lubrication problems, one usually deals with surfaces that are neither perfectly nor extremely smooth. Meaningful film thickness and traction experiments with rough surfaces are difficult to perform and difficult to interpret due to difficulties in controlling surface roughness and surface texture. After all, when the lubricant film thickness becomes very small, how important the surface films are is still an open question. Moreover, when the lubricant film thickness approaches the combined surface roughness, the validity of all conventional EHD analysis needs to be justified even from the physical standpoint, not to mention possible chemical effects. Nevertheless, a better analytical understanding of both film thickness and traction with rough surfaces down to the transition regime and of traction through transition into the boundary regime, even with chemical effects ignored, would be a great step forward. With such a nonchemical model at hand, the effects of chemistry can then be evaluated.

LECTURER'S CLOSURE

The valuable discussions contributed by my distinguished colleagues reminded me of still another Chinese expression, "Cast stone to attract jades." Since there is considerable overlap on subject matters among the discussions, I shall attempt to reply to the comments according to topic.

General Comments

Professor Dowson's caution to the general audience and machine designers is very well taken. As mentioned in my introduction, the rheological effects discussed here are more pertinent to bearings using polymer-thickened fluids and high-speed, heavily loaded concentrated contacts than to conventional bearings.

I appreciate the plea put forth by Professor Dowson that there should be a glossary of terms and definitions on rheology in lubrication. I think we should get together with the rheologists to come up with agreement on the exact definitions on rheological terminology in the literature. A common glossary would serve as an excellent guide for future conferences on rheology in lubrication.

Cavitation

Both Professor Dowson and Mr. Ku call for more understanding of the effects of rheology on cavitation. So far, the studies on cavitation in bearings and seals seem to be concentrated on the location of the film rupture, which determines the boundary conditions in the Reynolds equation (refs. 62 to 65), assuming the lubricant is Newtonian. The effects of non-Newtonian behavior of the lubricant on film rupture appear to be relatively unexplored. Tao and Philipoff's results, as shown in figure 1 of the lecture, appear to be some of the few experimental data for viscoelastic fluids. In their paper, they did point out that the level of subambient pressure for viscoelastic fluids is higher than that for normally Newtonian fluids. They also reported that for mineral oils the level of subambient pressure is about 2 psi, which confirms the value quoted by Professor Dowson for Newtonian lubricants. However, they have not given any satisfactory explanations as to why the viscoelastic fluids penetrate deeper into the subambient region.

Shear-Thinning Effects

The interesting evidence presented by Professor Dowson on the effects of mechanical and thermal degradation on the shearing-thinning relation is most welcome. The drastic reduction of apparent viscosity with shear rate for synovial fluid is indeed astonishing. Both Dr. Johnson and Mr. Dyson request a more detailed description of the hyperbolic shear-thinning model. The shear stress and shear rate relation is represented by the hyperbola

$$\Omega=\frac{C\,\tau/\bar{G}_\infty}{C-\tau/\bar{G}_\infty}$$

where Ω is the nondimensional shear rate $\frac{\mu}{\bar{G}_\infty}\frac{\partial u}{\partial y}$, τ is the shear stress, and $\bar{G}_\infty$ is the high-frequency limiting shear modulus.

The value C is not determined empirically from any experiments. It is the limiting value of $\tau/\bar{G}_\infty$ for $\Omega\rightarrow\infty$ and was found by Dyson (ref. 47) to be equal to 0.25 for the Barlow-Erginsav-Lamb liquid. The value of $\bar{G}_\infty$ is determined by the same procedure suggested by Dyson (ref. 47).

Dr. Johnson also raises a profound question on the use of a shear-thinning model based on steady-state shear for cases of unsteady shear where there is a pressure gradient present. I fully concur with his reservation that this application is not completely valid in the entry region of an EHD contact. However, in the parallel section, where the uniform shear dominates, the deviation from steady state is small, and the application of a steady-state shear-thinning model should yield a close approximation for the sliding traction.

I appreciate Professor Winer's comments on the effect of steady shear on the relaxation spectrum for cases where a steady shear is superimposed on an oscillatory motion in a lubricant film. In EHD contacts, the relaxation time of the lubricant in the conjunction most likely can exceed 10^{-6} to 10^{-7} sec. However, this does not necessarily mean that all relaxation phenomena associated with small-strain viscoelasticity would be eliminated because the reciprocal of the steady shear may not necessarily be as small as 10^{-6} sec.

Professor Winer's suggestion that there is a link between the limiting shear concept and the molecular degradation of polymers is worth pursuing. I endorse his plea that we should take advantage of the literature in polymer science to enhance our understanding in EHD.

Viscoelastic Effects

The comments to be answered under this heading are confined to the viscoelastic effects related to small strain. Comments on large-strain viscoelastic effects have been covered under shear-thinning effects.

The superimposition of a spin on pure rolling between a ball and two plates is certainly an elegant and ingenious method to separate the elastic shear from the viscous shear. My congratulations to Dr. Johnson for conceiving this excellent method, and we will look forward to reading a more complete coverage on this most interesting work.

Dr. Archard's alternative method in studying the small-strain viscoelastic effect by introducing an axial oscillation of the center disk of Crook's four-disk machine seems to be an extremely promising idea. If everything goes well with this venture, we should soon have some badly needed high-pressure shear modulus data available from his oscillatory rig.

Mr. Anderson calls for more intensive experimental efforts both in characterizing the non-Newtonian and viscoelastic behavior of lubricants at high pressure and high shear rates and to study the short-time transient effects. I could not agree more with his plea. It is certainly gratifying to hear that NASA's resources are directed to two very badly needed experimental programs.

I would like to make a comment on the present ball bearing dynamics computer program that uses a Newtonian model with exponential pressure-viscosity relations for the lubricant. This model is only valid if the local shear rate in the ball-race conjunction is small. Once the shear rate approaches the region corresponding to the peak traction of the EHD traction versus slip curve, the Newtonian model is inadequate; and one should employ a more realistic EHD traction model. To my knowledge, there are at least two groups trying to incorporate EHD traction in the ball bearing dynamics program. I expect before long we should have some new analytical results to correlate with future optical observations as proposed by Mr. Anderson.

I am most grateful to Mr. Kinner for calling my attention to the excellent work currently going on in Professor Hirst's group. I think the best feature of this experiment over the steady-state EHD experiments is its capability of sifting out the elastic effects of the fluid. I wonder how the value of elastic modulus deduced from this squeeze-film rig compares with that obtained by oscillatory shear experiments. The effects of film thickness and viscosity on the magnitude of the elastic effect described by Mr. Kinner seem to lend further support of the argument that viscoelastic effects increase with the Deborah number.

Transient Viscosity

I like to thank Professor Dowson for his encouraging remarks on transient viscosity. At present, there appear to be two mechanisms that could explain the loss of the effective viscosity $\left(\mu_{\mathrm{eff}}=\tau/\frac{\partial u}{\partial y}\right)$ at high rolling speeds in an EHD contact. The concept of a free-volume-dependent viscosity is only one of the approaches. The other approach used by Dyson (ref. 47) is one in which a small-strain viscoelastic model of the Maxwell type has been used to predict an effective viscosity as a function of rolling velocity for a Hertzian contact. Conceptually, these two mechanisms differ considerably because in one case the viscosity is related to free volume and in the other to shear. However, they both lead to the same trends for the effective viscosity. My belief is that these are two entirely separate mechanisms that can occur simultaneously in a high-speed EHD contact. It should be of interest if one can extend Dyson's small-strain viscoelastic analysis to include a time-dependent viscosity depending upon the free volume. I share the same feeling expressed by Mr. Anderson that more experimental evidence is needed on transient viscosity. Let us hope that his newly sponsored program will help us to clear some mysteries in this area.

I hesitate to take Dr. Johnson's measurement of an outward radial force of the ball as conclusive evidence of the absence of transient viscosity for two possible reasons. First, without knowing the exact magnitude of the local shear rate distribution in the contact, it is difficult to assess how the transient viscosity would affect the local traction. For instance, if the local shear rate falls in the region of the descending friction curve, then there will be practically no influence of transient viscosity on traction as indicated in figure 14 of the lecture. Second, the pressure distribution in an EHD conjunction is known to be asymmetric with respect to the centerline. A pronounced asymmetry would cause a net radial force acting outwardly on the ball.

EHD Film Thickness

I am fully aware that there is considerable skepticism concerning the film-thickness data measured by X-ray techniques at high loads. On the other hand, these film-thickness data appear to be the only ones available in the load range (>200 000 maximum Hertz stress), where practical rolling-element bearings operate. It would be unwise to ignore the X-ray evidence and to avoid seeking any explanation for this discrepancy between these data and EHD theories.

I am grateful to Professor Winer for calling my attention to the fact that their recent optical data for point contact have gone up to 175 000 psi, and that their data do not support the X-ray data. I regret that the significance of these data has escaped my attention because of the different representation of load parameters. It appears that the difference between optical and X-ray load exponents may be due to the following reason. Sanborn and Winer (ref. 40) showed that the minimum film in the side lobes is much lower than the center film. Gohar (ref. 39) showed that the ratio of minimum film to center film appears to decrease with load. Because one measures the exit film instead of the center film in the X-ray experiment, a close agreement between the optical center film and the X-ray exit film may not be expected at high loads.

Surface Roughness

Mr. Ku's reminder on surface roughness effects are highly welcome. In reality, surface roughness definitely has a major influence in lubrication, particularly in EHD contacts where full film is frequently a luxury because of the cost of surface finishing. Analytical understanding of surface separation and traction during an encounter between two asperities is still in its very early stage of development. Some excellent work has been initiated by Fowles (refs. 65 and 66). Once the basic mechanism between two asperities is understood, then comes the tedious task of statistical analysis for the overall performance of the entire surface, assuming that the surface can be characterized statistically using the parameters suggested by Whitehouse and Archard (ref. 67). Assuming all these analyses can be carried out successfully, one inevitably confronts next the question of surface film for which no physical properties are available. From the viewpoint of an analyst, this looks enormously complex. I am more inclined to agree with Mr. Anderson's comments to rely more on experiments for studying the surface roughness effects.

Finally, I wish to thank Mr. Derner for his interesting remarks concerning the elastic effects of the bearing-lubricant system. I assume Mr. Derner is referring to the response of the solid deformation to the sudden application of normal and tangential load. In EHD theories, one generally assumes that the solids are Hookean containing no viscous element, that the tangential displacement is negligible, and that the problem is quasi-static; i.e., the deformation is steady state with respect to the center of conjunction. For the conditions usually encountered in rolling-element bearings, all three assumptions are indeed valid. The response of solid deformation will gradually become out of phase with the imposing traction if the rolling speed is approaching the square root of the Young's modulus of the solids divided by its density. This value is approximately 2×10^5 in./sec for steel, which is very unlikely to occur in practice.

NOMENCLATURE

e_{ij} strain rate component

E' equivalent Young's modulus $=2\left(\frac{1-\nu_1^2}{E_1}+\frac{1-\nu_2^2}{E_2}\right)^{-1}$

E_1	Young's modulus of upper roller
E_2	Young's modulus of lower roller
$f_{\max}$	maximum obtainable frictional coefficient with respect to the variation of sliding speed
G	shear modulus
h_0	inlet film thickness
h^*	film thickness at which $dp/dx=0$
k	thermal conductivity of the fluid
k_0	thermal conductivity of the fluid corresponding to the inlet temperature
n	exponent used in the power-law model
p_e	entrance pressure
p_{Hz}	maximum Hertzian pressure
R	$\dfrac{R_1R_2}{R_1+R_2}$
R_1	radius of the upper roller
R_2	radius of the lower roller
t	time
T	temperature of the lubricant
T_1	surface temperature of the upper roller
T_2	surface temperature of the lower roller
T_0	inlet temperature
T_c	center-film temperature
u	velocity of the lubricant
U	rolling speed of the contact $=\dfrac{U_1+U_2}{2}$
U_1	speed of the upper roller
U_2	speed of the lower roller
W	load per unit width of the contact
$\bar{W}$	$\dfrac{W}{E'R}$
x	coordinate along the film
X	Ree-Eyring parameter
X_0	X at ambient pressure and temperature
y	coordinate across the film
α	pressure-viscosity coefficient
β	in equation (4), temperature-viscosity coefficient in equation (7), Ree-Eyring parameter in equation (14), temperature-viscosity coefficient used in $\dfrac{\mu}{\mu_0}=e^{-\beta(T-T_1)}$
γ	temperature-pressure-viscosity coefficient

γ_1	exponent in Ree-Eyring parameter
γ_2	exponent in Ree-Eyring parameter
δ	time-delay constant
λ	$\frac{\mu_0}{G}$ = relaxation time
μ	viscosity of the fluid
μ_0	viscosity at the inlet
μ_1	viscosity corresponding to T_1
σ_{ij}	stress component
τ	shear stress
τ_{max}	maximum shear stress with respect to variation of sliding speed
ϕ	equivalent viscosity function
ϕ_T	thermal reduction factor

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Mechanics and Thermodynamics in Lubrication

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It is argued that the breakdown of the lubricant film is of greater industrial importance than its formation. With straight mineral oils this occurs when the conjunction temperature reaches a critical value. The critical point is caused by desorption of the naturally occurring surface active agent and can be described by thermodynamic analysis. Langmuir's model fits the data adequately. The effect of friction polymers, atmosphere, and additive competition is discussed. The reaction kinetics of extreme-pressure action are considered. As examples of the concepts put forward, the effect of different metals in lubrication is briefly surveyed.

In contrast, breakdown in elastohydrodynamic (EHD) lubrication is difficult to predict because the behavior of the lubricant under the extreme pressures, shear rates, and temperatures inside the contact is not well understood. This problem is treated phenomenologically by studying traction. The topics considered are classical and non-Newtonian explanations, anomalous film thickness and viscosity effects, surface roughness contribution, and solidification of the lubricant. Possible reasons for the apparent granular traction characteristics are examined.

IN THIS PRESENTATION a comprehensive description of the scuffing process will be put forward. It is hoped to show that the scuffing process, the breakdown of lubrication, is quite different from the formation of the lubricant film. It is governed by different laws. Because recently almost all the pure research has been concentrated on the generation of the film, which is the province of theoretical mechanical engineers, this has resulted in relatively little research being done on the subject. Breakdown is probably of greater industrial importance than film formation.

There will be a differentiation between the discovery of the mechanism of failure and finding numbers to help the designer. The one follows from the other; but it is dangerous to produce design data using an insufficiently tested theory. A simple example can serve as illustration. It will be shown that breakdown in gears lubricated by plain oils is often caused by the thermal desorption of the polar materials in the oil, which occurs at a certain critical temperature. This constitutes the critical-desorption-temperature theory. This critical temperature is influenced by a number of things, primarily by the heat of adsorption of the lubricant on the given metal, but also by the surface roughness of the steel and the load. Therefore the value of the temperature will be different in different applications. There will not be one universal temperature that can be quoted along with the oil's viscosity grade. Hence trying to force all gears to fail at one temperature is harmful. It hinders a search for the correct mechanism of failure.

The paper therefore will describe the mechanism of failure in qualitative terms. It will indicate what must be done, and in some cases is being done, to advance to a quantitative description for the designer's benefit.

FORMATION OF THE LUBRICANT FILM

When the oil film is built up and runs at a thickness comparable with the surface roughnesses, about 5 to 10 μin., the decisive properties of the system are the bulk properties. The speed and geometry of the rubbing surfaces, and in elastohydrodynamic (EHD) contacts their bulk mechanical strengths, together with the viscosity of the lubricant, decide how thick the film is. These are all continuum properties. It is not necessary to deal with the molecular character of the system.

The determination of the viscosity is a matter that has attracted the interest of many people, and the equations governing it occupy an advanced realm of mechanics. There is a growing body of evidence to show that in concentrated contacts there may be a change of state; the treatment of its properties is also a branch of continuum mechanics. The additional feature, involved in a change of state due to pressure, is the nonsteady-state thermodynamics situation, still a bulk effect.

Once the operation of the film is known, the engineer applies this to the design of machinery. It has been for many years the complaint of lubrication engineers that the engineering world does not use existing knowledge effectively. In 1734, for instance, Jacob Rowe (ref. 1) published a booklet after having obtained patents in 1727, in which he calculated the transport industry of Britain could save £947 500 per annum by the reduction of friction in carts and carriages. But as Kelley (ref. 2) pointed out at the last symposium, savings in one sphere often bring disadvantages in another, and Rowe's ideas were never extensively applied.

Engineers remain largely unconcerned about saving money in running expenses. They are interested almost exclusively in preventing dramatic losses resulting from failure. They seem to associate the reduction of running expenses with reduction in safety margins, which naturally are unacceptable.

It is therefore to the mechanism of failure that this contribution is directed.

MECHANISM OF FAILURE

The engineer, who has been able to predict with such accuracy the oil film thickness between rubbing surfaces, would naturally imagine that the surfaces will seize or score when the film is so reduced that the roughnesses interact beyond a tolerable level. Burwell (ref. 3) in 1941 calculated the failure film thickness of a 147° partial bearing and compared it with the roughness of the surfaces using the recently developed surface roughness meters. Cameron did the same (ref. 4) for Michell pads and found that seizure occurred when the oil film thickness calculated for smooth finite pads equaled twice the total average roughness of the two surfaces. The two studies were in agreement with intuitive thoughts on failure.

These ideas were rather sharply shaken when Ibrahim and Cameron (ref. 5) studied the oil film thickness between running gear teeth. They found that the scuffing of gears had nothing to do with film thickness. The gears ran with quite a thick film and then suddenly failed. This was especially marked at high speeds. At low speeds the normal process was followed: the film thickness reached zero and the gears scuffed. Figure 1 (redrawn from fig. 20.9 of ref. 5) makes the two types of failure quite clear. The film thickness is measured in volts, a method that had been quite heavily criticized (ref. 6) but recently vindicated (ref. 7). It will be noticed that the 1350-rpm line gives a thicker film than the 135-rpm one but scuffs much sooner. A similar finding, that scuffing of disks is independent of film thickness, has been described by Kelley and Lemanski (ref. 8), but consideration of it will be reserved till later.

The most obvious explanation of these results was that even though the gear teeth were separated by a considerable measured oil film, there was sporadic short circuiting of the electrical system used to determine the film thickness, evidence of intermittent metal-to-metal contact; i.e., random touching of asperities. If at some critical condition, as yet undeter-

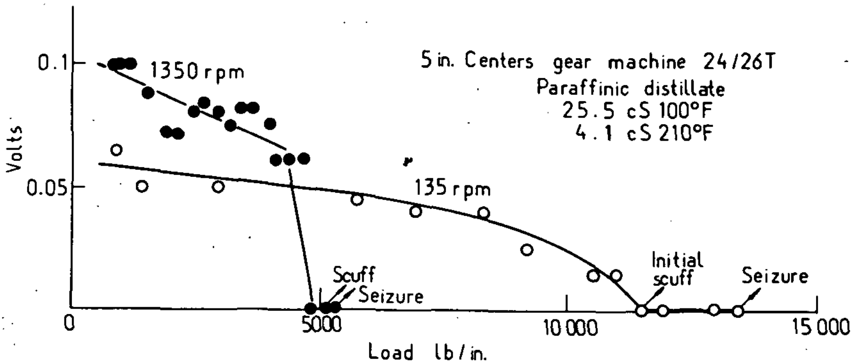

FIGURE 1.—Breakdown of lubrication in gears.

mined, the lubricating quality of the oil completely vanished, then the gears would scuff. This would be independent of the film thickness, providing, of course, the film was not so large and thick that there was no intermittent asperity contact and breakthrough. The description and evaluation of this critical condition is discussed next.

Breakdown of Lubricity

If the preceding analysis is correct, then the problem is to find what makes the oil cease lubricating. It is generally assumed that temperature plays a large part in the process. It was shown quite early by Bowden (ref. 9) that there was a change from smooth sliding to stick slip. A further great boost to this concept was provided by Blok's analysis (ref. 10) of the flash temperature produced in gear contacts.

If the effect of temperature on oils is in fact paramount, then it should be possible to study it in a slow-speed machine without needing to generate the temperature in fast-running (and complex) equipment. Such an apparatus could run in an oven or on a heated platen instead of generating the heat by frictional heating. The variation of slow-speed friction with temperature was first studied (as far as can be found) by Hardy (ref. 11) in 1920. He showed that for a mineral oil sliding on steel there is a rise of friction at about 60° C. A similar result was given by Tabor in 1941 (ref. 12).

A more important effect is a dramatic rise at 150° C, which was found by Khrushchov and Matveevsky (ref. 13). They showed that one apparent feature of mineral oils is that they cease to lubricate at about 150° C. It is surprising that this phenomenon has not been studied more extensively. Whatever other factors may overlay it, this effect must play such an important role in lubrication that it should be evaluated.

The effect itself is similar to the change from smooth sliding to stick slip that was studied so extensively by Bowden in the 1930's. It must be admitted that the very high hopes raised at that time of an increase in performance by the addition of a small amount of surfactant were not found in practice. The effect of 0.1 percent stearic acid added to a neutral white oil was dramatic at room temperature, but at operating temperatures performance was not improved at all. Frewing (ref. 14) in 1940 showed that the transition temperature at which smooth sliding changed to stick slip was a function of the concentration of surfactant. Using the standard plot of the logarithm of the concentration against the reciprocal of the absolute transition temperature resulted in a straight line. Analyzing this with the help of the van't Hoff isochore, he found the heat of adsorption of the 22 surfactants he used.

The fact that the transition temperature with even 1 percent of surfactant was so low, considerably less than 100° C, militated against the application of this concept in lubrication. Furthermore, Bristow (ref. 15) in

1947 showed that the change from smooth sliding to stick slip was very much influenced by the design of the test apparatus itself. The elasticity of the mounting and the sliding velocity of the frictional pair all affected the transition. These findings probably made people believe that this whole approach had no significance for practical systems.

The realization that the higher the molecular weight, the higher the transition temperature of the surfactant, and that mineral oil contains some $\frac{1}{2}$ percent of a very active surfactant (previously described by Groszek and Palmer (ref. 16)) led Askwith, Crouch, and Cameron (ref. 17) to suggest that the 150° C transition found by Matveevsky was due to the desorption of this natural material. This supposition was subsequently proved by Grew and Cameron (ref. 18).

What in effect was postulated is that, as the temperature is raised, the concentration of surface active materials adsorbed on the surface is steadily lowered. This concentration is a statistical affair. Molecules come and go, but at any one instant a certain fraction of the surface is covered. A model of the process has to be put forward to enable an equation to be derived to describe it, and the Langmuir model gives a useful insight into the mechanism.

The equation (ref. 17) that emerges is

$$-\frac{\Delta H^\circ}{T}+\Delta S^\circ=R\left[\ln\frac{\theta}{(1-\theta)}-\ln C\right]$$

where

ΔH° = change heat of adsorption
ΔS° = entropy change
θ = fractional coverage
$\theta/(1-\theta)$ = ratio of covered to uncovered sites
R = gas constant
T = absolute temperature (here the temperature at which θ becomes critical)
C = concentration of material in solution

Hence if log C is plotted against $1/T$, the slope gives ΔH, the heat of adsorption, and the intercept is $\{\Delta S^\circ/R-\ln\theta/(1-\theta)\}$. The variables ΔS° and θ cannot both be determined from this plot. To achieve this adsorption, studies were carried out using stainless steel powder and hexadecylamine in a hydrocarbon solvent, at a series of fixed temperatures, which is the same system used in the friction tests. From the isotherm the variation of coverage as a function of temperature is found. At 50 percent coverage the heat of adsorption is equal to the value found by the Bowden machine and is the subject of a paper (ref. 19). What is helpful is that θ occurs as a logarithm, and over quite a large range, in fact from $0.1 \leqslant \theta \leqslant 0.9$, the expression $\ln\{\theta/(1-\theta)\}$ can be approximated by $5(\theta-\frac{1}{2})$ to within 0.1

unit. As ΔS is of the order of 30 cal/°C or so, this is accurate enough. The main concern is that θ does not approach zero or unity too closely. This has fortunately been ruled out by the direct adsorption measurements. One result that has not yet been fitted into the theory is the effect of load, and another is that of surface finish.

To measure the critical temperature discussed here, we use a Bowden-Leben machine, while Matveevsky has a slow-running four-ball machine in an oven. The critical temperature is usually defined as the rapid increase of friction at a given temperature. It has been found that this temperature varies with load. In these tests, using cetyl amine or stearic acid as the additive and a ½-in. stainless steel ball loaded against a flat heated plate as the friction pair, the transition temperature drops about 4° C for every pound load on the ball. The results for various loads are displayed in figure 2, taken from (ref. 19), which is the standard log concentration versus reciprocal transition temperature plot. It is seen that the slope, which corresponds to the heat of adsorption, is unaltered; the lines move to the right as the load is increased. This means the load squeezes the adsorbed chains flat and in so doing provides additional energy to the system. The temperature needed to displace the chains is therefore less. The thermodynamics has been discussed by Adamson (ref. 20), though he applied it to a slightly different model. This work also uncovered the interesting fact that surface roughness plays a not inconsiderable role in the temperature at which the friction increases. It has of course been known for a long time that in some pieces of machinery, e.g., piston pumps, the bore could be finished too finely. It was usually thought that this had to do with the provision of micro oil reservoirs. These boundary friction studies and their thermodynamic analysis show that roughness can have an effect capable of description in terms of surface energies.

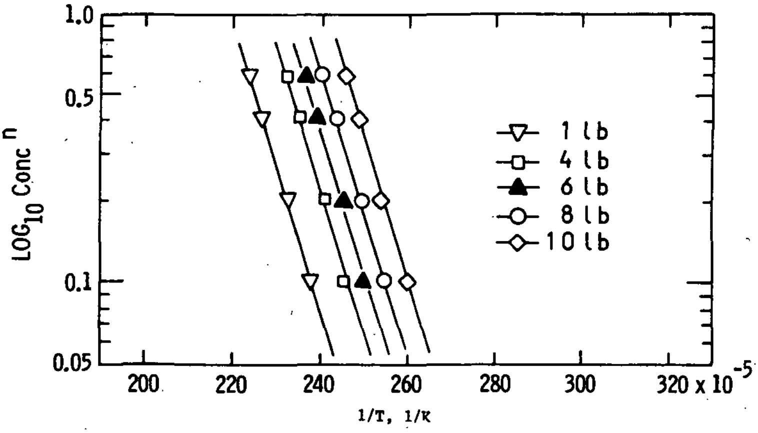

FIGURE 2.—Variation of critical temperature with load.

This double variation with surface finish and with load makes it difficult to apply immediately results from slow-speed tests to real systems, though some notable successes have been achieved that will be discussed later.

The purpose of such basic work is to discover the underlying processes of lubrication and of failure and then to see how they can be applied in practice.[1]

Pure Liquids

One other feature of this analysis is that it only treats lubricants containing polar additives. The Langmuir equation deals with the concentration of surfactant in solution, and the $\Delta H°$ and $\Delta S°$ are the changes in heat of adsorption and entropy when 1 g-mol of additive goes from the surface and into solution.

If a pure lubricant such as pure kerosene or pure mineral oil (i.e., with all surfactants removed) is used, there is clearly no adsorption of the liquid on the surface. The technique at the moment is not able to deal with this situation. Such a defect is all the more regrettable as pure synthetic lubricants are coming more and more in use, and it would be very useful if their heats of adsorption could be found by such simple means as measuring transition temperatures. Various ideas are being tried and perhaps may be useful in the future. On the other hand, the normal operating temperature of such synthetics is generally so high, about 200° C and higher, that anything adsorbed onto the surface will have vanished long ago.

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[1] This work by J. P. Sharma and A. Cameron was presented at the Amer. Soc. Mech. Eng.-Amer. Soc. Lubric. Eng. Lubric. Conf. (New York), Oct. 1972.

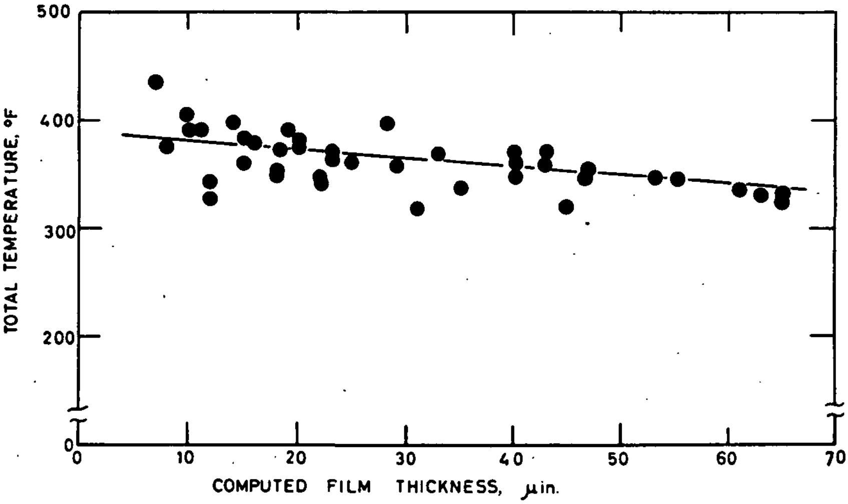


Figure 3.—Independence of critical temperature with oil film thickness.

Application of the Critical-Temperature Concept

Kelley and Lemanski (ref. 8) showed that on a disk machine the surfaces scuffed when total conjunction temperature reached 200° C. This value was independent of film thickness over a considerable range, from 8 to 64 μin. This is given in figure 3, which has been redrawn from the original publication. The temperature, which is made up of skin temperature plus Blok's temperature flash, drops somewhat with increasing film thickness. This may be as much the method of calculation as anything else and cannot necessarily be taken as being of significance.

Unfortunately, the critical temperature of Kelley and Lemanski's oils were not measured. O'Donoghue, Manton, and Askwith (ref. 21) analyzed some casehardened disk scuffing tests described by Thomas and Ali (ref. 22) and also measured the critical temperature of the oil used in a 20-rpm machine using stainless steel disks. The critical temperatures found were very close indeed to the temperatures calculated from Thomas and Ali's results. The agreement was impressive. In many cases, such as Kelley's, O'Donoghue's, and the data analyzed by Blok (ref. 23) in the last symposium, the scuffing temperature is indeed constant, but other work has shown that it varies. This was pointed out by Dyson in his contribution to the discussion of Blok's paper (ref. 23). It seems certain that desorption must play a dominant role in scuffing. After all, if the coefficient of friction doubles at one particular temperature, it must have a very considerable influence on the running of the machine in question. The desorption can be masked by other effects, which are considered next.

Friction Polymer

It has been shown by Fein and Kreuz (refs. 24 and 25) in a series of very elegant papers that if a particular sequence of running in is followed, a type of varnish forms on the surface of the disks. They called this material friction polymer and studied its properties at some length.

They have shown that when it is generated, a coherent layer of plastic forms on the surfaces, which therefore do not scuff.

The formation process of this polymer seems clear enough. When the steel surfaces wear, fresh nascent iron is exposed. Such a material is extremely active chemically, and it is able to make the oil molecules polymerize. The polymerized material then attaches itself to the iron surface where it acts as a solid lubricant. An adherent layer of this type is presumably impervious to the desorption process described above. If this friction polymer is formed in sufficient quantities, the desorption mechanism advanced earlier will be overlain by it and scuffing will therefore no longer be governed by the transition temperature. The formation of this friction polymer would seem to depend on the production of suitably active wear particles; i.e., of the active iron that enables the process to proceed.

What has not yet been settled is the limits of the operation of polymer formation. A great many gear tests certainly indicate that a critical temperature is a limit of about 180° C that can be passed only with great caution (or with extreme-pressure (EP) additives), so its protective action is difficult to assess.

This is not to decry in any way the existence or importance of the friction polymer. The excellent work of Fein precludes such a course of action. It, however, would be valuable to know how far it can be counted on to increase the load-carrying capacity of any given system.

Effect of Atmosphere

Allied to friction polymer is the extremely interesting series of papers from Appeldoorn and colleagues (ref. 26), which started with the finding that a number of mechanisms worked better in an atmosphere of pure dry nitrogen than in air. It was generally thought that some oxygen was needed for good lubrication.

A reasonable explanation of this new finding is that during the wearing process, nascent metal is formed. The metal will react with the lubricant itself if there is no oxygen available. Should there be oxygen present, it will get there first and form an oxide. This also explains, or partially explains, the variation of base stock response. Paraffinic oils were affected far more than aromatics, while there was a very considerable synergistic effect when the two were mixed.

Paraffin chains are far more easily broken than aromatic rings. Thus the nascent metal will react much more readily with lubricant having long chains and form a reacted layer, an embryo friction polymer. Aromatics, on the other hand, are very chemically stable and so will not react.

The cause of the mixture of the two behaving so very well is a puzzle. It could possibly be that the aromatic rings provide the bonding conditions for the aliphatic bonds to break and re-form on the surface more easily than they do on their own.

These examples show the importance of the surface. It is reasonable to suppose, though no evidence has been published on the subject, that as the metal acts as a catalyst, the type of metal and its crystal structure will play an important role in this process. It is strange that there is so little work done on the influence of metal type on lubricated sliding. It is possible that metallurgists often understand engineering and hence friction; but only very few appreciate organic chemicals and the reactions caused by lubricated metal surfaces in frictional disciplinary studies.

Extreme-Pressure Action

Once the adsorbed film has broken down and the various polymer layers have worn away or ceased to be effective, the surfaces are then chemically clean and will scuff. It may be surprising to talk about metals immersed in oil being chemically clean. At the desorption temperature the surface coverage by adsorbed molecules falls below the critical point and unless a layer of some other more adherent material can then be interposed between the rubbing metals, they will seize together. It is in the sense that they will seize unless they are protected that the surfaces behave as though they are chemically clean.

The protection most readily provided is to add to the oil an active chemical that forms a chemically bonded layer on the surface. This layer keeps the surfaces apart and prevents seizure. Classically the active agents form sulfide or chloride compounds with steel. Originally they were formed by heating a fatty oil and blowing in chlorine. Since then, their chemistry has become a little more sedate. A further series of compounds are phosphates, tricresyl phosphate being an early member of this class. The phosphates are puzzling because the mechanism of their action is almost entirely unknown.

There are two main functions of EP agents. One is to prevent wear, and the other to prevent seizure while accepting a relatively high rate of wear.

There are a number of points of interest about these extremely widely used compounds that will be discussed later. The most impressive, however, is that there is a very large amount of empirical practical knowledge about the knowledge of them but almost nothing at all is known, or at any rate published, of their detailed mechanism. They are assumed to act by chemical attack; their reaction kinetics should therefore be amenable to standard analysis, but if this is so, no one has studied it or published anything on them.

First an interesting phenomenon that occurs when surfactants and EP additives are mixed will be described.

Additive Competition

There have been many examples in the Lubrication Laboratory at Imperial College of the phenomenon known as additive competition between surface active agents and EP additives (ref. 27). This can be explained by the postulate that the surfactants get to the surface faster than the EP agents. Once there they prevent them from forming a chemically bonded layer. As soon as the temperature increases and the surfactant gets desorbed, the EP agent is able to get in and perform its office of laying down a chemically bonded layer. This phenomenon has been noted in the additive response of back axle oils in service (ref. 28). Their EP agent is depressed by the addition of dispersants. It is also noticed in the commonly reported comment that sulfides do not start their action till the temperature is raised to 150° C. This is partly the desorption temperature of the surfactant naturally occurring in mineral oil. It seems reasonable to suppose the surfactant keeps the sulfide away till it is desorbed. The detailed action of this competition is not quite clear. What is not obvious is why it is necessary to reach the desorption temperature, which our work seems to show occurs when about 50 percent of the possible desorption sites are uncovered, before the sulfide can react. One would have thought that as physical adsorption is a dynamic affair with molecules coming and going, enough of the surface would be free for the sulfide to react. The answer may lie in the fact that the residence time of surfactants at about 150° C is in the order of microseconds, while the reaction time of EP agents in the contact zone is in milliseconds, so the surfactant always gets there first.

The material naturally occurring in mineral oils, which confers lubricity to oil, behaves both as a physically adsorbed oiliness agent as well as an EP agent. Below 150° C it is adsorbed physically, but at the physical desorption temperature it apparently changes over and becomes chemisorbed. This is no doubt how EP agents of the sulfurized or chlorinated sperm oil type work. They are physisorbed to begin with at low temperatures and then become chemisorbed at the physical desorption temperature.

Four-Ball Machine

This is one of the oldest of the EP testers, but its mode of action is still very much a mystery. When the wear scar diameter is plotted against load on a log-log scale, two straight lines are usually found with mild EP agents, as shown in figure 4, taken from Fein (ref. 25). Both lines have slopes of 1/3 as elastic theory predicts, but the lower line, the wear line, is usually above the theoretical. The reason for this is not at all easy to explain. The fact that diameter is proportional to $W^{1/3}$ is evidence of elastic behavior, but why is the proportionality constant larger than it should be? Some few comments were made in reference 17 where the scar

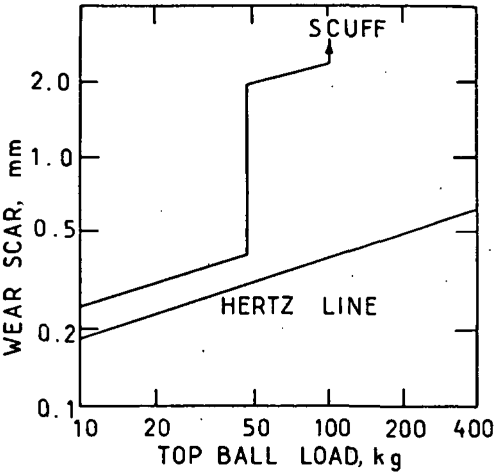


FIGURE 4.—Two zones of four-ball wear track.

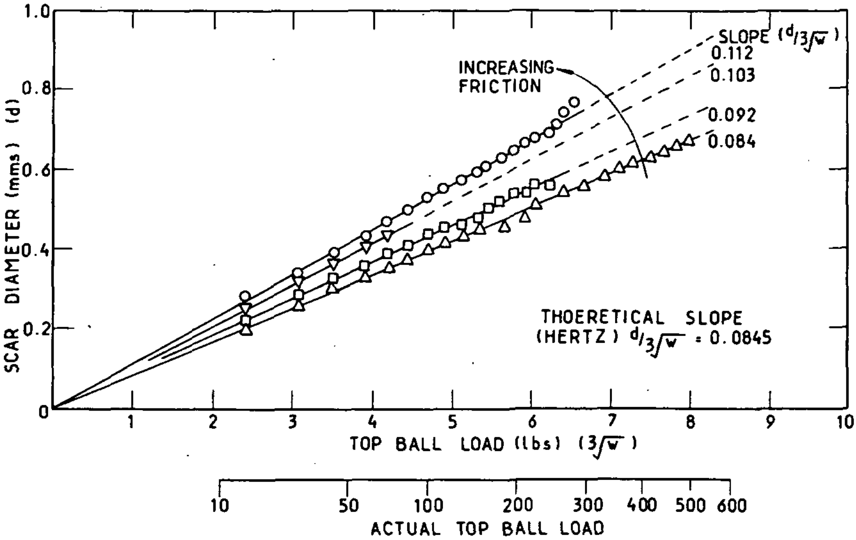


Figure 5.—Wear scar diameter as a function of the cube root of the load for different conditions.

diameters of a medium-speed four-ball machine (200 rpm, 1-in.-diameter balls) were given. Straight lines were found when scar diameter was plotted against $(\text{load})^{1/3}$. Their slope increased with increasing friction (fig. 5). It was only at the very lowest friction ($f=0.04$) that theory and measurement coincided. The suggestion was made that the greater the friction, the larger the wear debris and hence the wider the wear scar. No other reason was forthcoming.

Furthermore, no explanation has been seen why the two regimes shown in figure 4, the antiwear and antiscore sections, exist. Could it be that the antiwear zone is lubricated by a physisorbed film that is desorbed when the contact temperature reaches a critical value? The antiscore zone could be the region, above the desorption temperature, where the surfaces are chemically clean and the EP additive attacks the surface between successive contacts.

Extreme-Pressure Reaction Kinetics

As far as is known, there has been no study in the reaction kinetics of EP agents. One question typical of many concerns the four-ball machine with an oil containing an EP agent such as sulfur. How many layers of sulfide or how many fractions of layers formed between contacts? Does the EP agent attack the surface during the contact or between successive contacts? In our laboratory we are attempting to answer this by studying the reaction rate of *dibenzyl disulfide* in a four-ball machine. Barcroft (ref. 29) used a hot wire device to measure the reaction rates of *dibenzyl disulfide* and iron. It is hoped to apply this to the four-ball machine. At the time of writing, no conclusion has been reached, but if all goes well some results should be available for the symposium.

The need for knowledge of EP reaction kinetics becomes very clear as soon as one tries to tailor an EP additive for advanced lubrication systems. They all seem to rely on exotic metals and demand equally exotic high-temperature lubricants. If one knew what was needed in the way of layers of reacted materials for successful EP action in simple well-known systems, such as sulfur on hard steel, it would make one's job much easier with a new synthetic fluid and newly developed alloy.

Metallurgy

Every engineer knows that some metals are compatible and some are not. No one has yet been able to find out why. Clearly a three-component system must be considered: metal-oil-metal. An extremely promising start on metal-metal compatibility has been made by Buckley (ref. 30) using some very elegant crystallographic techniques. The task here is to consider lubricated compatibility. Matveevsky (ref. 31) has published some very important studies on the critical temperature of copper alloys. Figure 6 shows clearly that the effect of a small amount of tin causes a rise of 30° C in the transition temperature of pure copper. The beneficial part played by tin is, of course, well known in practice. The fact that aluminium bronze and silicon bronze are worse than tin bronze is also fully appreciated in the worm-gearing industry.

These findings are presumably explained by the effect of physisorption. The full thermodynamic relationships between lubricants and alloys have not yet been discovered.

Using the Langmuir model, ΔH° and ΔS°, the steady-state heat of adsorption and entropy for any given alloy and system can be found. As stated earlier it is possible to evaluate only additives because ΔH° and ΔS° cannot be obtained for pure fluids using the transition temperature method. For mineral oils this is not so serious, as it is the naturally occurring additive that is the important factor in the lubricity of oil anyway. This material is comparatively easy to extract from mineral oil, and so all the thermodynamics are carried out using it.

This desorption mechanism accounts for the lubricating quality of straight oils, without EP additives and a given metal-metal pair, while the chemical reactivity is, of course, of paramount importance at the stage after the surfactants desorb.

This was shown (ref. 32) during the checking of Matveevsky's data, which showed a very sharp critical temperature. All the results were similar to the lower curve of figure 7. Everything that could be thought of was done to achieve the sharp change found in Moscow. Eventually it was achieved by the use of stainless steel instead of the tool steel that had been tested till then.

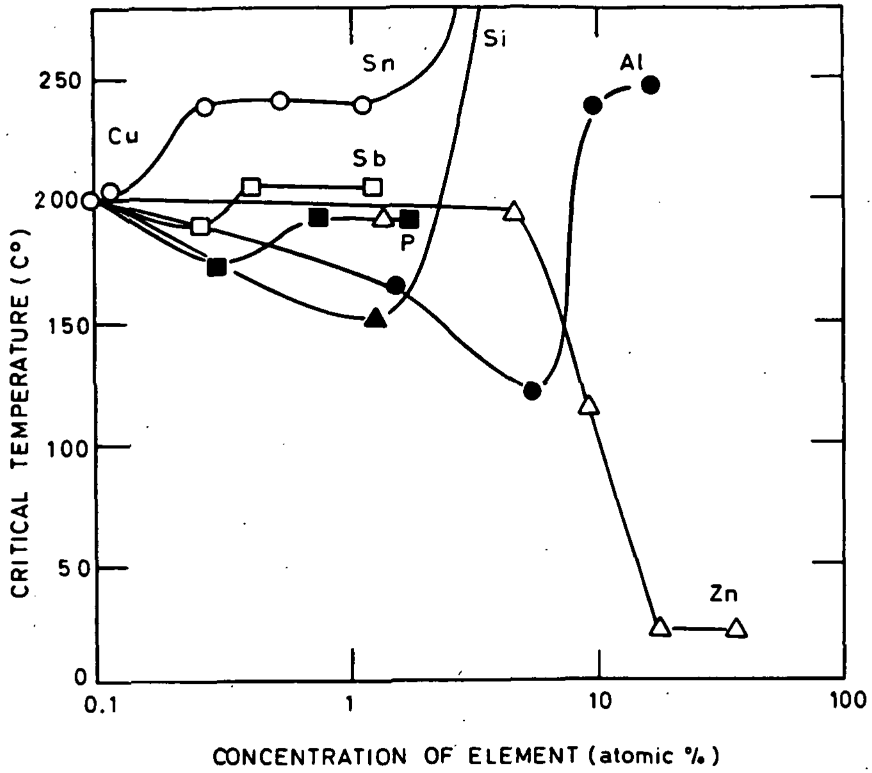


Figure 6.—Critical temperature of copper alloys.

Different alloys will respond to EP materials differently. This has been known in general terms for many years. No supplier or user of EP additives, however, is quite certain of the exact mechanism. There is a very large effect when a given steel is largely austenitic rather than martensitic. How large is open to question. Our laboratory has recently been involved in the question of scuffing of diesel piston rings. It is not known how chromium plating alters the action of an EP additive originally developed for steel. As far as can be found, no one has made (or published) any studies of the kinetics of these effects.

Another question one would like answered is what the factors are that cause sulfur compounds to break down. Is it that under extreme conditions of speed, the iron sulfide does not have time to re-form in between contacts? On the other hand, could it be that the surface or track gets so hot that the iron sulfide melts. Or is it that at these temperatures it yields plastically, and it is so expelled by pressure?

It would seem clear that some more work should be done on the reaction kinetics of EP film formation using steels of known composition and heat

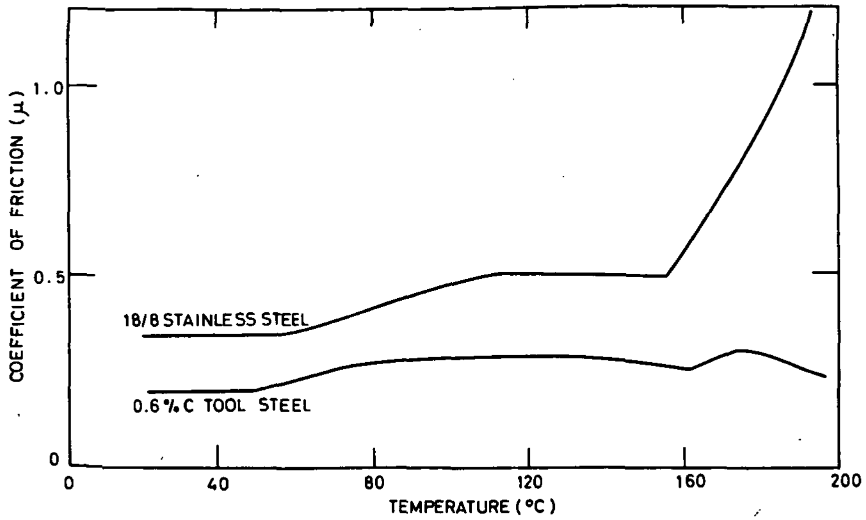


FIGURE 7.—Friction versus temperature plots for stainless and tool steels.

treatment. This would put the subject on a much safer footing in a quite simple way.

In this paper, sulfur or chlorine additives have been talked about, yet it is realized that phosphorus compounds are most important commercially. These have not yet been mentioned because no one knows how they act. Each time a paper appears on this subject, it normally starts by indicating how all the previous publications were in error. In the following discussions, the same previous authors return the compliment. In this branch of the subject one cannot plead for more work clarifying a known system. It needs the discovery of some as yet unrecognized mechanism. Is it too much to hope that the additive manufacturers and oil companies, who are surely replete with brilliant theoretical chemists, would allow one or more of them to do some speculative research to elucidate this very elusive problem?

Conclusion

In conclusion, one can say that, except for phosphorus compounds, the main outlines of the action of boundary and EP agents is tolerably clear. What is needed is some careful detailed work applying known physicochemical laws to known systems using wherever possible pure or at least well-characterized materials. It is only by doing this and thoroughly understanding the processes that go on in thin or marginally lubricated systems that progress will be made. It should then be possible to measure lubricant properties in the laboratory with precise apparatus and apply the results so found to actual machinery. It seems rather unreal that the whole industrial world runs on lubricants whose detailed action no one has yet bothered to put on a sure numerical basis.

ELASTOHYDRODYNAMIC BEHAVIOR

In contrast, the subject of EHD lubrication is described very well mathematically in general, even in some cases where the qualitative treatment is hard to believe. A good example of this is the agreement between theory and experimental measurements of Westlake (ref. 33) on films of as little as 200-Å thickness. This represents only a few molecular dimensions and so the success of continuum mechanics is somewhat surprising. Discrepancies do exist, however, between the classical predicted film thicknesses, such as those of Dowson and Higginson (ref. 34) and the experimental values in some situations, but these have largely been resolved. The most difficult to treat was the problem of viscoelasticity. No lubricant can respond instantaneously to the enormous pressure it meets on passing through an EHD contact, and a certain amount of time is necessary for the fluid molecules to rearrange themselves to the applied pressure. This relaxation time is generally about 10^{-12} sec for most lubricants and so they can experience the full pressure during their stay in the contact (usually 10^{-2} to 10^{-4} sec). For some special lubricants such as silicones, the time needed to respond to the pressure is much greater and so the lubricant entering the contact barely starts to feel the applied pressure before it abruptly leaves the contact. Consequently, the viscosity of the lubricant does not reach to full expectation, and the film thickness is lower than the classical prediction. This explanation has been put on a firm mathematical basis by Dyson (ref. 35), and it is now possible to compensate for these viscoelastic effects to a fair degree of accuracy, although precise calculations are hindered by the lack of data on lubricants at EHD conditions.

A second major point of discrepancy was found under conditions involving sliding of the bearing elements in addition to the rolling. In the extreme case of the elements traveling in opposite directions, there was a full oil film where classical theory predicted there to be none at all. Fortunately, this had already been described by Cameron (ref. 36), who showed that the thermal imbalance across such a contact produced an additional lubricating action that is predominant in cases of large sliding. This action has been treated mathematically by Dyson and Wilson (ref. 37), who have obtained once again a fair agreement with experiment. Happily, this additional form of lubrication need not be considered in most practical situations, even for 100 percent sliding (i.e., one element stationary).

EHD film formation theory can therefore predict to a fair degree of accuracy the size of the lubricant film in the contact and shows that these films persist even for viscoelastic situations, large amounts of sliding, or down to molecular dimensions. However, this good agreement is of little use in a treatment of the breakdown of the oil film and the onset of scuffing.

Behavior Inside the Conjunction

The purpose of this section of the paper is to look for a mechanism as a result of which the film would collapse under certain conditions to failure, rather than be involved in the steady random interaction of asperities. Breakdown occurs inside the contact region, whereas the generation of the film is governed almost entirely by the inlet region, which is outside the Hertzian zone. EHD theory therefore tells us little about the nature of the lubrication inside the contact because this is largely irrelevant to the film formation. Once the lubricant is inside the contact it is difficult for it to leak out except at the normal exit, and so the film thickness is maintained no matter what properties the lubricant shows.

This is illustrated well by the work of Jacobson (ref. 38), who considered the effect on film thickness of solidification of a mineral oil. Having measured the freezing point and yield strength of the oil statically at the appropriate pressure, Jacobson assumed there was time for the oil to solidify in the Hertz zone and obtained excellent agreement for film thickness predictions and measurements.

Jacobson's work highlights the fact that to study the lubricant inside the contact, we must examine some aspect of lubrication that depends on the contact itself and not on the inlet zone. The obvious choice is the traction force caused by sliding, as this is transmitted over the Hertz region. We cannot study the lubricant directly in bulk because the EHD conditions of high transient pressure and high shear rate are difficult to reproduce elsewhere, and so a phenomenonological approach is required. The nature of the lubricant must be deduced from its traction characteristics before we can predict a breakdown.

The Traction Behavior

The first thing to note is that the traction transmission in EHD contacts cannot be explained satisfactorily either quantitatively or qualitatively by classical Newtonian theory. Various attempts have been made at this along the lines of Crook (ref. 39) and most conclusively by Johnson and Cameron (ref. 40). The general feeling is that force transmission obeying Newton's law of viscosity is not an adequate model, even including thermal effects. For very low sliding speeds, some quantitative agreement has recently been found by ten Naple, Moes, and Bosma (ref. 41), but the qualitative agreement even here is still poor. The main points of disagreement can best be considered by looking at a typical set of traction results (fig. 8). The features of this family of curves are as follows:

(1) Results at different rolling speeds $\bar{u}=\frac{1}{2}(u_1+u_2)$ and varying sliding speeds (u_1-u_2) can largely be condensed to single curves by plotting the traction coefficient against the slide-to-roll ratio

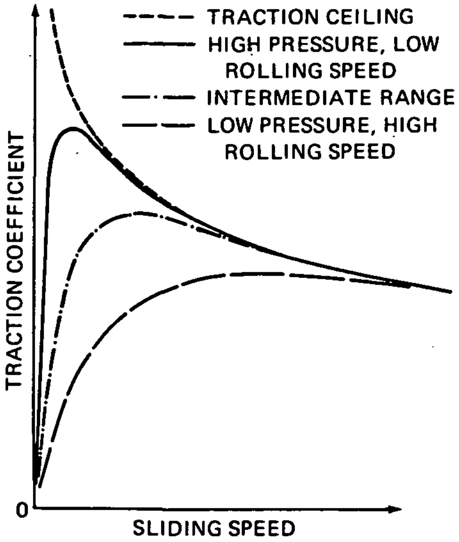


FIGURE 8.—Typical traction results.

$$\Sigma=(u_1-u_2)/\tfrac{1}{2}(u_1+u_2)$$

particularly near the origin, where there is a region of linear proportionality.

(2) At conditions of high pressure and low temperature, the curves exhibit a strong peak, whereas at lower pressure and higher temperature they reach a plateau region.

(3) There is a traction ceiling approached by all curves except at very high temperature.

Newtonian theory has been able to indicate the existence of the peaks or plateaus by introducing the effects of frictional heating, but has not succeeded in offering any explanation of the other two features. In addition, the absolute height of the traction peaks predicted has been far too large. Overall, this leads to the conclusion that Newton's theory of viscous traction is not valid under these conditions, that something unusual must be occurring in the lubricant inside the contact to make its properties completely different from normal.

A number of ideas have been put forward as alternatives to the Newtonian concepts. Not surprisingly, the idea of viscoelasticity has been introduced because it has been shown to be fairly important in certain circumstances even for the film formation in the inlet region. Dyson (ref. 42) has shown that the best way to treat this rheological behavior is in terms of the Barlow-Lamb liquid model, as opposed to the earlier and somewhat simpler Maxwell model. Both methods combine the viscous properties of a Newtonian fluid with the elastic properties of a Hookean solid, and they differ mainly in the choice of parameters involved in the combination. In both cases it is the shear rate in the lubricant that is the controlling feature when compared against some relaxation time. The familiar example used to illustrate this is the case of pitch, which will flow on a long time scale but can be shattered by a hammer blow. Once again the unique conditions of EHD lubrication prove to be a great obstacle, however, because the Barlow-Lamb model applies to oscillatory shearing, not continuous shearing as in a sliding contact and there seems to be no independent method of obtaining viscoelastic data for an EHD application. Nevertheless, by making certain assumptions, Dyson was somewhat successful. He showed that a traction peak could be predicted, that a fall in apparent viscosity over the whole contact with rolling speed was predicted, and that a fall in α, the pressure-viscosity coefficient, could be expected at high pressure. This was indeed found from the results of Johnson and Cameron (ref. 40) in figure 9. The success was only limited, however, when examined in greater detail. Consider this apparent viscosity of the contact defined in a Newtonian manner:

$$\eta_{\text{apparent}}=\frac{h}{u_1-u_2}\,\frac{T}{2a}$$

where $2a$ is the contact width, h is the film thickness, and T is the traction force. But at the origin, the slope $T\bar{u}/(u_1-u_2)=C$ (a constant) and since $h\sim\bar{u}^{0.7}$, it follows that

$$\eta_{\text{apparent}}\sim\frac{1}{\bar{u}^{0.3}}$$

In other words, this fall in apparent viscosity with rolling speed is the same for all fluids, since the linear region has been found by Gentle (ref. 43) for many lubricants. This conclusion cannot be explained by viscoelastic

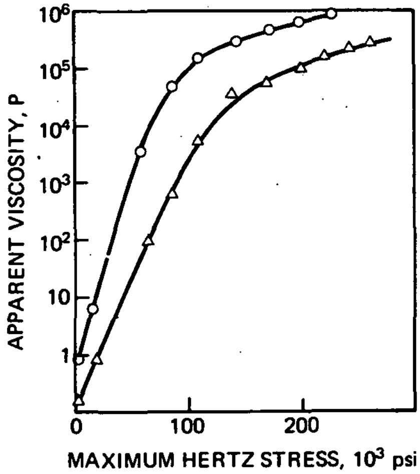


FIGURE 9.—Apparent viscosity versus pressure relationship from Johnson and Cameron's results.

theory, which recognizes wide variation in rheological behavior from fluid to fluid, and indeed it seems implausible. It can only mean that the traction force cannot be obtained from an expression of this form even when variable viscosity is introduced, and the force must be truly independent of the film thickness.

Another point against the viscoelastic formulation is that the fall in the α value predicted at high shear rates because of the fluid's inability to respond to the EHD conditions has also been found by Paul (ref. 44), using a low-shear-rate viscometer. It would seem fairly reasonable to assume from this that the lubricant actually undergoes a physical change at a sufficiently high pressure, not just a saturation of its viscosity under the EHD conditions. This approach was suggested by Smith (ref. 45), followed up by Plint (ref. 46) and Johnson and Cameron (ref. 40), and is now known as the plastic shear plane hypothesis. In principle, it considers the lubricant as behaving more like a Bingham solid, which exhibits elastic properties up to some critical shear stress at which it fractures and flows plastically. The advantages of this idea are immediately apparent as it explains easily the traction peak, which is associated with the rupture of the film, and the traction ceiling, which would relate to the critical shear stress, once frictional heating was taken into account. However, once again there are important drawbacks. First, the independence of traction and film thickness before the rupture occurs cannot be explained; second, the idea of a sudden transition at the point of rupture cannot be reconciled with the continuous curves approaching the traction ceiling at low pressure or high temperature. Plint's method of semilogarithmic plotting to highlight the transition in his results fails to give any indication of a sudden rupture of the film in other workers' results at lower pressures.

The Phenomenological Approach

None of the concepts so far introduced totally meets the experimental facts either qualitatively or quantitatively, so we are no nearer in our search for the true nature of lubricant inside the contact, the fact needed for a description of film failure and scuffing. Could it be that we have overlooked the possibility that the traction is apparently so largely independent of the fluid film simply because it is transmitted by some other mechanism such as asperity contact. A quick examination shows there to be many points in favor of this idea, particularly the fact that the traction curves at low pressure reach a plateau region in an exponential manner. This typically suggests a statistical kind of behavior as though the transmission of the force was caused by discrete events occurring in greater and greater numbers as the slide-to-roll ratio increases, until it reaches a steady-state value. The most obvious explanation of such a phenomenon is that the surface roughness asperities are transmitting most of the traction. To understand this easily, consider the analogy between these asperities and the bristles on a brush. Suppose two brushes are held at a fixed distance apart facing each other so that the two sets of bristles are meshed, but not touching the opposing brush base (fig. 10). If one brush is then moved parallel to the other to simulate sliding of the bearing surfaces, then the force is transmitted between them as a result of individual pairs of bristles colliding. The size of the force depends on the number of bristle collisions per unit time. When there is no relative motion of the brushes there is no force because there are no collisions, and when there is considerable sliding the force is at a steady value. For conditions in between, the force increases with increased sliding.

But the effect also depends on the time during which the brush bristles are observed. If observed for a long time, the collisions are seen to occur at an average, steady rate. However, if the observation is performed for very small intervals, then there is a chance that no collisions will be seen and therefore for that small time the force will be truly 0. By analogy, the traction in an EHD contact, if caused by surface roughness asperities, would tend to 0 for low sliding speeds or small observation times; i.e., high rolling speeds. Traction would depend therefore statistically on the slide-to-roll ratio and would vary little according to the nature of the fluid in the contact since this would be largely irrelevant. Both of these predictions are experimental facts, but as always there are drawbacks.

The weight of experimental evidence concerning surface roughness and traction, such as that of Jefferis and Johnson (ref. 47), leads to the conclusion that little force is transmitted by the asperities. In addition, the quite considerable stresses involved in EHD contacts would cause appreciable scuffing of the surfaces if caused by asperities because presumably these contacting peaks of the roughness could not spring back like the bristles, but would tend to be torn from the surface. An additional point that has not been mentioned much previously is that out of all the

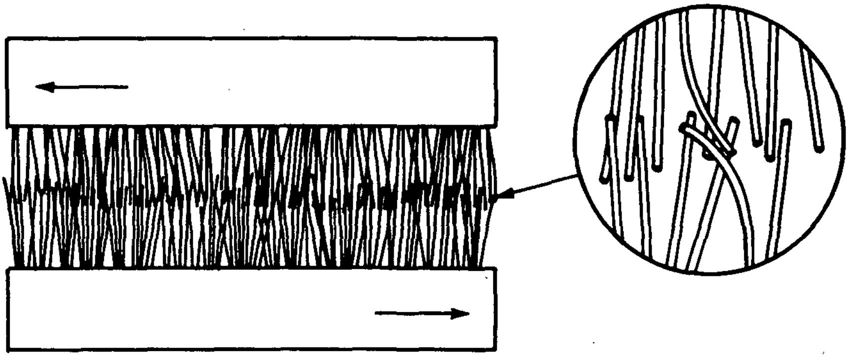


FIGURE 10.—Statistical nature of force transmission in brush bristles.

optical work carried out on EHD contacts, there has been no observation of surface roughness inside the Hertz region. Many people believe that this is not just caused by lack of resolution in the optical system but that the asperities are actually flattened under the enormous pressure of the lubricant in the contact. Measurement of roughness by ordinary techniques would therefore be of little use for knowledge of the roughness inside the contact.

In conclusion to this section, even though the idea of surface roughness as the main mechanism of force transmission is appealing in some respects, there are many reasons for abandoning it, not the least of which is the inability to explain traction peaks, in addition to the plateau regions, statistically.

The statistical nature of the force transmission can, however, be combined with the concept of solidification of the lubricant by introducing granularity. This bizarre concept outlined by Gentle (ref. 43) has some attractive features. Friction in a substance such as sand exhibits statistical dependence on the shearing, provided the period of observation is short enough to expose the granularity. Plots of stress against strain (equivalent to the traction curve axes) for sand, such as those of Golder (ref. 48) shown in figure 11, are remarkably similar to traction curves for lubricants. The difference between low-pressure and high-pressure behavior is caused by different types of packing of the granules. Loose-packed granules predominate at lower pressures, giving an arrangement that is broken down gradually by the shear until a steady traction force is produced by randomly colliding granules. At high pressures, hexagonal-packed granules offer more resistance to shear owing to the more rigid configuration, but once the order is broken by the shearing, the force is once again caused by collisions of random granules. This granular lubrication hypothesis therefore can explain in essence the traction curves that are obtained from

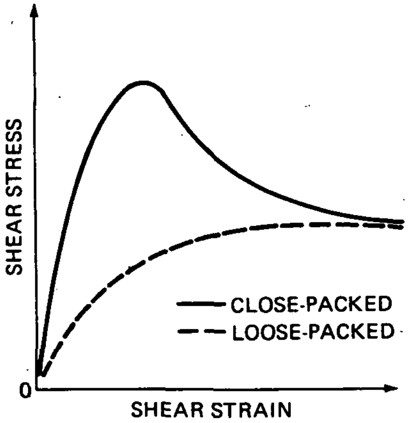


FIGURE 11.—Shear stress versus shear strain for sand.

EHD contacts, including the independence of film thickness, the traction peak, and the traction ceiling. The only drawback is to find some physical basis for the granularity.

The most likely possible cause is that the region of constant viscosity of lubricants at high pressure corresponds to solidification or glassing of the fluids. In a sliding contact the nucleation centers around which molecular aggregates grow both in glasses and crystals and are prevented by shearing from uniting to form a continuous medium. The result is that the lubricant would behave as a granular solid if the temperature in the contact was below the pour point corresponding to the pressure of the Hertzian region. Unfortunately few data are available concerning the raising of the pour point with pressure, and so the concept of granular lubrication remains as pure supposition, as do all other explanations of EHD traction, until some independent method of testing lubricants inside the contact may be found.

Conclusion

What conclusion can we draw from this discussion of traction that will help explain scuffing in EHD contacts? It seems that from models which assume the lubricant remains a liquid, whether Newtonian or not, that there is no mechanism which could cause severe scuffing, provided a full film is maintained, as asperity interaction is generally thought to be small. The provision of a full film has been shown to be important by Wedeven (ref. 49), who found a suitable criterion for the onset of starvation. If the lubricant inlet boundary approaches within about two Hertzian diameters of the contact, then the pressure cannot build up fully in the fluid and the film thickness is reduced.

It seems therefore that we must interpret data on failures with some caution because the cause is more likely to be starvation, which is difficult to observe except by optical methods, rather than any instability in the fluid form.

A problem of this nature would offer more hope of solution than the disturbing idea that a fluid film could suddenly collapse. Let us hope that this is the case.

DISCUSSIONS

J. F. Archard (University of Leicester, Leicester, England)

Dr. Cameron and Dr. Gentle have presented a paper that contains a number of interesting and speculative ideas. It is to be hoped that, even when we utterly disagree with them, we will recognize their important function in provoking discussion and argument, which are undoubtedly a spur to more constructive thinking.

I therefore start with a disagreement about one of the central points of the authors' paper, their assertion "that breakdown in gears lubricated by plain oils is often caused by the thermal desorption of the polar materials in the oil, which occurs at a certain critical temperature." After Professor

Blok's long paper (ref. 23) at the last symposium and the discussions which it provoked, perhaps we should not spend too long in discussing this issue. As in the courts of law, one is obliged to consider all the evidence, not just one's own selection. I think that at the present time the verdict must be one allowed under Scottish law (but not, I think, in many other places) of "not proven."

As Mr. Dyson pointed out in his discussion of Professor Blok's paper (ref. 23), there exist a number of results in the published literature in which the failure load increases with increasing sliding speed and which are difficult, if not impossible, to fit into the hypothesis of a constant total contact temperature for failure. To these results must now be added a new investigation by Bell and Dyson (ref. 50). In their experiments, when a disk machine was lubricated with a plain mineral oil, the calculated total contact temperatures at failure covered a range from 127° to 289° C.

In this connection it is salutary to recall a similar controversy about the role of surface temperatures that has occurred in the discussion of dry wear under oxidizing conditions. An earlier review (ref. 51) pointed out the need for experiments that distinguish clearly between the influence of the bulk temperature T_b and the superposed flash temperature T_f. Because in these experiments T_f is a function of $W^{\frac{1}{2}}V$, where W is the load and V the sliding speed, constancy of $W^{\frac{1}{2}}V$ has often been taken to indicate the influence of T_f. However, in some typical dry rubbing experiments, it has been shown that both T_f and T_b are a function of $W^{\frac{1}{2}}V$, so that it becomes difficult to distinguish between the role of these two temperatures (ref. 52).

Returning to our discussion of lubricated experiments, it therefore appears essential that a critical examination of failure criteria should be based upon a set of experiments, performed under otherwise identical conditions, in which both the bulk temperature and the flash temperature are controlled independently. To make myself clear, I suggest that the sort of data that we seek are best illustrated by some earlier results (ref. 53) produced to show, unequivocably, that the film thickness under EHD conditions is determined by the bulk surface temperature and not by the lubricant supply temperature (fig. 12).

The total contact temperature hypothesis for failure is critically dependent upon our ability accurately to forecast flash temperatures. It seems likely that some of these forecasts may be in doubt because of uncertainty about the variation of the intensity of heat generation q through the conjunction. Three such possible distributions are shown in figure 13. A constant measured value of friction is assumed. The uniform distribution A used in the earliest theories is usually replaced by the Hertzian or semielliptic distribution B. But under full EHD conditions, distribution C is likely to be more sharply peaked toward the center because of the influence of pressure upon viscosity. Although the peaked distribution shown here is based upon a new analytic solution of temperature distributions

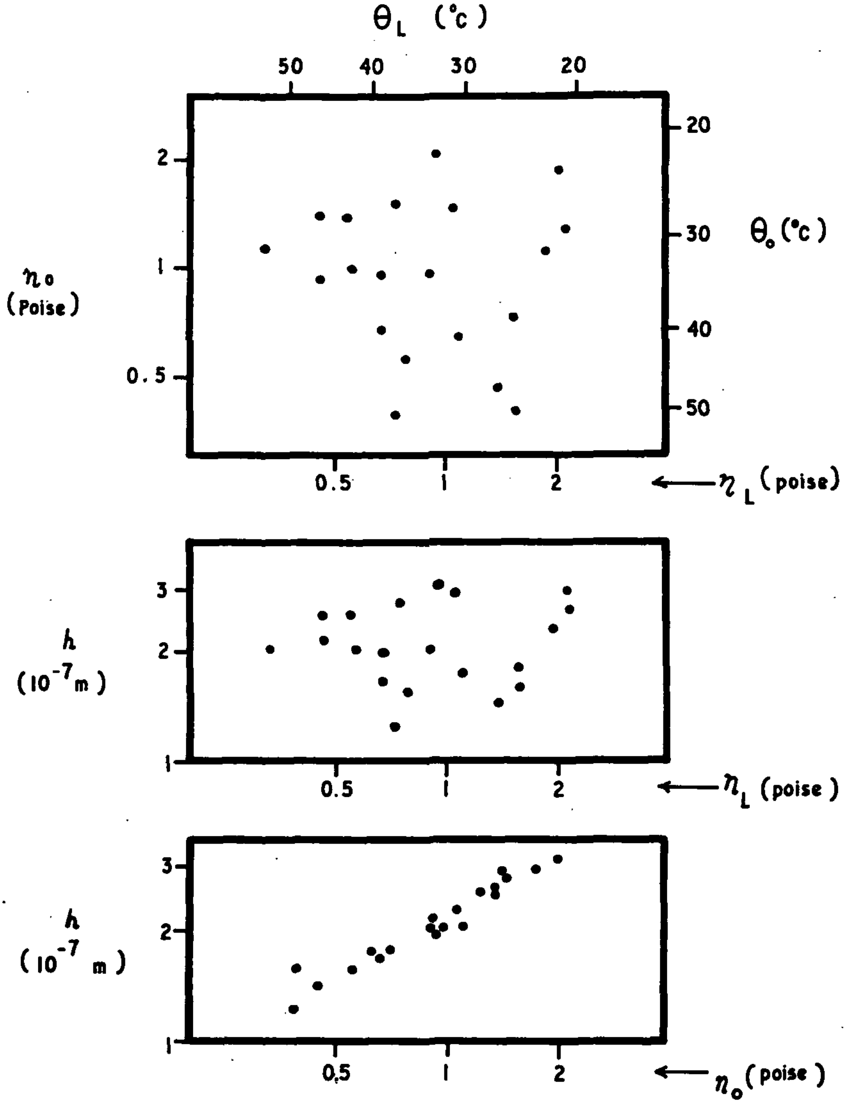


FIGURE 12.—Zero correlation of film thickness with inlet oil viscosity.

(ref. 54), it is in general accord with the variation of viscosity through the conjunction shown in the computer solutions of Manton, O'Donoghue, and Cameron (ref. 55). For the same total dissipation of energy, the maximum flash temperatures arising from these different distributions are likely to differ by 40 to 50 percent. While full EHD conditions may give distribution C, the existence of appreciable mitigated solid contact could well re-

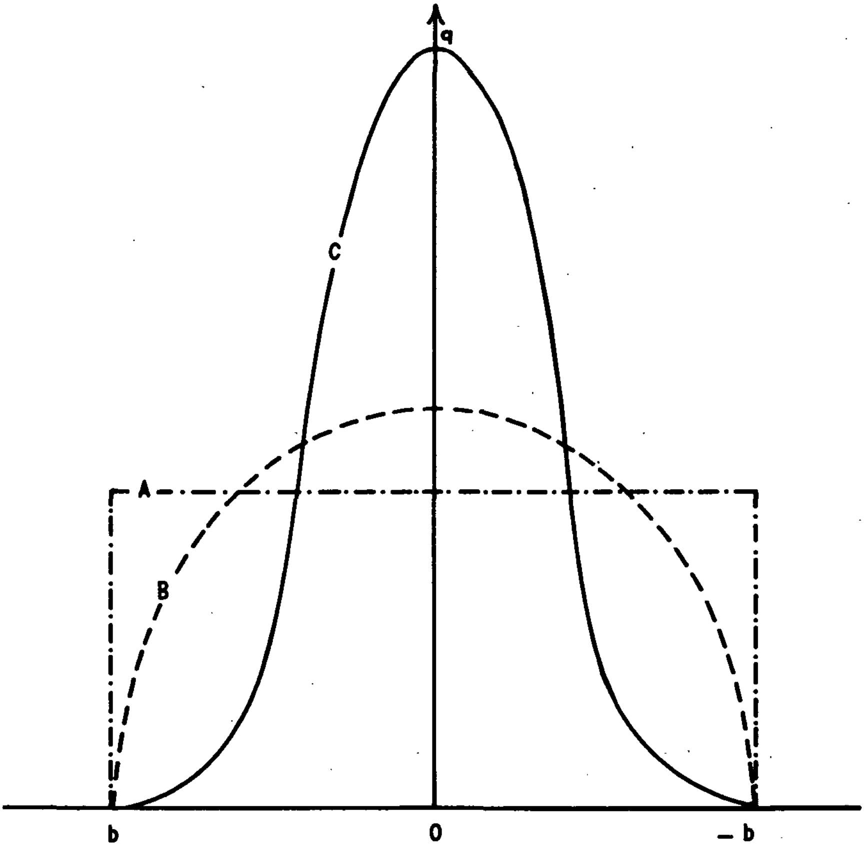


FIGURE 13.—Alternative distributions of the intensity of heat generation. *A:* uniform; *B:* semielliptic; and *C:* peaked.

sult in something nearer distributions *A* or *B*. Clearly, to validate the constant contact temperature hypothesis, we need a better understanding of methods of estimating the flash temperatures. A useful start to such an understanding, based upon theoretical analysis combined with measurements of transient surface temperatures, will be found in a paper by Kannel and Bell (ref. 56).

Dr. Cameron and Dr. Gentle attempt to relate the constant contact temperature hypothesis to a detailed mechanism of failure by assuming that it corresponds to a desorption temperature. A very large body of interesting scientific work exists in the literature on the thermodynamics of physical adsorption and its role in lubrication. But most, if not all, of the direct evidence supporting the idea that rubbing surfaces can be protected by physically adsorbed films is concerned with low-speed rubbing under idealized conditions. To stimulate the subsequent discussion, I ask the following question: What direct evidence exists to suggest that physical adsorption of surface active materials is a significant factor in lubrication under conditions typical of engineering practice?

I think that an unbiased review of evidence drawn from experiments under typical engineering conditions would suggest that chemisorption is the dominant mechanism and that the nature of the products of chemical reactions is of prime interest. If this be so, then the problem becomes similar to that described in the earlier reference to unlubricated wear. Once again definitive experiments are required that distinguish clearly between the roles of the bulk temperature T_b and the flash temperature T_f.

The authors raise a very pertinent question in their discussion of the four-ball machine. In effect, they suggest that we really do not know how some of our standard tests for additive behavior work. It may therefore be appropriate if I outline an exploration of this problem that has been carried out in my laboratory. A feature of many of these tests is that rubbing starts under nonconforming conditions, but after a period of wear local conformity is achieved by a wear scar. Sometimes the size of this wear scar is taken as a measure of the efficiency of the additive. We have shown, using simple electrical resistance techniques, that during the period of wear a low electrical resistance is maintained. The development of a stabilized wear scar is accompanied by a high electrical resistance showing that under these conditions hydrodynamic lubrication exists. A first simple theory, which forecasts the thickness of the film under these conditions, has been developed. The work suggests that the role of additives is to insure that the surfaces can survive, without complete seizure, during the period of wear so that hydrodynamic mechanisms of lubrication can reassert themselves after a wear scar of appropriate size has been formed.

The authors also include some qualitative discussion of rheological models for lubricants in EHD situations, a topic that is discussed with considerably more rigor in Professor Cheng's paper at this symposium. Dr. Cameron and Dr. Gentle quite rightly emphasize the differences between the entry region and the Hertzian, or main load-bearing, region. However, in the opening paragraph of this section of their paper their presentation creates the impression of confusion between simple viscoelasticity, i.e., in shear, and time-dependent pressure-viscosity effects, which Professor Cheng calls compressional viscoelasticity. There is an important difference between these two effects, and if we are to establish viable models of rheological behavior, it is vital that the distinction between them should be clearly maintained. Indeed, in the discussion of Professor Cheng's paper, it was shown by Dr. K. L. Johnson that, under certain circumstances, these two effects can produce forces of opposite sign.

One aspect of the authors' discussion of traction results seems to call for further elucidation. In discussing figure 8 they claim that, particularly at low sliding speeds, traction results are condensed to a single curve when plotted as a function of the slide-to-roll ratio. Later they express this same result in the equation

$$\frac{T\bar{u}}{u_1-u_2}=C$$

This seems an important result, particularly as the text seems to imply that it has been found for many lubricants. Therefore, in the reply to the discussion, it would be valuable if the authors could justify these statements by showing some experimental results plotted in this way. Also it would be helpful if they could indicate how the constant C varies with the type of lubricant.

It seems important that rheological models adopted for EHD conditions should, at least, be understandable in terms of the very large body of knowledge drawn from the main stream of rheology, as set out so well in Mr. Hutton's paper at this symposium. The combination of conditions encountered in EHD (pressures, shear rates, transient conditions), although unusual, are surely not so outlandish that an entirely different type of rheological behavior is to be expected. For this reason the hypothesis of granular behavior seems unlikely and, indeed, is probably unnecessary. The authors' text on this point is not specific, but it seems to imply that granular behavior is postulated because a mechanism for the initiation of failure is sought in the complete absence of solid contacts through the film. Is such a mechanism needed? Can scuffing occur without the existence of any type of mitigated solid contact through the film? I suggest that the answer to both of these questions is "No."

I opened this discussion by suggesting that an important function of these review papers is that they should stimulate thought, argument, and disagreement. Having expressed disagreement with many of their ideas, I must end on a note of sympathy to the authors in their task. I offer them my own defense when faced with the problem of writing an earlier paper in this series (ref. 51) of critical and provocative reviews: "it must be feared that what the author considers to be critical and provocative, the reader may regard as perverse and idiosyncratic."

A. Dyson (Shell Research Ltd., Thornton Research Centre, Chester, England)

The authors state that mineral oils cease to lubricate steel at a temperature of 150° C and express surprise that this phenomenon has not been studied more extensively. One possible reason for this apparent neglect may be that their contention is not valid as a general statement, although it is undoubtedly true in particular cases.

If the conditions in a lubricated contact between steel surfaces are made more severe, the contact will ultimately fail, but, in my experience, the temperature at failure will vary in a systematic way with the conditions of operation.

At high sliding speeds and low rolling speeds, we have observed scuffing at a calculated total contact temperature lower than 60° C; at the other extreme, at high rolling speeds and low sliding speeds, the same mineral oil has lubricated steel surfaces of the same composition quite satisfactorily at calculated total contact temperatures of more than 380° C. Of these high total contact temperatures, the bulk metal temperature, measured by embedded thermocouples, was more than 320° C.

The authors also state that it seems certain that desorption must play a dominant role in scuffing, but I fail to see how this conclusion follows from the arguments that the authors advance. A doubling of the coefficient of friction obviously has an important effect on the operation of a piece of machinery, but we do not know whether desorption occurs during the scuffing process, whether it causes the rise in friction if it does occur, or whether a doubling in the coefficient of friction must necessarily arise from desorption and from no other cause.

We do not know much about the mechanism of scuffing, and therefore we do not know how EP additives work in avoiding or postponing scuffing, except in the most general terms.

The suggestion of the granular nature of the lubricating fluid is an interesting idea, but so far as I can see, it has not progressed beyond this stage. I should be interested to know if Dr. Gentle has been able to work out the consequences of his idea in quantitative terms.

Although I would be among the first to admit that the theory based on the viscoelastic properties of the lubricant has many unsatisfactory features, it has nevertheless had some success in describing the results of measurements of traction in various circumstances. This applies particularly to the theory as modified to take into account the effect of compressional viscoelasticity as described in Professor Cheng's paper. It would be interesting if we could compare these findings with similar quantitative results derived from Dr. Gentle's theory.

A. W. J. de Gee and G. H. G. Vaessen (Central Laboratory, TNO, Delft, The Netherlands)

In their very informative review, the authors maintain that for pure mineral oils on metal surfaces well-defined critical desorption temperatures can be found.

In the case of copper-based bearing alloys in boundary-lubricated sliding contact with SAE 1045 steel (refs. 57 and 58), such critical temperatures were found to depend quite markedly on the composition and the structure of the bearing alloys. However, they were found to be independent of load, speed, and surface roughness, at least within the limits of experimental accuracy of conjunction temperature measurement (±2° C). Obviously, this weakens the generality of the authors' conclusion that surface roughness and load influence the value of the critical desorption temperature. Can it be that in the cases cited by the authors, the effects of load and roughness were due to unobserved differences in equilibrium conjunction temperature rather than to mechanical or surface energy effects?

As to the authors' comments on film thickness, we think that their statement that the scuffing of gears has nothing to do with film thickness is perhaps too strong, if only because of their own observation that breakdown of boundary lubrication can occur only if intermittent metal-to-metal contacts occur. From recent work on small journal bearings (ref. 59), we conclude that this happens if the film thickness reaches a critical lower value h_c, defined as

$$h_c = c\,(\mathrm{rms}_{\mathrm{bearing}} + \mathrm{rms}_{\mathrm{journal}})$$

in which $c = 3.5$ for a roughness profile of Gaussian distribution. Actually this formula was found to give an excellent fit between calculated and measured data on film thickness, provided that process roughness data rather than design roughness data were used.

Finally, we would like to comment on, and in fact amplify, the authors' statements on friction polymers, catalytic action of metal surfaces, and the effect of oxidation. Figure 14 summarizes results on the boundary-lubricated sliding of tin bronzes against plain carbon steel, recently found in our laboratory. It can be seen that at a measured conjunction temperature of 130°±2.5° C, phosphorus-free Cu6Sn behaves exceptionally well, provided that the lubricant, a straight mineral white oil, is blanketed with air. However, if experiments are performed with the same material in an atmosphere of argon instead of air, the wear rate of the bronze is found to have increased by a factor of 50 or more. Figure 14 also shows that the same high wear rates are found if phosphorus-containing Cu6Sn is used, irrespective of the nature of the cover gas. Careful examination of the surfaces after termination of the tests showed that, when working with

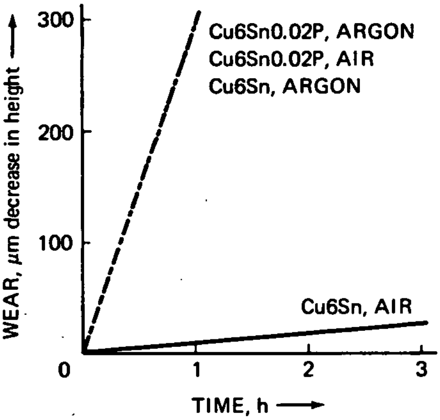


FIGURE 14.—Wear curves for bronze pins sliding against SAE 1045 steel rings. Speed of rotation of the rings: 125 rpm (linear velocity: 0.5 m/sec); load: 4000 N; average conjunction temperature: 130° C; lubricant: straight mineral white oil; cover gases: air and argon.

phosphorus-free bronze and with air-covered oil, a thin layer of carbonaceous material, probably a friction polymer, was present at the specimen surfaces.

At present we would like to put forward the following tentative explanation of the observed effects: It has been shown (ref. 59) that a phosphorus-free tin bronze contains a small percentage of finely divided SnO particles. In the initial stages of the contact process a thin, frequently invisible, film of transferred bronze is invariably formed on the steel journal surface. In this transferred film, the tin oxide is even more finely divided than in the original material. We consider it very probable that this finely divided SnO catalyzes the formation of a friction polymer. If the oil is blanketed with air, this friction polymer is activated by partial oxidation; i.e., formation of acid groups, and thus a substance is formed that can strongly adhere to a metal surface. If the experiment is performed with tin-oxide-free (i.e., phosphorus-containing) bronze or if the experiment is performed under argon, the necessary requirements for the formation of an activated friction polymer are not fulfilled.

E. Rabinowicz (Massachusetts Institute of Technology, Cambridge, Mass.)

The authors, under the heading "metallurgy," cite the work of Matveevsky and Lasovskaya, who studied the critical temperature of lubricated copper alloys sliding against steel. Matveevsky and Lasovskaya found that alloys containing the metals aluminum and zinc lowered the critical temperature, while alloys containing tin and antimony raise the critical temperature. The generally accepted explanation is that these results are in some way attributable to some interaction between the alloying elements and the lubricant. It seems to me that an explanation of a completely different type can explain the results much better. This other explanation considers the compatibility relations between the copper alloy and the mating steel surface.

As is well known, the metallurgical compatibility of copper with respect to iron (and hence steel) is marginal. Aluminum and zinc are fully compatible with steel, while tin and antimony are almost incompatible. Accordingly, it seems plausible to assume that aluminum and zinc are bad additives for copper when used for sliding against steel because they increase the metallurgical compatibility, while tin and antimony are beneficial because they reduce the compatibility.

This effect shows up clearly in tests with unlubricated sliding surfaces. Thus, unlubricated tin bronzes give less friction and wear against steel than do zinc brasses and aluminum bronzes. In the presence of lubricants, apparently, metallurgical incompatibility has the effect of extending the working temperature of a lubricant that has been heated to the point that it no longer interacts well with the sliding surfaces.

M. Godet (Institut National des Sciences Appliquées, Lyon, France)

It is a hopeless task to attempt to discuss Drs. Cameron and Gentle's paper in a few lines, as practically all aspects of lubrication have been touched upon. I will therefore limit my discussion to a few well-defined points.

Breakdown of Lubricity.—I will attempt to study from the applied mechanics point of view the consequences of lubricity breakdown. The argument can be read to say that scuffing occurs when a critical temperature T_c is reached and is independent of film thickness even when thick and continuous films are formed. Let us consider the two following cases, occurring only instants apart in the same mechanism operating under identical conditions.

Case 1.—The surface temperature T is slightly lower than the critical temperature T_c, $T=T_c-\epsilon$, where $\epsilon \ll T_c$. A thick film is observed, pressure is generated, and a load is carried. The laws of hydrodynamics apply; pressure and load can be calculated from the Reynolds equation.

Case 2.—The surface temperature T is slightly higher than the critical temperature T_c, $T=T_c+\epsilon$. The oil film has disappeared, the oil is no longer entrained in the contact, and scuffing occurs. The question that naturally comes to mind is what exactly has happened from the point of view of the hydrodynamics of the problem.

The fact that the polar materials of the oil have been desorbed from the surface is not an acceptable answer, even if it is physically correct, as the Reynolds equation, which instants earlier governed the whole phenomenon and described it accurately, does not know about desorption. Hence it is necessary to see how a critical temperature can affect either values or basic assumptions contained in the Reynolds equation.

The Reynolds equation is a second-order partial-derivative equation with two unknowns: the film thickness and the pressure. Its parameters include viscosity, film shape, and boundary conditions on both pressure and velocity. It further supposes that adequate oil supply is available. Oil viscosity is a continuous function of temperature. It varies rapidly around 20° C and very slowly around 150° C, which appears to be a representative value for critical temperatures. It therefore seems unlikely that changes in viscosity can explain why the Reynolds equation is not applicable above critical temperatures. Film shape does not vary directly with small temperature differences, boundary conditions on pressure are unchanged, and oil starvation decreases rather than increases (ref. 60) with a drop in viscosity. This leaves boundary conditions on velocities as the only possible parameter that can be affected by critical temperatures. The Reynolds equation is only valid if there is no slip between the liquid and solid molecules at the wall. Should slip occur, theory (ref. 61) shows that pressure and load may be considerably reduced leading to likely scuffing conditions.

In conclusion, the thermal desorption criterion for scuffing appears to be only applicable to mechanisms operating with thick hydrodynamic films if thermal desorption provokes boundary slippage.

Contact Temperature and Scuffing.—In an experimental study of mixed friction (refs. 62 and 63) in which we tried to determine the load division between the parts P_H and P_M of the load P that are carried, respectively, by the fluid and by the metal asperity contacts, we had to run an exhaustive evaluation of temperature-measuring techniques, as contact temperature appeared to be one of the dominant factors. This was done on a much modified Timken machine that used original Timken rings and blocks. The measurements undertaken were (fig. 15) inlet oil temperature, oil-ring temperature at two points, Timken block temperature, oil-ring temperature at contact exit, and contact temperature.

The inlet oil temperature was measured by a thermocouple positioned in the inlet flow. The oil-ring temperatures were measured at 90° and 270° of the contact by placing fine thermocouples in thin tubes linked to a vacuum pump. The oil is sucked into the tube, and the thermocouple junction is situated at approximately 0.2 mm from the ring surface. A hole was eroded in the Timken block at 1.5 mm below the original contact surface. Finally a reasonably complex infrared (IR) measurement method was used by Deyber in our laboratory to determine contact temperature. The technique (fig. 16) consists in measuring two IR beams emanating, one from the contact surface (1) and conducted through a hole in the test ring, the other from a temperature reference (5) source situated at 180° from the contact and seen through the same optical path. The IR beam is reflected off both flat (2) and parabolic mirror (3) and focused on a lead sulfide cell (4). A full description and discussion of the technique is given in references 63, 64, and 65. A representative graph giving the variation of the coefficient of friction and of the various temperatures obtained for an applied load of 900 N and a speed of 1000 rpm, with an EP oil is given in figure 17. A fairly

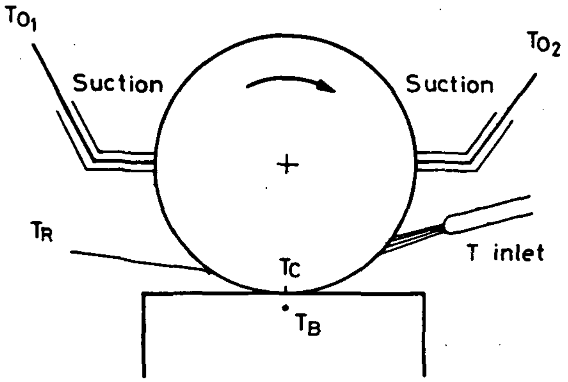


FIGURE 15.—Inlet oil, oil ring, Timken block, and contact temperatures.

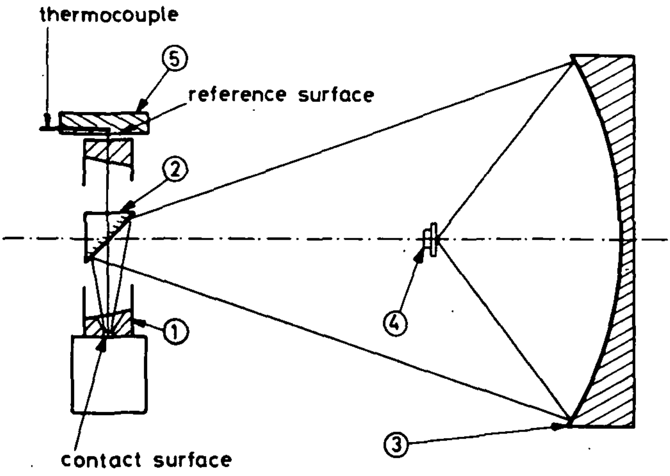


FIGURE 16.—Infrared temperature-measuring system.

comprehensive theoretical study that was undertaken by Van Schoors (ref. 66) and conducted for the Timken ring and block geometry with oil-covered surfaces gave values which came surprisingly close to the experimental results given by the IR technique. It is also notable that the contact temperature variations follow very closely the variations in coefficient of friction. This led us to choose that temperature as the representative temperature in our mixed friction analysis. The data show that large differences exist between *external* and *direct contact* temperature measurements, which cautions us against conclusions drawn from data based on trailing thermocouple measurements, and that the temperature inside and not before the contact appears to determine the fluid load carried in mixed friction.

The data also show, and this is closer to the problem at hand, that no critical scuffing temperature can be determined from the data presented in figures 18 and 19. In figure 18, all curves were obtained with the same base oil, and the same additive and scuffing can be seen to occur anywhere between 100° and 250° C. In figure 19 scuffing occurred after a steady run at 130° C with relatively low coefficient of friction ($f \simeq 0.10$) with another EP oil that under two different conditions (900 N, 1000 rpm, $f \simeq 0.13$ (fig. 20) and 700 N, 1000 rpm, $f \simeq 0.15$ (fig. 21)) gave very satisfactory performance for up to 1 hr at temperatures above 160° C and sometimes in excess of 200° C. This was followed in both cases not by scuffing, but by a drop in friction and temperature introduced by an increase in fluid load brought about by a change in contact geometry caused by wear (ref. 67).

Proceeding as we did earlier concerning lubricity breakdown, it appears that one way to look at the above data, in the light of the thermal desorp-

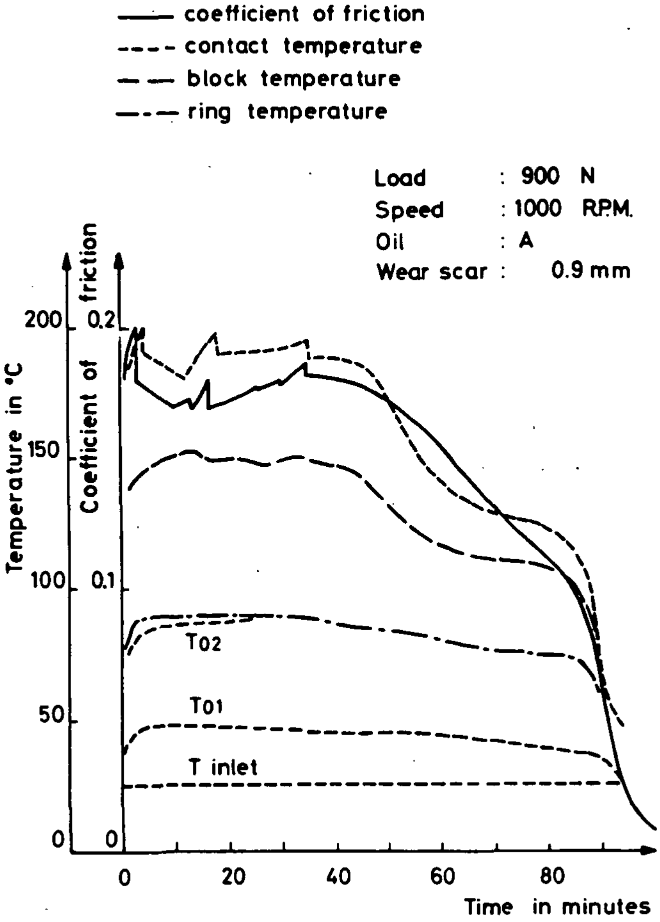


FIGURE 17.—Variation of coefficient of friction and temperatures with time.

tion theory, is to state that the scuffing shown in figure 19 is due to thermal desorption occurring around 130° C and that there is no relation between scuffing and contact temperature for EP films. In this particular case evidence obtained from analysis of contact resistance measurements leads us to believe that the additive with 30 percent sulfur and 2 percent phosphorus did act to protect the surfaces. In the other cases, figures 20 and 21, in which satisfactory performances were obtained even though larger friction power was generated at the contact, the EP additives were able to form protective films.

Traction.—We were quite surprised to find reasonably good agreement (fig. 22) between theory and experiment in work done by Dalmaz (refs. 60 and 68) on point contacts for load and traction in lightly loaded cases run-

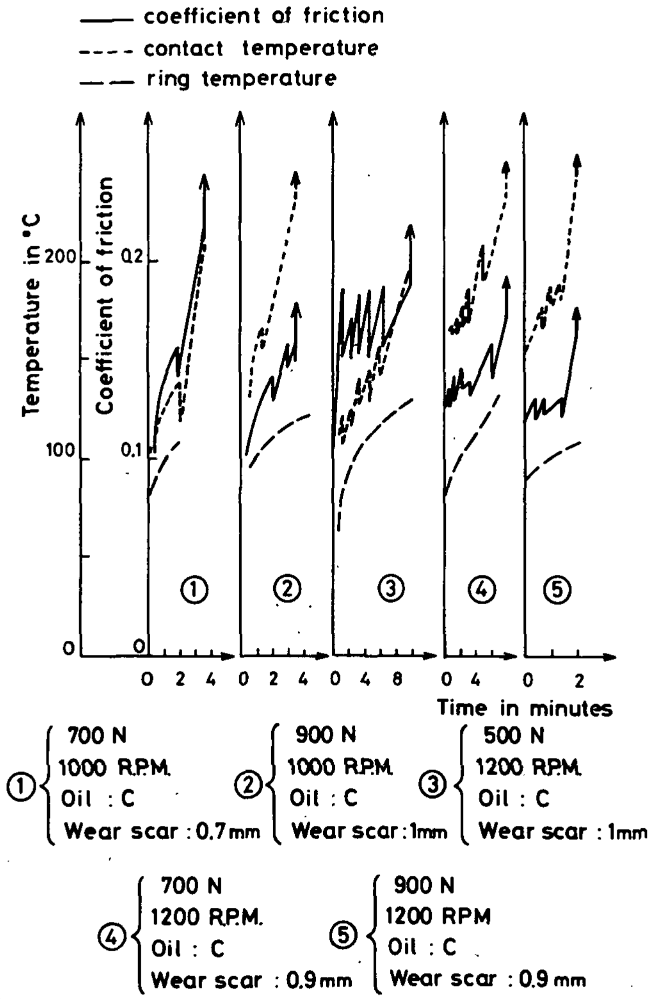


FIGURE 18.—Variation of coefficient of friction and contact temperature with time.

ning at moderate speeds. As far as traction is concerned, our theoretical results, which were slightly lower than observed experimental values, show that the total friction force depends on the exact dimensions of the domain over which the integration of the shear stresses is performed. This has to be taken into account in any comparison between theoretical and experimental traction results. No apparent non-Newtonian behavior was, however, observed when we compared traction results measured at shear rates equal to 2.5×10^6 sec^{-1} obtained with two oils of identical viscosity. The first was a pure mineral oil, the second an oil of the same base nature but very highly loaded with viscosity index (V.I.) improver. It was as-

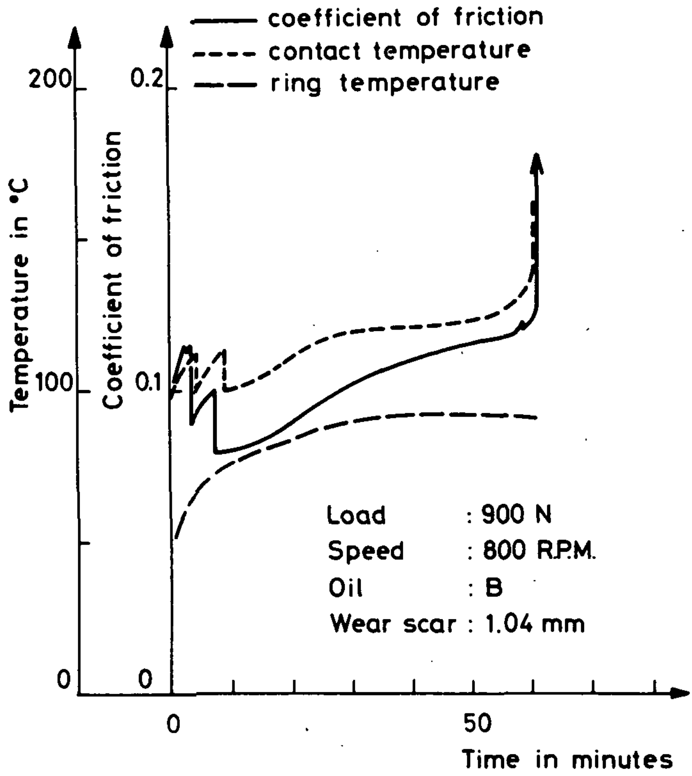
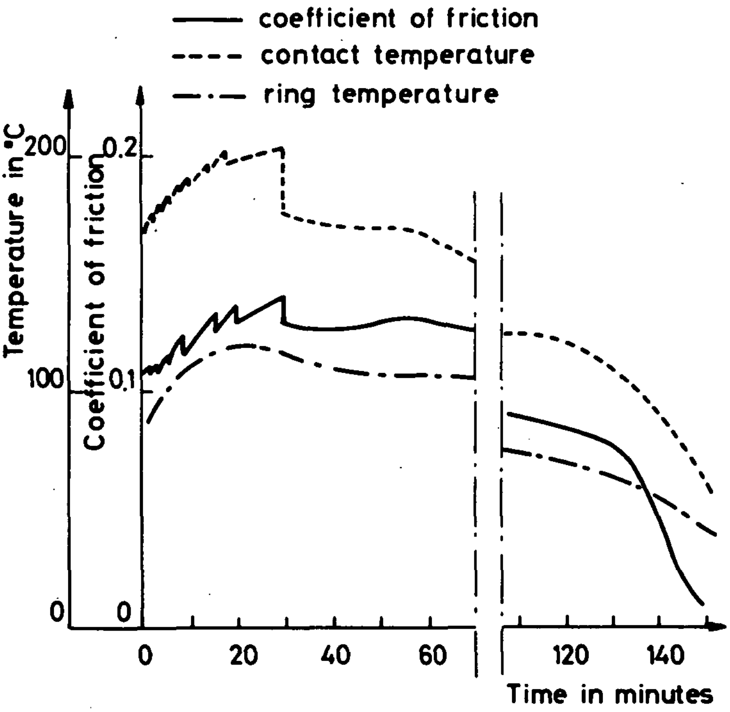


FIGURE 19.—Variation of coefficient of friction and contact temperature with time.

sumed that the high-shear-rate domain is very small next to the entire integration domain in point contacts and that even a large increase in traction over that small area would not modify the global results. This, of course, would not hold for line contact systems such as disk machines. A large increase in traction accompanied by a sudden drop in film thickness (fig. 23) was however observed by Dalmaz when inlet oil conditions were perturbed by oil starvation.

Conclusion.—While it is clear that desorption can play an important role in bringing about scuffing, it appears that it can only do so if some further conditions are met. In thick films, desorption should bring about gross boundary slippage. In mixed or boundary lubrication, scuffing can only occur if EP additives are unable to act.

From the technological or number-finding point of view, further research of the kind done recently by Bell and Dyson (ref. 50) must be undertaken to help designers. From the fundamental point of view, even if our understanding of the factors that can bring about scuffing is improved, the scuffing mechanism is still not understood. Hence new views, however contro-



Load : 900 N
Speed : 1000 R.P.M.
Oil : B
Wear scar : 1.17 mm

FIGURE 20.—Variation of coefficient of friction and contact temperature with time.

versial, such as the one presented recently by Rozeanu (ref. 69), are necessary and welcome.

H. Christensen (Technical University of Norway, Trondheim, Norway)

It is sometimes observed that the failure of the sliding surfaces in heavily loaded, lubricated contacts is preceded by a sudden drastic change or collapse of the oil film (ref. 70). Several hypotheses purporting to explain this phenomenon have been advanced. One is that the collapse occurs when the film thickness reaches the value of about three standard deviations of the total surface roughness. Another hypothesis relates the collapse to a structural breakdown of the lubricant. Another theory associates failure with the reaching of a critical temperature, which may or may not be connected with a physical desorption of active surface films. It is the purpose of the

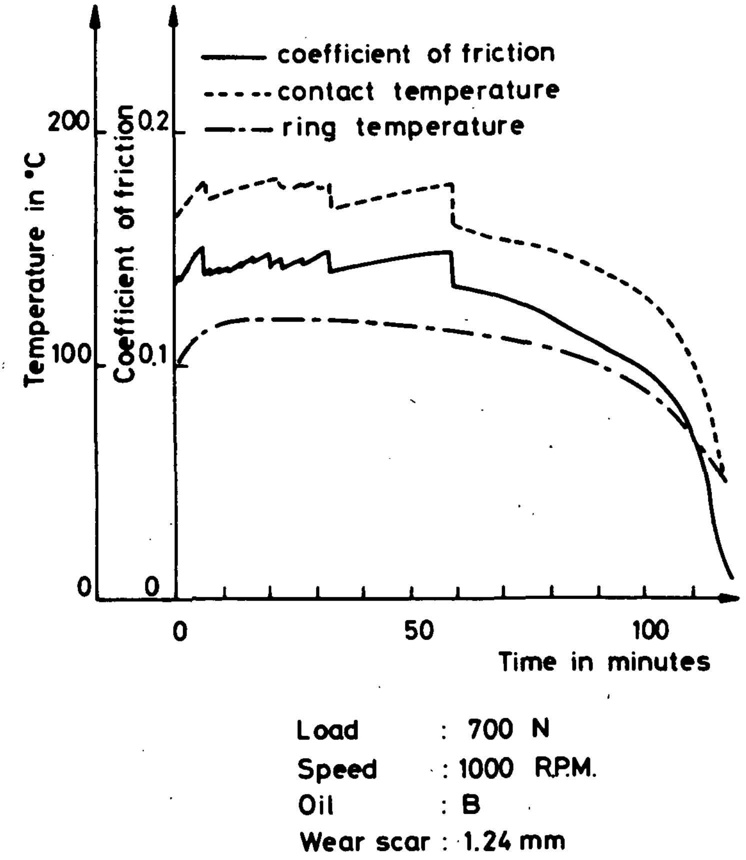


FIGURE 21.—Variation of coefficient of friction and contact temperature with time.

present note to demonstrate the theoretical possibility of film thickness instability without the need for introducing any hypothesis about new, and somewhat mysterious, changes in the fluid properties. The mechanism is provided through the well-known lubrication theory augmented with the concept of surface roughness interference under mixed lubrication conditions. The tools are available in the form of the probabilistic theory of hydrodynamic lubrication (ref. 71) and its extension to deal with mixed lubrication conditions (ref. 72).

The Mechanism of Film Collapse.—The central concept is that the mean or operative viscosity of the film is to be regarded as a function of the mean rate of heat generation in the film. More specifically, use is made of the old idea that in the mixed lubrication region, the load is carried partly through hydrodynamic action and partly by direct surface asperity interference.

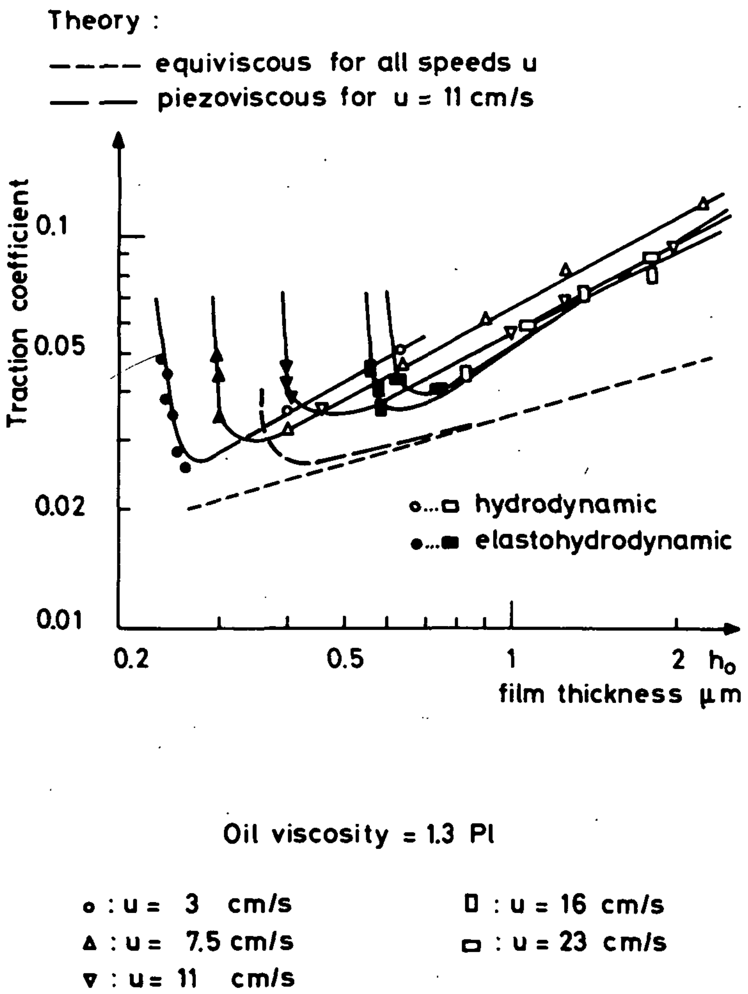


FIGURE 22.—Experimental and theoretical variation of the traction coefficient versus film thickness.

Similarly, friction is generated partly by the hydrodynamics and partly by asperity interference in a boundary type of friction mode. Assuming now that the mean temperature rise in the film is related to the mean total frictional heat generated, which in its turn implies that the mean or operational viscosity is related to the total frictional heat generated, the mechanism is complete.

To get a physical feeling for how the mechanism operates, consider a lubricated contact running at constant speed under a given load. Let the load receive a small increase. The contact must respond by a corresponding small decrease in film thickness. But this will result in an increase in

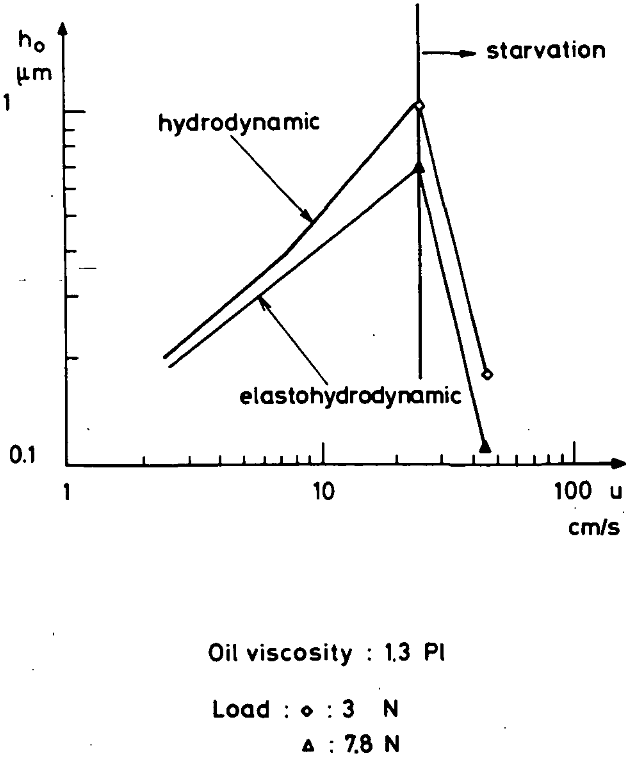


FIGURE 23.—Film thickness variation versus speed when starvation occurs.

asperity interference and, hence, an increase in temperature and a consequent decrease in operating viscosity. Because the load is mainly being carried by hydrodynamic action before the collapse, a decrease in operating viscosity must be followed by a further decrease in film thickness. However, as long as the load-versus-film-thickness curve has a negative gradient, equilibrium is possible. If at any point this gradient should turn positive, stable operation cannot take place. Thus, film collapse occurs at the operating point where the load-versus-film-thickness gradient first passes through a zero value.

To illustrate the operation of the mechanism, a fixed inclination sliding pad with no side leakage was chosen. A sliding pad rather than an EHD line contact was chosen because performance curves for this type of bearing are available in connection with an application of the probabilistic theory of mixed lubrication (ref. 72). It turns out that the following four dimensionless numbers or parameters are of importance in controlling the collapse: stiffness ratio parameter $N_1 = p_v l m^2/(\eta_0 U)$, the thermal parameter $N_2 = \beta \gamma p_v/(c_t \rho)$, the boundary friction parameter $N_3 = \mu_b/m$, and the roughness parameter $N_4 = c/ml$, where p_y is the yield stress of the bearing material, l is the bearing length, m is the fixed bearing inclination, η_0 is the reference viscosity at the bearing inlet, U is the sliding speed, β is the constant in the Reynolds viscosity-temperature relation, γ is the fraction of total heat determining the mean temperature rise, c_t is the specific heat of the lubricant, ρ is the density of the lubricant, μ_b is the boundary friction coefficient, and $2c$ is the surface roughness peak-to-peak value.

Because the number of influential parameters is so large, a complete analysis must be very comprehensive. The following partial analysis deals with the limited situation of a given bearing system being run at constant speed while the load is being slowly increased. Minimum nominal film thickness is continuously measured. The result is shown in figure 24. For the system, the parameters N_2, N_3, and N_4 are all fixed, while the four curves correspond to four different values of N_1 corresponding to the sliding speeds of $0.5U$, U, $5U$ and $10U$.

Consider the curve labeled $10U$. At small loads film thickness is large, and, in the present example, when the film thickness is greater than 0.5, the bearing is operating under pure hydrodynamic conditions. Increasing the load will decrease the film thickness. When film thickness gets smaller than 0.5, the bearing is entering the mixed lubrication region and asperity interference starts to take place. However, at first nothing drastic results from this action. After further load increase, the bearing will have reached point A in the diagram. At this point the bearing is unable to match any further (infinitesimal) increase of load by a corresponding continuous decrease in film thickness. Its only course is to jump, discontinuously, across to point B where stable operation may, in principle, be resumed. The drastic discontinuous change or collapse in film thickness will cause corresponding changes in the lubrication conditions. To see this, details of the calculation in the vicinity of the point of collapse (point A) are shown in table 1. The most significant fact is that even at the point of collapse itself, the total area of asperity interference is exceedingly small, only a small fraction of a percent of the total bearing area. From this fact it follows that the load is carried almost entirely by hydrodynamic action. On the other hand, hydrodynamically generated friction and friction related to asperity interaction are of about the same order of magnitude. The temperature rise at the point of collapse does not appear to be very high, of the order of 20° to 40° C, while the coefficient of friction gives no indication that collapse of the film is imminent. At the end of the collapse at point B, conditions are very different. The calculated temperature rise is great indeed, and as a consequence, practically all of the load is now carried by the asperity interference. Since the load-carrying capacity of the asperity interference action is independent of viscosity, the bearing has again, at least in principle, entered a mode of stable operation. However, the calculated temperature increases indicate that destruction of the sliding sur-

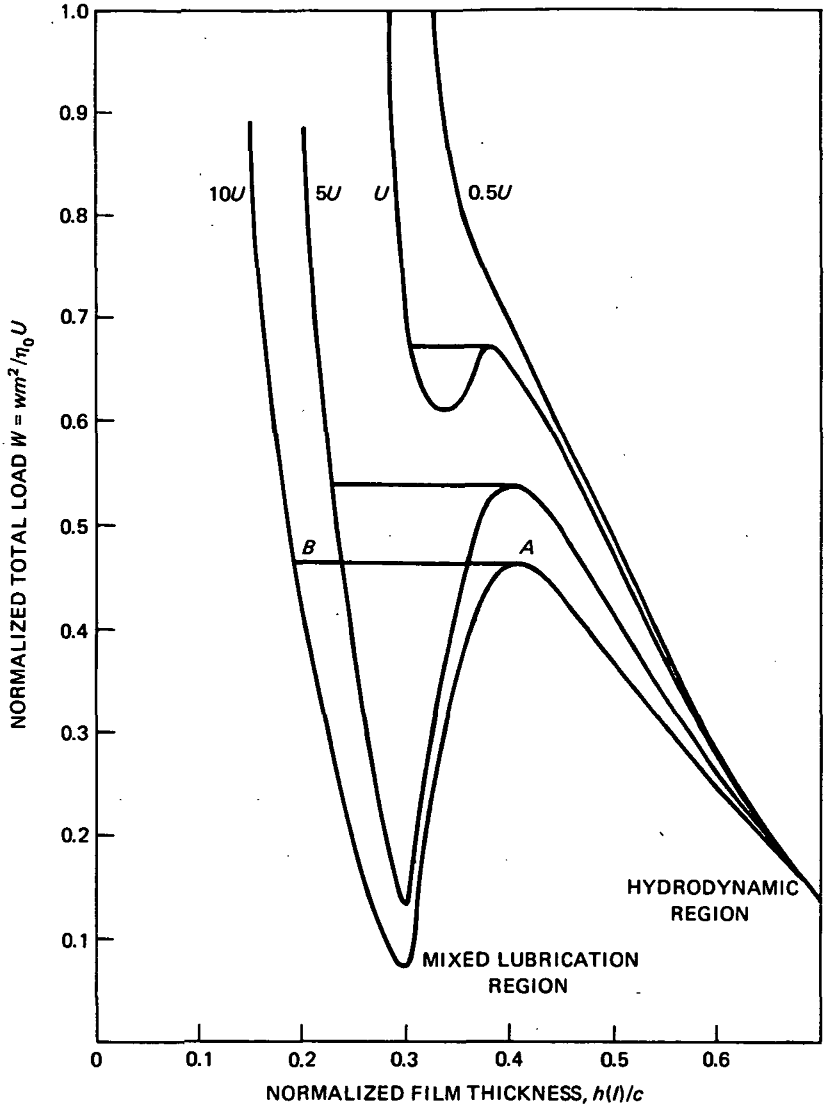


FIGURE 24.—Collapse of oil film.

faces follows as a consequence of the collapse. It appears from the curves shown that the film collapse will only take place provided that the sliding speed is high enough. This is in agreement with observational evidence.

Conclusion.—The intent of this note has not been to propose a theory of scuffing failure of gears, but merely to demonstrate that the phenomenon of lubricant film failure can be explained upon a basis of accepted mechanical lubrication theory. The generalizations needed in the theory to ac-

TABLE 1.—*Details of Calculation at Point of Collapse*

	0.5U	U	5U	10U
$\Delta\theta$	No collapse	27	29	40
μ		0.0120	0.0035	0.0030
a		1.35×10^{-2}	5.7×10^{-3}	5.7×10^{-3}
w_h/w		89.6	98.8	99.5
f_h/f		17	70	80

$\Delta\theta$ =calculated temperature rise above ambient, °C
μ =coefficient of friction of bearing
a =asperity interference area as fraction of bearing area, percent
w_h/w =ratio of hydrodynamic to total load, percent
f_h/f =ratio of hydrodynamic to total friction force, percent

complish this are merely to allow operational viscosity to change with temperature and to take proper account of the surface roughness interaction that takes place under mixed lubrication conditions. Qualitatively, at least, there is no need for postulating new, bizarre properties of lubricants. That the film must suffer a collapse under certain operating conditions follows as a simple, logical consequence of the mechanics of the lubrication situation.

LECTURERS' CLOSURE

Following Dr. Archard's lead and using a proverb, we feel that "half a loaf is better than none" sums up the purpose of this paper. It seems far better to have an understanding of a logical mechanism of failure and then try to examine the exceptions in the light of it. Not all cases of failure are attributable to polar desorption, and we fully agree that a given critical temperature "is not valid as a general statement, although it is undoubtedly true in particular cases," as Mr. Dyson puts it. In fact, the final sentence of our section on application of the critical temperature concept says the same thing in different words. Where we differ from Dyson is that we first try to find out why it is true in the particular cases and what the mechanism is there and then study what masks the desorption. This masking by polymer formation or chemical attack is clearly illustrated in figure 4 of the text. The question of direct evidence is partly answered in references 21 and 22, but is made difficult by the fact that work is still proceeding and will hopefully be presented to the ASLE–ASME Conference in New York in October 1972 by Bailey and Cameron (ref. 73).

The independence of critical temperature with respect to load and surface roughness noted by de Gee and Vaessen is very interesting. We are hoping to do more work on this and obtain a better insight into the effect.

The effect of film thickness is also most interesting since in earlier work by Cameron (ref. 4), a similar value for the constant C was found. With thrust or journal bearings, the minimum friction is very low, so on reaching the critical value of the film-thickness-to-surface-roughness ratio, a rise in friction will produce a large rise in temperature, leading to failure. With EHD contacts, on the other hand, increased contact makes very little change to the friction. We note that there is no failure theory of EHD contacts at all available.

The results for air and argon are fascinating. The whole question of the reaction kinetics in various atmospheres has still to be explained satisfactorily. We wonder whether the surfactants desorb from a layer of friction polymer or whether the temperature 130° C is the melting point of the polymer. This could be decided by running tests with oils containing various quantities of surfactant as done in reference 18.

Is it at all possible for Professor Rabinowicz, who is the expert in these matters, to develop his thesis further. Is such a term as "compatibility" of the metal surfaces capable of a mathematical description in surface energetics with the oil as an active component? In other words, can the alteration to the critical temperature be calculated?

Moving on to EHD contacts, we are very doubtful if there is slip at the boundaries, as suggested by Professor Godet. It seems to us that this would be less likely to occur at high temperatures (low viscosities) than at low temperatures. The desorption theory, together with the observed postulate of steady intermittent contact, explains the sudden collapse of a film, which cannot be explained otherwise.

The section on the mechanics of lubrication was intended as an attempt to analyze from a phenomenological point of view why a stable thick film should ever break down. It was argued that since such breakdowns would occur in the lubricant inside the contact, it was logical to start by examining some manifestation of the fluid properties in this region; namely, the sliding traction. If the results from an EHD traction experiment performed inside a black box could be presented graphically to a disinterested and well-informed observer, he would surely conclude that inside the black box was a bed of sand undergoing a shear. The origin of the granular approach presented here is therefore that the traction behavior is directly analogous to the behavior of a powder bed, and it is worthwhile examining it further to see if there is a physical basis for the granularity. It cannot compete for rigor with the rheological approaches explained at this symposium, but if it enables more people to think of the traction problem in a qualitative manner, then it has done its job.

The drawback to this granular approach is that it seems impossible to put numbers into it, owing to lack of evidence on the size of granules. However, it does indicate that if a fluid forms granules, there should be little difference in behavior from fluid to fluid. This can be observed in fact by looking at the low-pressure traction results of Gentle (ref. 43). These fit quite well to the granular theory prediction:

$$1-\frac{f}{f_{\max}}=\exp(-A\Sigma)$$

where

$$\Sigma=\frac{u_1-u_2}{\bar{u}}$$

f = traction coefficient reaching a plateau value of $f_{\max}$
A = a constant

In response to Dr. Archard's discussion, it is the exponential coefficient A that is more meaningful to look at, in conjunction with the value of $f_{\max}$. The value of A changes very little from fluid to fluid, which would indicate that any granules would be of the same size approximately in these fluids. It is the value of $f_{\max}$ that shows more variation, in fact, approximately over a range of one decade, although any correlation with temperature, load, or fluid properties has yet to be found. This is not surprising, however, since $f_{\max}$ would represent the coefficient of friction between individual granules, and presumably this would depend little on the nature of the fluid.

It was gratifying to find that the approach to this section drew such widely different responses as those of Professors Godet and Christensen. Professor Godet raises the question that is a logical response to any suggestion of a sudden collapse of a hydrodynamic film: What characteristic of a fluid can change so suddenly? Professor Christensen attempts to answer this in a most ingenious way and with a good deal of success. The process described seems plausible, but it is difficult to see if it would apply equally well to an EHD line contact. Here the argument, for example, that a small increase in load produces a decrease in operating viscosity as a result of asperity interference is by no means easy to support. However, we look forward to a fuller presentation of this work.

In conclusion, it would be diplomatic to quote Mao Tse-Tung (ref. 74): "Revolutionary truth is the sum of all the possibilities."

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Environmental Capability of Liquid Lubricants

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The purpose of this paper is to provide in compact form as complete as possible an array of the methods available for predicting the properties of liquid lubricants from their structural formulas. These methods carry with them the ability to design lubricants by forecasting the results of changing the structure. In a more general way, they serve to map out the ultimate limits to which liquid lubricants can cope with extremely hostile environments.

The methods are arranged roughly in the order of their rigor from thermodynamic properties through empirical physical properties to chemical properties. As far as possible, these discussions have been kept on a common basis, using group contributions to solubility parameters, even at the sacrifice of rigor and precision, to show how adjustment of one property affects all the other interactions with the environment.

1. INTRODUCTION

THE HISTORY OF LIQUID LUBRICANTS is essentially that of a battle against increasingly hostile environments. Five years ago the author (ref. 1) prepared figures 1 and 2 to show that we had already encountered the worst that the universe had to offer, and there is no reason now to change that statement. What has changed enough to justify reopening the subject is our increased competence in dealing with the same problems.

Figure 1 shows the physical situation reduced to two variables, temperature and pressure. These are the two main forces that control three of the most vital properties of every liquid lubricant, its viscosity and the end-points of its liquid range at which it solidifies or evaporates. The means used to deal with this class of stresses include mainly the thermodynamic properties, or those that can be predicted from complete knowledge of the intermolecular forces within the lubricant.

Figure 2 shows the chemical stresses to which lubricants are subject. Temperature again appears as one of the three axes, but this time in its role as the principal accelerator of chemical reactions, usually with the rate

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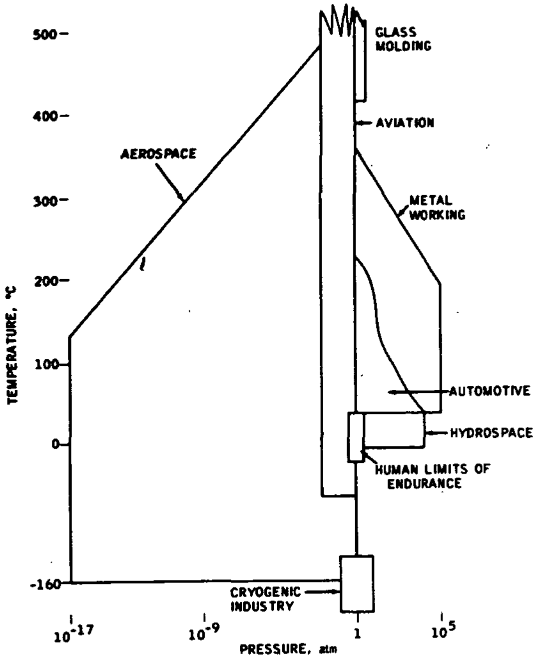

FIGURE 1.—The physical lubrication environment.

doubling for every 10° C rise, but sometimes with very different exponents. The radiation axis represents another form of energy. Infrared (IR) is exactly equivalent to heat, but as the wavelength decreases, ionization and free radical formation become increasingly important side effects. Molecular scission starts to become important at X-ray wavelengths and at gamma-ray energies dominates the reactions. However, all these processes have their thermal equivalents, so these two axes are, to some extent, redundant. The oxidizing power axis, on the other hand, conceals a hidden factor because it represents the partial pressure of oxygen, or its equivalent in some other element or compound. The necessity for such an axis is relatively recent. Until the coming of the aerospace age, such matters were of interest only to a few engineers in chemical industry.

Thus, the two variables in figure 1 also create problems in figure 2, but the means for dealing with them must be chemical rather than thermodynamic. At this point, the author must insist on excluding chemical thermodynamics as a phrase, because its use would lead to confusion with the purely physical aspects related to figure 1. Those chemical effects sometimes classified as thermodynamic will be discussed in terms of kinetics.

Another factor not explicitly included in figure 2 might be broadly classified as catalytic effects. These include those of humidity and bearing metals, and most especially those associated with freshly sheared metal

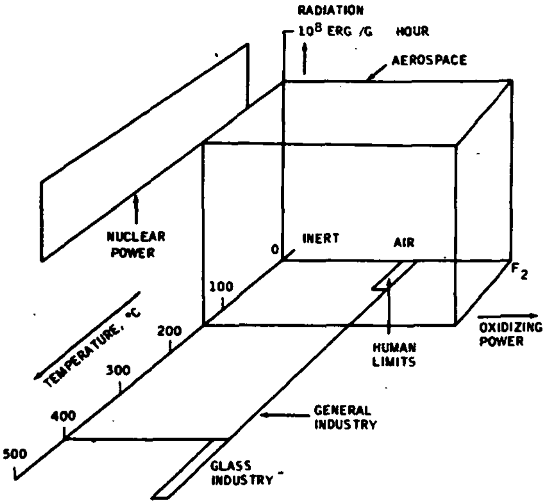

FIGURE 2.—The chemical lubrication environment.

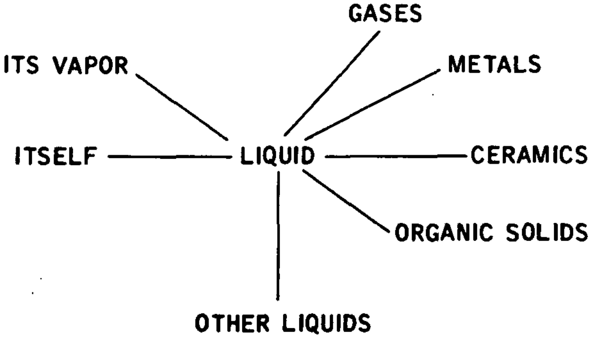

FIGURE 3.—The interactions of a liquid.

surfaces. Unfortunately, while these enter primarily into the oxidation axis, they also contribute to thermal degradation and so must be dealt with twice.

A third set of factors is shown in figure 3, which outlines the physical interactions of a liquid with its material environment. While these are seldom as drastic as the effects in figures 1 and 2, they are by no means trivial. The implications of figure 3 are discussed in more detail in section 2.2.

To discuss the effects of the environmental extremes on lubrication, it is necessary to go into considerable detail about their effects on lubricant properties. Most of the lubrication problems normally encountered result from the lubricant's being too thick, too thin, evaporated, burnt off, nonwetting, etc., and so are lubricant failures. The direct effects of the environment on the lubrication process are subtle enough to often be masked by these gross problems, and even now are we only beginning to be able to study them directly. If in the following discussion properties tend to overwhelm processes, this is merely an indication of the incomplete state of our knowledge.

Table 1 shows the various properties of any liquid lubricant, arranged in the order of their predictability. It is the plan of this paper to go through this list down to "corrosion," which Dr. Rowe will handle, discussing each property in terms of its relation to chemical structure. While these discussions progress from rigorous to quite empirical, it will be seen that all these properties are basically predictable. In addition, there are many relationships among the properties that are predictable, which should clarify the fact that certain combinations of properties are very difficult to achieve. Where feasible, the degree of control that these predictive methods provide over interactions with the environment will be indicated. Finally, an example of how one might use this approach to improve aircraft performance is lightly sketched in.

2. THERMODYNAMIC PROPERTIES OF LIQUID LUBRICANTS

It may be safely said that for the first few thousand years of lubricant technology, the thermodynamic properties of the lubricants in use were irrelevant to the problem, as technology slid along on the natural fats and oils. Until petroleum oils became available, there was little choice; olive oil was outstanding for its freedom from odor and its good stability, with fish oil near the other end of the spectrum. These differ from each other, and even from the stiffest tallow, only in the degree of unsaturation, which has only a minor effect on thermodynamic properties.

Petroleum lubricants were not exactly a welcome addition to this close-knit little family. Aside from having an unlimited variety of viscosities, relative freedom from gum formation, and freezing points as low as then desired, these hydrocarbons had little to offer. The natural ester lubricants were far superior in viscosity-temperature coefficient, volatility, and film strength under boundary lubrication conditions. The real reasons for these differences were slow to develop. The explanation offered was that the natural esters had oiliness, which really means "we don't know why, but we'd use olive oil if your hydrocarbons weren't so *cheap*."

In the end, the answers came from the chemical engineers, whose need for thermodynamic data was tied to the design of distillation and other separation equipment. This activity covers both the chemical and petroleum industries, but it was in the latter that the most rapid strides were made because of the large incentives in spite of the complexity of the problem. The chemists had, by analysis and synthesis, proved the existence of various individual compounds in mineral oil. Meanwhile, the engineers

TABLE 1.—*Classes of Lubricant Properties*

Class	Property	Environmental application
Thermodynamic	Heat of vaporization	Manufacture
	Density and expansivity	Essentially all
	Bulk modulus	High pressure, hydraulic response
	Vapor pressure	High temperature and/or vacuum
	Miscibility	Compatibility—additives and seals
	Gas solubility	Cavitation, compressors
Empirical	Heat capacity	Heat transfer
	Thermal conductivity	Heat transfer
	Freezing point	Storage and starting
	Viscosity and viscosity index	Hydrodynamic lubrication
	Work of adhesion	Boundary lubrication
Chemical	Thermal stability	Inert atmospheres
	Radiation stability	Powerplants, aerospace
	Oxidation stability	Ordinary atmospheres
	Flammability	Air, from low to high pressure
	Corrosion	Metals
Contamination	Color and color stability	Storage and use
	Foaming	Gears and circulation
	Demulsibility	Water
	Rust prevention	Metals and humidity

were compiling charts for whole families of compounds. At this point, J. H. Hildebrand (ref. 2) began to serve as a link between the two groups. After some contributions on correlating heat of vaporization, he concentrated on the mathematical structure, which, in the writer's opinion, is the key to all the physical interactions of liquids with their environment.

This mathematical structure is the set of equations that describe the cohesive energy ΔE_v as the heat of vaporization per mole ΔH_v, minus the work to expand the vapor to infinite volume $P\Delta V$. By this definition, the cohesive energy provides an exact measure of the intermolecular forces that prevent a liquid from quietly expanding into a gas because the energy is the integral of force times distance. If divided by Avogadro's number, it would give the energy per molecule, but a more practical unit can be obtained by dividing by the molar volume to obtain the cohesive energy density $\Delta E_v/V$. An even more useful unit is the square root of $\Delta E_v/V$, the solubility parameter δ. Assuming that the perfect-gas law holds for the vapor,

$$\delta^2=\frac{\Delta H_v-RT}{V} \tag{1}$$

This deceptively simple-looking formula contains the potential for predicting, when expanded as discussed in detail below, the thermodynamic properties of all lubricants from olive oil through synthetics so new that they are represented only by a scrawl on a tablecloth.

Meanwhile, the chemists had achieved a comparable insight. After many years of patient and frustrating analysis and synthesis of lubricant-sized hydrocarbons; they were suddenly relieved of this burden by the development of three new tools. Chromatography, both liquid and gas phase, permits separations into fractions of any detail desired. Mass spectroscopy provides details of the rings and chains, and nuclear magnetic resonance counts the terminal (CH_3) groups. What was only recently the work of years by highly skilled groups is now routinely surpassed by high school graduates.

The kinds of help to be had from these two groups are shown in table 1. While there are still loose ends enough to provide some job security, it is evident that the tools are ready to solve most present and anticipated problems.

2.1 Types of Cohesive Energy

Hildebrand's work (ref. 2) was specifically limited to liquids held together by London forces, sometimes called dispersion forces because of their relation to the refractive dispersion of light. They arise because each atom consists of electrons orbiting around a central positively charged nucleus. The moving negative charges create an electromagnetic field, which attracts all atoms to one another regardless of direction. The nature of the atoms and their assembly into molecules affect the size of the London force but not its existence.

Hildebrand's greatest contribution, published almost simultaneously by Scatchard, was that an equivalent $\Delta E_v/V$ between dissimilar molecules could be approximated by the product of their solubility parameters. This permitted the chemical engineers' tables and charts of the heats of vaporization of hydrocarbon families to be converted into energies of interaction with any sort of matter that is also held together solely by London forces. This limitation is extremely important, as the vast majority of materials are also held together by other forces. Two of these, the Keesom forces due to permanent dipoles and the donor-acceptor (H-bond) forces typified by hydrogen bonding, are discussed below. There are at least two others, less well understood. They are the ionic and metallic forces, which are not exactly within the scope of this paper.

2.1.1 The London Component of Cohesive Energy

In the many liquids that are held together by a combination of London, Keesom, and H-bond forces, it is not feasible to make a direct measurement of the London forces alone. Blanks (ref. 3) used the principle of corresponding states to arrive at a pragmatic solution to this problem by taking as a model a hydrocarbon of similar shape and the same molar volume. All such compounds must have the same heat of vaporization if measured at the same reduced temperature T_R; that is, the ratio of the actual to the critical temperature T_c in absolute degrees. A chart, developed by Blanks (ref. 3) but in expanded form, is shown in figure 4. It performs the entire calculation to obtain the London portion of the solubility parameter δ_D at 25° C, the usual reference temperature.

The most frequent problem in using figure 4 is how to obtain T_c values. These can be calculated from the Lyderson constants in table 2, provided the boiling point T_b at 1 atm is known, by

$$T_b/T_c = 0.567 + \Sigma\Delta T - (\Sigma\Delta T)^2 \tag{2}$$

2.1.2 The Keesom Dipole Component of Cohesive Energy

The Keesom forces arise from the fact that in many molecules the positive and negative charges are not evenly distributed. As a result, the molecule is subject to a torque when placed in an electrostatic field, which is usually reported as the dipole moment μ, and measured in Debyes. The electric field may arise from another molecule of the same type, or another type, rather than from a measuring instrument. This situation was analyzed by Keesom, but a more satisfactory solution was reached by Böttcher, who also used the dielectric constant ϵ and refractive index n of the liquid:

$$\delta_P{}^2 = \frac{12108(\epsilon-1)(n^2+2)\mu^2}{V^2(2\epsilon+n^2)} \tag{3}$$

Beerbower and Dickey (ref. 4) give a much simplified, but less precise, empirical equation

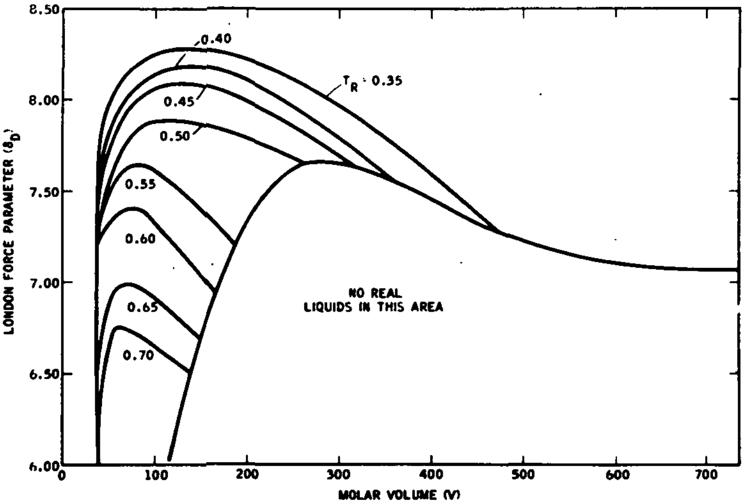

FIGURE 4.—Homomorph chart for noncyclic compounds.

TABLE 2.—*Group Contributions to Total and Partial Solubility Parameters*

Functional group	Molecular weight M, g/mol	Molar volume V, cm³/mol	Bondi volume V_w cm³/mol	Total parameter[a] $V\delta$, (cal×cc)$^{0.5}$/mol		Polar parameter $V\delta_P$, (cal×cc)$^{0.5}$/mol	H-bond parameter $V\delta_H^2$, cal/mol		Lyderson increments[c]		
				Aliphatic	Aromatic		Aliphatic	Aromatic	ΔT nonring	ΔT ring	ΔVc
CH_3—	15	34.2	13.67	148.3	--------	0	0	0	0.020	--------	55
$>CH_2$	14	16.15	10.23	131.5	--------	0	0	0	.020	0.013	55
$>CH$—	13	0	6.78	86.0	--------	0	0	0	.012	.012	51
$>C<$	12	−14.2	3.33	32.0	--------	0	0	0	.000	−.007	41
H—	1	[a] 14.7	[a] 3.5	--------	--------	[a] 0	[a] 0	[a] 0	--------	--------	--------
CH_2=olefin	14	26.5	11.94	126.5	--------	[a] 25	[a] 150	--------	.018	--------	45
—CH=olefin	13	11.8	8.47	121.5	117.3	[a] 25	[a] 150	--------	.018	.011	45
=C=olefin	12	0	[a] 5.01	84.5	98.1	[a] 25	[a] 150	--------	.000	.011	36
Phenyl	77	74.7	45.84	--------	795.4	[b] 50±25	--------	[b] 50±50	--------	.066	221
C–5 ring (sat.)	0	14.2	--------	21.0	--------	0	0	--------	--------	--------	--------
C–6 ring	0	12.1	--------	−23.4	Same	0	0	--------	--------	--------	--------
Para substitution	0	0	--------	--------	40.3	0	0	0	--------	--------	--------
—F	19	17.5	[a] 5.8	41.3	Same	[b] 225±25	~0	~0	.018	--------	18
—Cl	35.5	25.3	[a] 12.0	205.1	161.0	300±100	[b] 100±20	[b] 100±20	.017	--------	49
=Cl_2 twin	71	50.6	[a] 24.0	342.7	--------	175±25	[b] 165±10	[b] 180±10	.034	--------	98
—Br	80	29.1	[a] 14.6	257.9	205.6	300±25	500±100	500±100	.010	--------	[b] 70

—I	127	[b]32.2	[a]19.6	[b]320	270[b]	[b]325±25	[b]1000±200		.012		[b]95
—O—ether	16	3.6	[a]3.5	115.0	Same	200±50	[c]1150±300	[b,c]1250±300	.021	.014	20
>CO ketone	28	10.7	11.7	263.0	Same	390±15	[c]800±250	[b]400±125	.040	.033	60
—COO—ester	44	8.2	15.2	326.6	Same	250±25	1250±150	[b]800±150	.047		80
—CN	26	[b]20.5	14.7	354.6	Same	525±50	[c]500±200	[b]550±200	.060		[b]80
—NO_2	46	[b]19.9	16.8			500±50	[c]400±50	[b]400±50	.055		[b]78
—NH_2 amine	16	[b]19.0	[a]10.54	226.6	Same	[b]300±100	[d]1350±200	[c,d]2250±200	.031		28
>NH amine	15	[b]3.6	[a]8.08	180.0	Same	100±15	750±200		.031	.024	37
—OH alcohol	17	[a]10.5	[a]8.04	225.8	171.0	250±30	[d]4650±400		.082		[b]18
—OH phenol	17							4650±500	.031		[b]3
$(—OH)_n$	17n					n(170±25)	n(4650±400)	[b]n(4650±400)			
—COOH	45	[b]23.5		276.1	Same	220±10	2750±250	[b]2250±250	.085		80
>—PO_4	95	[b]33	25.8	[b]660		950±400	2500±800				
>CO_3 cyclic	60	[b]34.2		[b]600		[b]725±25	[b]380±50				
—NH_2 amide	16	[b]25.1		326.9	Same	500±25	2700±550				

[a] Varies according to adjacent group energies.

[b] Based on too few data to be reliable.

[c] Unpublished IR data included in correlation.

[d] Data from reference 10 corrected to 25° C and $V\delta_P^2$ subtracted. (For important steric shielding effects, see tables 7.6 and 7.7, p. 205, ref. 10.)

[e] "Base value" of 135.1 must be added to $\Sigma V\delta$.

[f] "Base value" of 40 must be added to $\Sigma \Delta Vc$.

$$\delta_P \simeq \frac{18.3\mu}{V^{0.5}} \tag{4}$$

Equation (3) is not applicable to alcohols (ref. 5), but equation (4) fits them as closely as it does other compounds.

2.1.3 The Hydrogen-Bond Type of Components of Cohesive Energy

Hansen (ref. 5) designated the remainder of the energy as hydrogen bonding, but it is now recognized that it includes other forces. These are all similar enough to permit lumping them as the H-bond CED, which can be obtained by difference

$$\delta_H{}^2 = \delta^2 - \delta_D{}^2 - \delta_P{}^2 \tag{5}$$

This has resulted in a considerable number of values, consistent with each other but less satisfying than would be values obtained by independent measurements. The best known means for quantifying the H-bond is that of Gordy and Stanford, in which a small amount of a donor material is added to the pure liquid. A typical probe is methyl deuteroxide, CH_3OD. The change in O—D spacing is measured by IR spectroscopy. Unfortunately, this yields only a relative value, as each probe liquid requires a separate factor for conversion of the shift in wave number to absolute units. A second problem is selection of a baseline condition for the unperturbed probe molecule. While vapor phase readings would seem ideal, a dilute solution in a purely London-bonded liquid has experimental advantages.

Bagley (ref. 6) has recently described an experimental method that offers new help. By measurement of the internal pressure, he was able to obtain values for the sum of the London and Keesom cohesive energy densities, which removes some of the uncertainty from equation (3).

Table 2 lists values for the contributions of a number of groups to V, δ, δ_P, and δ_H. The δ and δ_P values follow the form set by Small (ref. 7), who showed that the best correlations could be obtained by

$$\delta = \frac{\Sigma(V\delta)_i}{V} \tag{6}$$

The actual $V\delta$ values shown are those of Hoy (ref. 8), who used a much larger data bank than Small. The $V\delta_P$ values were compiled from the experimental results of Hansen (ref. 5) and Beerbower and Dickey (ref. 4) and the tabulated dipole moments of McClellan (ref. 9).

The H-bond energies follow a different pattern. Both theoretically and from the uncertainties computed by both methods, these correlate best on a cohesive energy ($V\delta_H{}^2$) basis. The values shown are again from references 4 and 5, with some additional data from Bondi (ref. 10) and unpublished work by Beerbower and Elliott,[1] using an improved Gordy technique.

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[1] Beerbower, A.; and Elliott, J. J.: Unpublished data, 1969.

Because the contributions of δ_P and δ_H to ΔE_V have these different forms, accurate group contributions to δ_D are not easily tabulated. If the boiling point is not known, equation (2) cannot be used, and δ_D is best calculated by differences, as in equation (5).

It must be emphasized that the methods in this paper are not the best ones for precise calculations, nor are they the most soundly grounded in modern theory. They were selected on the basis of providing easy recognition of the roles of V and the three intermolecular forces in controlling liquid properties. They are also easily used for rough calculations, but caution must be exercised lest the oversimplifications spoil the result. These are most apparent in the V column, which should only be used when no better means are at hand.

What is available to those interested in serious pursuit of this branch of materials science is five books, authored by three physical chemists and three chemical engineers. Significantly, it is difficult to be sure in which of these disciplines any given author was trained, as all of them have tended to break down the fences.

Hildebrand and Scott began this process with a book, now in its third edition (ref. 2), which concentrates on solubility. The approach is semirigorous, with a number of approximations that are justified on pragmatic grounds. Their second book (ref. 11) is more rigorous and explores the consequences of the simplifying assumptions.

Bondi (ref. 10) is the third physical chemist of this team. His book appeared slightly after the second edition of Reid and Sherwood (ref. 12), and there was an effort on both sides to avoid overlap and conflict. Bondi's coverage of organic solids and glasses is unique and goes far beyond Hildebrand's interest in solids mainly as solutes. Reid and Sherwood ignore solids and are stronger on gases than the others, including liquid-gas interfaces.

Prausnitz' (ref. 13) approach is probably the most rigorous; he concentrates on those matters to which the corresponding states principle applies. Writing later, he was able to unify many points made by the others. He does not attempt to include solids or any interfacial phenomena.

The problem encountered on V is typical of those arising from different reference states chosen by these authors. Hildebrand tends to concentrate on 25° C and 1 atm; Bondi on 0° K; and the others on the critical point (T_c, P_c). In the case of V, the 25° C value creates a problem because group contributions to volume have consistent values only at points that are thermodynamically definable, such as 0° K, T_b, T_c, and probably T_g (the glass transition temperature). Bondi's V_w and the Lyderson ΔV_c from Reid and Sherwood are shown in table 2, but getting to 25° C from either or both of them is too complex. One minor complication is that, while $V_w = \Sigma V_{wi}$, $V_c = \Sigma \Delta V_{ci} + 40$. Fortunately, experimental values of V are so easily available that the problem rarely arises.

2.2 The Interactions of Liquids With Their Environment

The environmental capability of a liquid can be expressed in terms of its interactions. This may seem artificial and clumsy to those accustomed to another approach, but it has the potential of viewing all the limitations on a comparable basis rather than the customary hodgepodge of "flash, pour, seal-swell, and Ryder load." The possible interactions of a liquid are covered by the diagram in figure 3. The logical entry point is the simplest possible interaction, that of the liquid against itself under the influences of temperature and pressure.

2.2.1 Density

It is obviously ridiculous to predict the density of a liquid, which is available, because it is much easier to measure it. Traditionally, this is the first measurement any synthesist makes on a new product, which shows good intuition, because this leads to one of the key thermodynamic parameters, V. To reconstruct a density ρ at 25° C or predict that for a planned lubricant, calculate

$$\rho=\frac{\Sigma M_i}{\Sigma N_i V_i} \tag{7}$$

where ΣM_i is the molecular weight and $\Sigma N_i V_i$ is the sum of the group contributions to volume in table 2. Bondi (ref. 10), Reid and Sherwood (ref. 12), and Prausnitz (ref. 13) all provide more elegant solutions to this, but they are relatively complicated.

A very rough idea of the effect of each functional group on density can be obtained by dividing M by V, except for $V=0$ or less. A better way is suggested by some work by Bondi, who was frustrated by lack of V_c and T_c data and took another route (ref. 10):

$$\rho=\frac{MT_R}{V_c}+\frac{0.74M(1-T_R)}{V_w} \tag{8}$$

where 0.74 is the packing density at 0° K and T_R is that for the complete molecule at 25° C.

The results may seem rather trivial, as most chemists can recite from memory the effect on density of adding CH_3, F, I, or NO_2 to a molecule, but it is gratifying to see the success of this patched-together model.

2.2.2 Thermal Expansion

Unfortunately, table 2 is limited to the standard reference temperature of 25° C and hence provides no direct means for quantifying the expansion coefficient ($\alpha\equiv d(\ln V)/dT\equiv -d(\ln \rho)/dT$): Bondi (ref. 10) cites Wall and Krigbaum's equation

$$\alpha\simeq\frac{R}{\Delta H_v} \tag{9}$$

which may be computed from table 2 by the built-up equation

$$\alpha \simeq \frac{R}{RT+(\Sigma V\delta_i)^2/\Sigma V_i} \tag{10}$$

Bondi points out that α is widely but incorrectly believed to be constant with temperature. Actually, it is $\rho\alpha(=d\rho/dT)$ that is constant with temperature, so this may be more a useful property to compute. Differentiating equation (8),

$$\frac{d\rho}{dT}=\left(\frac{1}{V_c}-\frac{0.74}{V_w}\right)\frac{M}{T_c} \tag{11}$$

which gives some insight into the contributions of various groups. To design a lubricant for minimum expansivity requires maximizing T_c, which agrees with petroleum experience. Selection of groups to minimize the rest of equation (11) is less clear, especially since such changes affect T_c.

Thermal expansion is not very sensitive to structure; as implied in equation (10), the three sources of CED all participate equally and the situation is usually dominated by δ_D and V. The latter alone is sufficient if $\delta_p \simeq \delta_H \simeq 0$, as shown by the fact that the American Society for Testing and Materials (ASTM) (ref. 14) tabulation requires entry only of ρ at 60° F for any petroleum fraction.

2.2.3 Bulk Modulus

Wright (ref. 15) has provided a comparable model for the bulk modulus and its reciprocal, the isothermal compressibility, of petroleum fractions. He was able to show that the isothermal secant bulk modulus B_T, representing total change in volume between 0 and test pressure P, is a function only of pressure and density at test temperature and 1 atm. As noted in section 2.2.2, the density at any temperature may be obtained from the density at 60° F or any other reference temperature. Thus,

$$B_T \equiv \frac{P\rho}{\rho-\rho_0}=f(P,\rho) \tag{12}$$

where $f(P, \rho)$ is defined by figures 5 and 6.

The isothermal tangent bulk modulus K_T is defined as the rate of change of pressure with fractional volume

$$K_T=\frac{-V\,dP}{dV} \tag{13}$$

This can be approximated by the rule that K_T at any pressure equals B_T at half that pressure, though Wright gives a more accurate procedure (ref. 15).

Problems arise when nonpetroleum liquids are considered, but these are largely associated with long chains or with hydrogen bonds. Bondi (ref. 10) provides a special equation for polymers, but Wright found that small concentrations of polymer need not be taken into account so the Bondi equation is needed only for oils that are mostly polymeric; i.e., silicones.

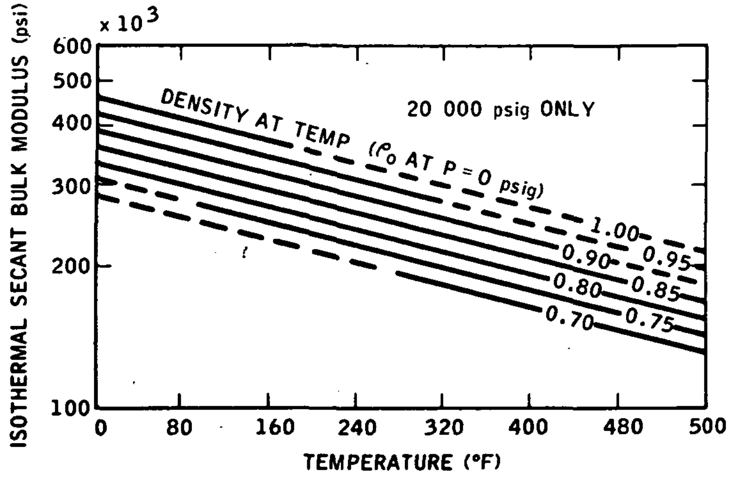
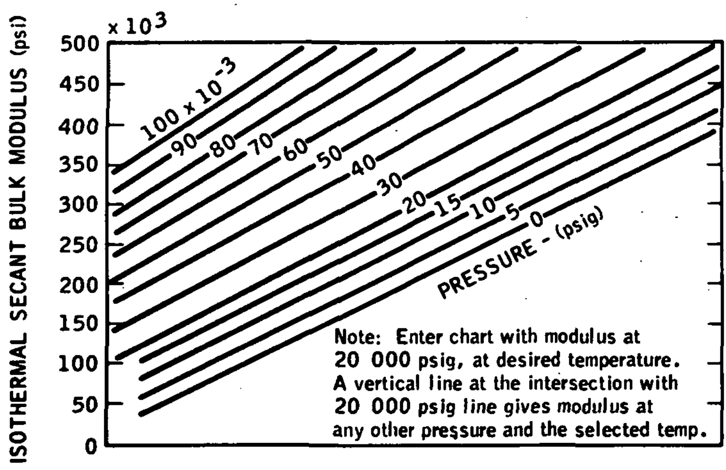


Figure 5.—Isothermal secant bulk modulus at 20 000 psig.



Note: Enter chart with modulus at 20 000 psig, at desired temperature. A vertical line at the intersection with 20 000 psig line gives modulus at any other pressure and the selected temp.

Figure 6.—Isothermal secant bulk modulus at any pressure.

Bagley (ref. 6) has recently shown that Hansen's H-bond energy is measured by the difference

$$\delta_H^2 = \frac{\Delta E_v}{V} - T\left(\frac{\partial P}{\partial T}\right)_V + P \qquad (14)$$

where $(\partial P/\partial T)_V$ is the thermal pressure coefficient at constant volume. This is equal to αK_T and $\Delta E_v/V = \delta_D^2 + \delta_P^2 + \delta_H^2$, so by combining and rearranging,

$$-K_T=\frac{P+\delta_D^2+\delta_P^2}{\alpha T} \tag{15}$$

This equation indicates that the H-bond energy contributes to K_T only through its effect on α. The reason for this appears to lie in the increase of the degree of polymerization of alcohols under pressure.

The most complex of the family is the isentropic or adiabatic bulk modulus K_s. While the isothermal versions are useful only when the pressure is applied slowly, as in high-pressure reactors or deep-sea exploration, K_s relates to the speed of sound U_s in the liquid by

$$K_s=\rho U_s^2 \tag{16}$$

For this reason it is useful in predicting the response time of hydraulic systems where a signal must travel some distance. It is interesting to note that the only bulk modulus ever recognized by ASTM (ref. 16) is K_s. Because designers tend to demand B_T values, which the chemists have laboriously computed from U_s, and then use B_T to recompute U_s, it appears that there is more waste motion in the information circuit than in the hydraulic loop.

The definition of K_s is

$$\frac{1}{K_s}=\frac{1}{K_T}+\frac{T(d\rho/dT)^2}{\rho^3C_p} \tag{17}$$

where C_p is the heat capacity of the liquid at constant pressure. This reintroduces some structural effects that will be dealt with in section 3.

2.2.4 Vapor Pressure

The absolute value of the vapor pressure may be obtained from table 2, but only by way of some other vaporization properties that are of equally great interest. As a start, the three parameters δ, δ_P, and δ_H and V should be computed. From these, δ_D is obtained by difference, and can be converted into T_c by means of figure 4 if this property is desired. The more useful T_b can be obtained from an equation derived from Burrell (ref. 17)

$$T_b=25\sqrt{563+0.080(3542+V\delta^2-V\delta_H^2)}-593 \tag{18}$$

unless T_b is available from experiment or literature. For lubricants other than petroleum, such information is very rare. For other methods, see Somayajulu (ref. 18).

This leads to a solution of the Clapeyron equation

$$\frac{d(\ln P_v)}{dT}=\frac{\Delta H_v}{T\Delta V_v}\simeq\frac{V\delta_D^2+V\delta_P^2+V\delta_H^2+RT}{RT^2} \tag{19}$$

By converting ΔH_v at 25° C from table 2 to that at T_b, the resulting Antoine equation is

$$\ln P_v = \frac{B}{T_b - C} - \frac{B}{T - C} \tag{20}$$

where

$$B = \frac{V\delta^2 + RT}{0.95R}\left(\frac{T_c - 273.2}{T_c - T_b}\right)^{0.38}\left(\frac{T_b - C}{T_b}\right)^2 \tag{21}$$

$$C = 0.19T_b - 18 \tag{22}$$

and P_v is the vapor pressure in atmospheres, as adapted from Reid and Sherwood (ref. 12).

Equation (20) provides a good computation model but is too complicated to be the basis for discussion of the separate effects of V and the partial parameters. The general picture may be seen by consideration of equations (18) and (19). These may be combined into an Antoine plot of $\ln P_v$ versus $1/T$, as in figure 7. Equation (18) shows that the boiling point is raised by increasing V, δ_D, and δ_P, but not by increasing δ_H. This may be

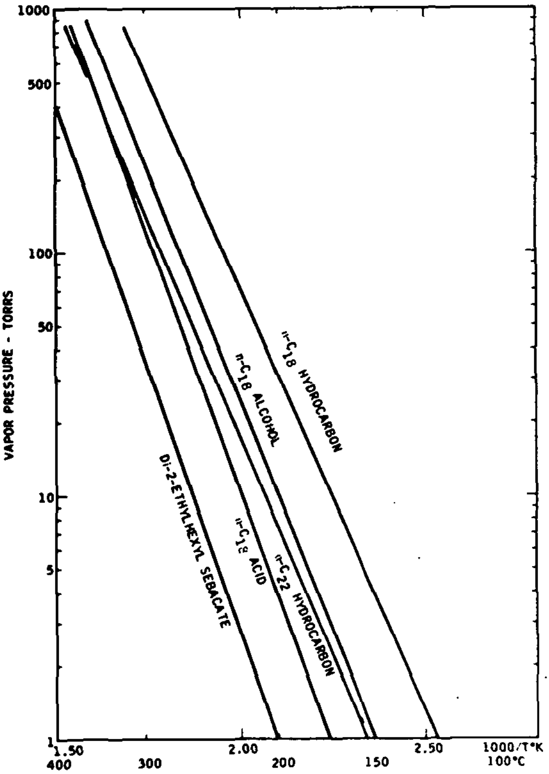


FIGURE 7.—Antoine chart for various prototype lube compounds.

an oversimplification, as it is based on Burrell's empirical corrections: "for alcohols add 1.4, for esters add 0.6, and for ketones boiling under 100° C add 0.5" to δ values calculated from T_b. For $V=100$ and $\delta_D^2+\delta_P^2=100$, these corrections average about the same as the $V\delta_H^2$ values in table 2. Thus, δ_H fails to contribute to T_b just as it does not contribute to bulk modulus.

The slope is predicted by equation (19) to increase with V and all three partial parameters. As this equation is only valid at the temperature (25° C) for which these four numbers are listed, and all four vary in different ways with temperature (ref. 19), it is unwise to draw detailed conclusions from figure 7. However, it is clear that using hydrogen bonding to control the vapor pressure of lubricants will be the least effective of the four possible ways.

The same reasoning applies to the evaporation rates. As shown by Coburn (ref. 21) and formalized in ASTM method D 2878, these two methods of expressing volatility are interchangeable, with due allowance for molecular weight.

2.2.5 Miscibility and Seal Swelling

The problem of solubility in nonelectrolytes was Hildebrand's principal target. While not properly an environmental problem, the compatibility of base stocks with one another and with the many additives included in finished lubricants should be briefly mentioned. This can be predicted by appropriate modification of Hildebrand's miscibility criterion (ref. 2), in which the entropy of mixing is equated to the heat of mixing. A further simplification can be made by assuming that the maximum temperature for miscibility T_M comes at 50 percent by volume of each component (1 and 2),

$$T_M=\frac{[(\delta_{D1}-\delta_{D2})^2+0.25(\delta_{P1}-\delta_{P2})^2+0.25(\delta_{H1}-\delta_{H2})^2](V_1+V_2)}{4R} \tag{23}$$

The 0.25 factors were empirically determined by Hansen (ref. 5) for a wide variety of solvents, polymers, and surfactants.

This work was applied by Beerbower and Dickey to the swelling of elastomeric seals (ref. 4). The equation for this phenomenon is a little different, as the restraint against infinite swelling is due to cross-linking of the polymer rather than entropy. As the volume increase Q approaches that at which all the slack is taken out of the polymer chains between cross-links Q_e, the work of swelling increases exponentially. Hence,

$$\log\frac{Q_e}{Q}=\beta V_1[(\delta_{D1}-\delta_{D2})^2+a(\delta_{P1}-\delta_{P2})^2+a(\delta_{H1}-\delta_{H2})^2] \tag{24}$$

where β is a factor depending on the elastomer and 1 and 2 refer to lubricant and elastomer, respectively. For vulcanized polyisoprene, $\beta V_1=0.08$

and $a=0.19$; the latter may simply represent a minor deviation from Hansen's 0.25.

One complication is that many elastomers are block copolymers or blended polymers that have been covulcanized. This results in having two sets of values for the partial parameters of the elastomer. In such cases, a graphical analysis must be substituted for equation (24).

2.2.6 Gas Solubility

The measurement of gas solubility has generated a surprising amount of literature in the past few years, especially in view of the fact that Prausnitz and Shair published an excellent predictive method (ref. 20) 10 years ago. In effect, their model required two steps. First, the gas was condensed to a hypothetical liquid at 25° C, which is actually far above its critical point, and 1 atm. This was then blended with the solvent in a manner analogous to equation (23). The basic method was limited to regular solutions in which for both gas and liquid $\delta=\delta_D$. Special methods were shown for polar gases, polar liquids, pairs forming temporary compounds, i.e., CO_2+H_2O, and for the light gases requiring substantial quantum-mechanics corrections, e.g., He, H_2, and Ne.

A special adaptation of this method to lubricants has been made and is awaiting publication as an ASTM method.[2] It differs from the original only in uisng δ_D for the lubricant, rather than δ, on the basis that the gases of interest are nonpolar. The basic equation is

$$\frac{1}{x_2}=\frac{f_2{}^L}{f_2{}^G}\exp\frac{V_2(\delta_{D1}-\delta_2)^2}{RT} \tag{25}$$

where x_2 is mole fraction of solute gas; $f_2{}^G$ is the fugacity of pure gas, equal to pressure in most cases; δ_2 is the solubility parameter of the hypothetical liquid (table 3).

Prausnitz provided a chart for estimating $f_2{}^L$, the fugacity of the hypothetical liquid, from P_c and T_R of the gas. For computation, this was fitted with two empirical equations:

For $T_R \leqslant 2.6$,

$$\log\frac{f_2{}^L}{P_c}=12.353T_R-8.494T_R{}^2+2.723T_R{}^3-0.3357T_R{}^4-6.3931 \tag{26}$$

For $T_R>2.6$,

$$\log\frac{f_2{}^L}{P_c}=0.5160T_R-0.1012T_R{}^2+0.1724 \tag{27}$$

Table 3 also lists V and δ_D parameters for some lubricants in which the nitrogen solubility has been successfully predicted by equation (25). The

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[2] Proposed Method for Estimation of Solubility of Gases in Nonpetroleum Liquids. Amer. Soc. Testing Mater., to be published.

TABLE 3.—*Liquid Volumes and Solubility Parameters for Gases and Liquids at 25° C*

Substance	V, cm^3/g-mol	δ, (cal/cc)$^{1/2}$
N_2	32.4	2.58
CO	32.1	3.13
O_2	33.0	4.0
Ar	57.1	5.33
CH_4	52	5.68
CO_2	55	6.0
Kr	65	6.4
C_2H_4	65	6.6
C_2H_6	70	6.6
Rn	70	8.83
Cl_2	74	8.7
Di-2-ethylhexyl adipate	399	7.4
Di-2-ethylhexyl sebacate	465	7.0
Trimethylol propane ester	477	7.2
Pentaerythritol ester	539	7.3
Di-2-ethylhexyl phthalate	377	8.1
Poly-(C_2F_3Cl)	[a] 770	7.0
Polyphenyl ether (4 ring)	373	10.0
Polyphenyl ether (5 ring)	430	10.0
Dimethyl siloxane	[a] 345	5.9
Methylphenyl siloxane	[a] 600	7.0

[a] These values are to be used regardless of the molecular weight.

volumes are needed to convert x_2 to more useful units. It should be noted that V values for polymers are to be used regardless of the molecular weight. These purely empirical values are based on the concept that the gas molecule can only interact with a certain volume of the polymer molecule. A sounder approach, based on the entropy of mixing, is under development.

3. EMPIRICAL PROPERTIES

There are a number of properties listed in table 1 that are dependent on intermolecular interactions but which do not fall into the neat pattern so far discussed. They are purely physical but depend on details of structure to such a degree as to eliminate all hope of a rigorous solution. Even for pure compounds, the task would be sizable, and for mixtures it would be hopelessly complex. As a compromise, empirical methods have grown up, most of which follow essentially thermodynamic models with adjustable parameters.

3.1 Heat Capacity

Thermodynamics denotes the amount of heat needed to raise the temperature of a mole of liquid 1° at constant volume, C_V, as being fairly accessible to rigorous treatment. However, the heat capacity at constant pressure C_p is almost universally the value desired, and it is more difficult to evaluate, although

$$C_p - C_V = TVK_T\alpha^2 \tag{28}$$

This relationship, combining the uncertainties of C_V, K_T, and α, is not very precise. Bondi (ref. 10) gives a detailed analysis of the various oscillations and rotations involved in C_V. This includes a table of dipole orientation energies similar to table 2 in general nature, but by no means compatible with it, and a table of group contributions to the heat capacity of the ideal vapor. Table 4 shows some group contributions to C_p (ref. 10). From these, it is possible to deduce that δ_P always makes a substantial contribution to C_V and hence to C_p, while the contribution of δ_H is less noticeable. Since Bondi lists nine methods, ranging from crude to quite precise, there does not seem to be much justification for further work, but if anyone desires to do so, C_p could probably be computed from table 2. ASTM D 2766 provides a standard method for ΔC_p (ref. 21).

TABLE 4.—*Group Contributions to Heat Capacity at 20° C*

Group	Contribution, cal/g-mol-°K
H— (formic acid and formates)	3.55
CH_3—	9.9
—CH_2—	6.3
$\diagdown$ —C—H $\diagup$	5.4
—COOH	19.1
—COO— (esters)	14.5
$\diagdown$ C=O $\diagup$	14.7
—CN	13.9
—OH	11.0
—NH_2	15.2
—Cl	8.6
—Br	3.7
—NO_2	15.3
—O— (ethers)	8.4
—S—	10.6
C_6H_5—	30.5

3.2 Thermal Conductivity

There is much less theoretical background on thermal conductivity in liquids, though Reid and Sherwood (ref. 12) cite several good models for gases. Bondi (ref. 10) devotes an entire chapter to liquids but is not able to establish a simple general rule. This arises from the fact that nonassociated liquids can transfer heat only by interchange of translational and rotational energies, while associated, i.e., H-bonded, liquids have what amounts to a parallel pathway in which the heat of association is also being transferred by an essentially independent mechanism.

For nonassociated liquids, the dense-gas correlation cited by Reid and Sherwood (ref. 12) could be used, but it involves several properties that are not readily accessible. Bondi adapts this idea to his special reduced parameters and arrives at a linear equation with two empirical constants

$$\lambda=\frac{3.20\times10^{-20}}{V_w^{2/3}}\left(\frac{E^\circ}{M}\right)^{1/2}-\frac{8.70\times10^{-20}cRT}{V_w^{2/3}(E^\circ M)^{1/2}} \tag{29}$$

where V_w is the van der Waals volume, E° is the standard energy of vaporization at $V=1.70\ V_w$, and $c=1/3$ of external degrees of freedom. Values of V_w can be built up from table 2. The variable E° is not listed in table 2 but is roughly proportional to $V\delta^2$, and c may be taken as 2 for rigid molecules and somewhat higher for elongated ones.

Equation (29) establishes linearity of λ with T, at least up to about $T=0.9T_b$, where the well-known anomalies surrounding T_c begin to appear. This is a very valuable contribution, as the literature contains a great deal of questionable data. Jamieson and Tudhope (ref. 21) surveyed the matter up to 1963 and found about one-third of the values to be outside the ±5-percent limits they considered borderline for acceptability. This did not include screening against equation (29), but "consistency of data" was one of their five criteria. Hopefully, the new ASTM D 2717 Method (ref. 21) will help to avoid generating further erroneous data.

The decision as to when equation (29) is not applicable involves three criteria including $T>0.9T_b$. For aliphatics of $T_b<100^\circ$ C (up to octane), special constants are required. These two points are academic to the lubrication engineer. The problem of flexible molecules responsible for the T_b anomaly also causes trouble in certain elongated lubricant molecules. Of these, polyphenyl ethers are especially troublesome, with a reversal of slope reported (ref. 23). Other data obtained by the method used have not been very precise, so there is room for doubt here. A special formula, developed for polymer melts, is suggested for such cases as long-chain esters, silicones, etc.

The third criterion, deciding when a liquid is sufficiently associated to justify addition of a nonlinear term, can be satisfied by three subcriteria, all of which must be met: The alternate path must be by H-bonds; the association must be 20 to 80 mol percent; and in our symbols, $V\delta_h^2>2RT$.

On this basis, any experimental data on liquids other than water, glycerol, glycol, etc., that is nonlinear with temperature must be considered suspect.

Bondi considers one empirical model worthy of reference (ref. 24), but it is too complex to offer any insight into the roles of δ and M. In general, it may be said that λ shows the responses forecast by the two terms in equation (29), with due allowance for the fact that the first term will be about twice the second at $T_R \simeq 0.5$, a typical situation for lubricants. This is because the first term represents λ at $V = 1.70 V_w$, and the difference at T_c will be λ for the vapor. As a result, the response to δ is positive but not very strong, while the response to M is negative and fairly strong.

The temperature dependence $d\lambda/dT$ is dominated by dV/dT, and tends to parallel it, though this is by no means evident by differentiating equation (29). Bondi offers the empirical relationship

$$\left(\frac{\partial \ln \lambda}{\partial T}\right)_p = 1.35 - 2.7\alpha \tag{30}$$

which implies that $d\lambda/dT$ becomes negative at low temperatures. This has been verified experimentally. He also cites

$$\left(\frac{\partial \ln \lambda}{\partial P}\right)_T \simeq \frac{2.15}{K_T} \tag{31}$$

as empirically correct though not in agreement with theory.

3.3 Freezing Point

Surely the most frustrating of all these semithermodynamic properties is the freezing point T_m. It has a clear-cut basis in that

$$T_m = \frac{\Delta H_m}{\Delta S_m} \tag{32}$$

where ΔH_m is the heat of fusion, and ΔS_m is the entropy of fusion.

As Bondi points out, ΔH_m is roughly proportional to the heat of sublimation ΔH_s, which equals the sum $\Delta H_v + \Delta H_m$. Thus, the first problem lies in evaluating ΔS_m, which "is essentially a function of the number of different positions a molecule can occupy in the liquid as compared to the solid state. Hence, ΔS_m is small for spherical rigid molecules and large for anisometric flexible molecules," and T_m responds inversely. He proceeds to establish a set of rules, rather intricate but logically consistent, for various types of nonpolar molecules ranging from the simplest diatomic gases up through the complications of linear molecules of high flexibility.

Before discussing these rules, it seems wise to review briefly the concept of entropy, which seems to become less understood with each passing year. Not only was it poorly taught in the 1930's and 1940's, resulting in lapses of memory, but it has also grown in breadth and depth since then. The simplest concept is of a well-insulated gearbox, which receives 20 J of work on the input shaft in a brief period and delivers only 19 J from the output shaft. Where is the missing joule? It is still in the box, as frictional heat, but no longer available because it is now 0.239 cal at essentially ambient temperature T. The change in entropy, $\Delta S = 0.239/T$, is a standardized measure of its unavailability.

From the gearbox to a steam engine that takes in 0.478 cal of heat at high temperature T' and produces 1 J of work is a rather large step, but not a great strain on logic. The byproduct is the same, 0.239 cal of unavailable energy at ambient temperature T, and again $\Delta S = 0.239/T$. In current terminology 0.478 cal of enthalpy (ΔH) has become 1 J of free energy (ΔG) and 0.239 cal entropic energy ($T\Delta S$).

The next step is not so easy to accept, but the logic is perfect. The gearbox is an irreversible process, while the steam engine is reversible, except for frictional losses. Both have their counterparts on the molecular scale. As an irreversible process, consider mixing two kinds of molecules, different in size, shape, or both. This might be compared to a macroscale process such as buttering bread, easier to do than to undo. The result can be expressed as a change in entropy of mixing, the use of which is discussed below.

The reversible process, however, is the real source of a whole set of relations such as equation (32), covering entropy of vaporization and surface formation as well as freezing or fusion.

Returning to Bondi's rules, the first is that all first-order crystalline transitions must be included in the melting process, and $\Delta S_{m,\mathrm{tr}}$ is so defined. The second is that ΔS_m consists of two parts; $\Delta S_m{}^v$ is due to change in volume, and $\Delta S_m{}^j$ to fusion at constant volume. He avoids the term "configurational entropy of fusion" for the latter, as it popularly implies (wrongly) that this portion is calculated by molecular theories.

$$\Delta S_m{}^v = \alpha K_0 \, \Delta V_m \tag{33}$$

where K_0 is K_T at zero pressure. Subtraction of this from $\Delta S_{m,\mathrm{tr}}$ permits examination of $\Delta S_m{}^j$ alone.

A lengthy process of analysis results in the equations in table 5, which need be entered only with the number of carbon atoms per molecule N_c to yield $\Delta S_{m,\mathrm{tr}}$. All the constants are empirical, and some are more trustworthy than others, but at least a solid base has been provided. The next step is to introduce the effect of certain groups within the nonpolar structure, and Bondi goes through olefins, noncondensed aromatics, and tetraalkyl metals.

The strong dipole interactions have the effect of reducing hindrance to internal rotation and simultaneously hindering external rotation, so the net effect must be obtained. Using a homomorph approach more direct than that discussed above, Bondi simply subtracts ΔS_m for a specific

TABLE 5.—*Equations Relating the Total Entropy of Fusion of Long-Chain Compounds to the Number of Carbon Atoms per Molecule* [a]

Homologous series[b]	Formula
n-Paraffins (N_c = even)	$\Sigma\Delta S_{m,tr}/R=0.80+1.33N_c$
n-Paraffins (N_c = odd)	$\Sigma\Delta S_{m,tr}/R=1.10+1.18N_c$
2-Methyl-*n*-alkanes	$\Sigma\Delta S_{m,tr}/R=-1.24+1.2N_c+20/N_c^2$
2,2-Dimethyl-*n*-alkanes	$\Sigma\Delta S_{m,tr}/R=-6.26+1.33N_c+83/N_c^2$
n-Alkyl-cyclopentane	$\Sigma\Delta S_{m,tr}/R=-5.1+1.30N_c+131/N_c^2$
n-Alkyl-cyclohexane	$\Sigma\Delta S_{m,tr}/R=-6.3+1.45N_c+56/N_c^2$
n-Alkyl-benzene[c]	$\Sigma\Delta S_{m,tr}/R=-5.6+1.18N_c+100/N_c^2$
n-Alkane thiols (N_c = even)	$\Sigma\Delta S_{m,tr}/R=3.3+1.2N_c$
n-Alkane thiols (N_c = odd)	$\Sigma\Delta S_{m,tr}/R=3.90+1.33N_c$
n-Alkyl bromide (N_c = odd)	$\Sigma\Delta S_{m,tr}/R=2.4+1.38N_c+0.54/N_c^2$
n-Alkanoic acid (N_c = even)	$\Sigma\Delta S_{m,tr}/R=-2.56+1.33N_c+36/N_c^2$
n-Alkanoic acid (N_c = odd, >5)	$\Sigma\Delta S_{m,tr}/R=-2.7+1.25N_c$
Na-*n*-alkanoates (N_c = even)	$\Sigma\Delta S_{m,tr}/R=-6.6+1.35N_c$

[a] Generally not valid for the first 2 members of the series.

[b] The available data for 1-alkenes and 1-alkanols are too irregular (and probably unreliable) for representation.

[c] The datum for ethylbenzene is appreciably higher than predicted by this equation.

TABLE 6.—*Entropy of Fusion Correction Due to the Presence of Polar Groups* [a] [b]

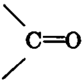
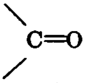
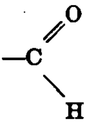
Polar group	Functional group	Correction [c]
Aliphatic ether	—O—	[d] −0.5 ±0.1
Aliphatic thioether:		
n-alkyl	—S—	[e] −1.0 ±0.5
sec-alkyl		
one		0.85±0.2
both	—S—	1.0
t-alkyl	—S—	−0.3 ±0.2
Aliphatic and diaromatic ketone		−1.5 ±0.1
Quinone		−0.7 ±2
Aliphatic aldehyde		0.8 ±0.3

TABLE 6.—*Entropy of Fusion Correction Due to the Presence of Polar Groups* [a] [b]—Concluded

Polar group	Functional group	Correction [c]
Aliphatic ester	$-O-\overset{\overset{O}{/\!/}}{C}-$	
Aliphatic alcohol	One OH group per molecule	-1.2 ± 0.2
Aliphatic primary amine	$-NH_2$	0.9 ± 0.3
Aromatic amine (unhindered)[f]	$-NH_2$	0.3
Aliphatic and aromatic secondary amine	$>NH$	-0.9 ± 0.1
Monocyano alkane	$-C \equiv N$	0.7 ± 0.2
Dicyano alkane	$-C \equiv N$	-1.8 ± 0.1
Alkane amide	$-\overset{\overset{O}{/\!/}}{C}-NH_2$	-0.5 ± 0.1
Alkane thiols	$-SH$ (N_c = even)	1.0 ± 0.2
	(N_c = odd)	1.8 ± 0.1
Secondary alkane thiols	$-SH$	0.25 ± 0.15
Tertiary alkane thiols	$-SH$	1.2 ± 0.5
Dialkyl disulfide	$-SS-$	-1.2
Dialkyl or diaryl sulfone	$-SO_2-$	3.3 ± 0.3
Heterocyclic sulfone	$\diagdown\ \diagup$ SO_2	-1.4

[a] Weighted to emphasize extrapolation toward $N_c > 3$.

[b] For details on haloalkanes, see table 6.20, ref. 10.

[c] In units of R.

[d] This is the most common value; a range *trans* −1.4 (vinyl and ethyl ether) to +0.2 (1,4-dioxane) is found with lesser frequency.

[e] Very irregular.

[f] Hindered primary amine = −0.9.

homomorph from that of the compound. There is no need for T_R, as both are measured at their melting points. His corrections for polar and H-bond groups are shown in table 6.

Obviously, this system has a few loose ends, and Bondi discusses them very frankly. The reader is advised not to plunge into calculations without reading his work thoroughly. One major gap, for the present purposes, is that he presumes T_m to be known and hence does not undertake to predict ΔH_m. As pointed out at the beginning of this section, it tends to parallel ΔH_v, so hope for a solution from δ_D, δ_P, and δ_H is not unreasonable.

If the freezing points of pure compounds are difficult to predict, it might appear that those of mixtures would be nearly impossible to handle. Actually, the problem is relatively easy, and the van't Hoff equation, which first appeared in 1887, requires only minor adjustments to solve many cases, if the higher of the two freezing points is known. This is because mixed freezing points depend on the relatively well-understood solubility phenomena.

In lubricants, three types of cases commonly arise: (1) miscible liquids depositing immiscible crystals, (2) miscible liquids depositing "solid solution" crystals, and (3) miscible liquids depositing addition compounds. If the liquids separate before freezing, there are several other cases but these will not be considered.

For case 1, Hildebrand gives

$$-\ln x_2 = \frac{\Delta H_{m2}(T_{m2}-T)}{RT_{m2}T} + \frac{V_2\phi_1^2(\delta_2-\delta_1)^2}{RT} + \phi_1\left(1-\frac{V_2}{V_1}\right) \tag{34}$$

where x_2 is the mole fraction of the solid in solution.

The first term is the entropy of fusion of the solid ΔS_{m2}, adjusted to the actual temperature T but with the terms involving the change in heat capacity on fusion ΔC_p omitted as an approximation. Near $x_2=0$, $\phi \simeq 1$ and the temperature gradient dT/dx_2 depends primarily on ΔS_{m2} and secondarily on the nonideality correction $V_2(\delta_2-\delta_1)^2$. A third dependence is on the entropy of mixing $\phi_1\ [1-(V_2/V_1)]$. To summarize, the effect of a small addition of a high-melting component on the first crystal formation, i.e., cloud point, is minimized by it having a small ΔS_{m2} and by close matching of δ_D, δ_P, δ_H, and V.

The eutectic temperature T_e may be estimated by simultaneous solution of the pair of equations

$$\ln(1-x_2)_e = \frac{\Delta S_{m1}}{R}\left(\frac{T_{m1}}{T_e}-1\right) \tag{35}$$

$$\ln(x_2)_e = \frac{\Delta S_{m2}}{R}\left(\frac{T_{m2}}{T_e}-1\right) \tag{36}$$

While petroleum lubricants are usually so nearly ideal mixtures that eutectics are not significant, substantial lowering of the freezing point of synthetics by blending is a common practice; e.g., mixed terphenyls.

3.4 Viscosity and Viscosity Index

Early work on correlating viscosity with structure was frustrating, and so were attempts at a purely thermodynamic approach. It has only recently become evident that part of the trouble was the lucky accident that so much data was fitted so well by the completely empirical ASTM (or Walther) equation

$$\log\log\left(\frac{\eta}{\rho+0.6}\right) = m\log\left(\frac{1}{T}\right)+k \tag{37}$$

where η is the viscosity in centipoises and η/ρ is the kinematic viscosity in centistokes. (The term "absolute" is controversial, as is the European term "dynamic," so in this paper "viscosity" without any adjective will be used for centipoises.) This form of equation has no logical connection with the thermodynamics of flow, but its widespread use in the form of the ASTM D 341 charts (ref. 21) will make it hard to displace.

Appeldoorn (ref. 25) reviewed the situation on empirical relationships, and concluded that Roelands' version (refs. 26 and 27) may prove even more satisfactory in fitting a wide range of lubricants. It covers the variation not only with temperature but also with pressure, and in addition shows a correlation against the percentage of total carbon atoms in aromatic C_A and naphthenic C_N rings. His general equation is

$$\log \eta = \frac{A_0}{T^x} + C\frac{P^y}{T^x} + DP^y + B_0 \tag{38}$$

where A_0 and B_0 are empirical constants characteristic of the liquid, $C = A_0/P_p^y$, $D = (B_0 - \log \eta_p)/P_p^y$, P_p is the pole pressure at which all the lines converge, and η_p is the viscosity at this pole.

The relation to composition is limited to petroleum products and uses a number of empirical constants. However, it is worthy of reporting here as an example of what can be done on a less than fundamental basis. Roelands (ref. 26) illustrates this for the pressure part of the equation by

$$\log (y - 0.890) = 0.00855(C_A + 1.5C_N) - 1.930 \tag{39}$$

$$P_p = 500 \frac{500}{(C_A + C_N + 27.5)^{1/y}} \tag{40}$$

$$\log \eta_p = \frac{-114}{C_A + 1.5C_N + 27.5} \tag{41}$$

No method for computing x is given because Roelands found that a constant value of $x = 3.5$ gives very satisfactory results for the oils studied, even at pressures up to 3000 atm.

Despite the sweeping generality of the Roelands equation, it still has little relation to thermodynamics. Bondi (ref. 10) points out that a more logical form was proposed 50 years ago by Vogel, though he could not at that time give any physical meaning to its three adjustable parameters. Various efforts since then have brought it to the form

$$\ln \frac{\eta}{\rho} = \ln \frac{A + E'}{T - T_0} \tag{42}$$

where A is an empirical constant depending on the liquid, E' is the energy of activation independent of temperature, and T_0 is the reference temperature, related to the glass transition T_g.

While this has a better foundation than equation (38), its application to petroleum is less well worked out. Bondi (ref. 28) made a vigorous effort to relate viscosity to molecular structure by means of equation (42). Though he met with considerable success above T_b, the region between T_g and T_b proved to be relatively difficult. The best correlating parameter was the reduced form of the equilibrium glass transition temperature, $5cRT_0/E^\circ$, but the relationship between T_0 and T_g remains incompletely resolved. If N_c is greater than 15 and the molecules are aliphatic or cyclic with unbranched side-chain lengths of more than 4 atoms per chain, then T_0 is about $0.8T_g$. To quote, "Even that covers a range and can be related only very approximately to currently known structure parameters, primarily the number of external degrees of freedom per unit volume." In addition, hydrogen bonding presents special problems that will have to wait for better data. Of course, the reader can pick out a good many semiquantitative rules from his analysis, and in his book (ref. 10) these are made more accessible. Thus, anyone wishing to design a lubricant from first principles will get a good deal of help but not quantitative predictions.

Appeldoorn (ref. 25) offers a few suggestions on the effects of structure on the temperature and pressure coefficients: "Straight-chain, flexible molecules have low coefficients; bulky, branched and rigid molecules have high coefficients." He cites extensive studies in this area, in addition to reference 28.

In view of the lack of success of many sophisticated attempts to produce a unified structural explanation of viscosity, it is evident that the final model will have to be complex, nearly to the point of being useless. Viscosity is affected by both the intermolecular forces of section 2 and every possible sort of intramolecular force so far considered.

The problem of blending, as with freezing point, was solved long ago. Almost any model will do; the Walther function [log log $(\eta/\rho+0.6)$] gives quite good results, and Bondi's partly completed $5cRT_0/E^\circ$ functions also can be used satisfactorily. Even the viscosity loss due to dissolved gas has been successfully predicted (ref. 29).

3.5 Work of Adhesion to Metals

The ability of a lubricant to resist being wiped off the bearing is obviously important. This is usually described in terms of contact angle (ref. 30), which is unfortunate as most lubricants show zero contact angle on the surfaces they are to lubricate. Except for some rare cases of autophobic liquids that cannot spread on their own monolayers, liquids which ball up on the surface are generally nonlubricants. Even worse, it is frequently stated that all solids on which a given liquid shows a contact angle of 0° have the same work of adhesion to it, because this work is calculated for nonwetting liquids as $\gamma_1(1+\cos\theta)$, where γ_1 is the surface free energy of the liquid and θ the contact angle. The fallacy of using this expression for wetting liquids was exposed long ago by Philipoff (ref. 31) and more recently by Gans (ref. 30). Their method for estimating the work of adhesion by extrapolation from contact angles of nonwetting liquids is shown in figure 8. The results must be used with some caution as the data were obtained by Bernett and Zisman (ref. 32), on metals that had been polished under water and hence were both oxidized and hydrated. However, they do compare favorably with older data obtained in vacuum.

Means for estimating γ_l from table 2 was published by Beerbower (ref. 40) who showed that for most organic liquids,

$$\gamma_l = 0.0715 V^{1/3} \left[\delta_D^2 + 0.632(\delta_P^2 + \delta_H^2)\right] \tag{43}$$

where 0.0715 includes the fraction of bonds cut by the liquid surface slicing across the octahedral space occupied, on a time-averaged basis, by a liquid molecule. This can be broken up into the partial free energies required for the Fowkes model of wetting (ref. 34), though there is some lack of numerical agreement on

$$\gamma_l^d \simeq 0.0715 V^{1/3} \delta_D^2 \tag{44}$$

Fowkes' polar surface tension corresponds roughly to

$$\gamma_l^p \simeq 0.0451 V^{1/3} (\delta_P^2 + \delta_H^2) \tag{45}$$

but might well be further subdivided. Corresponding values for the bear-

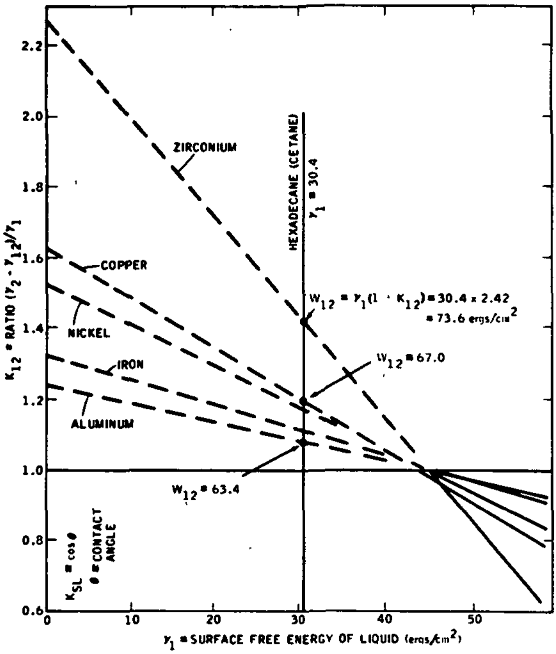


FIGURE 8.—Zisman-Gans plot of wetting power of organic liquids on metals (at relative humidity of 0.6 percent).

ing surface, $\gamma_2{}^d$ and $\gamma_2{}^p$, are difficult to obtain and impracticable to precompute. However, his equation for the work of adhesion W_{12} has yielded the useful information

$$W_{12}=2[\sqrt{\gamma_1{}^d\gamma_2{}^d}+\sqrt{\gamma_1{}^p\gamma_2{}^p}] \tag{46}$$

A different approach was taken by Hansen (ref. 35) who plotted δ_p and δ_H of a number of probe liquids on the surface and drew a circular contour line through all those just wetting. A further adaptation of this, to drawing the circle through borderline coefficients of friction, was worked out for polyethylene at various levels of surface sulfonation (ref. 36). This method of plotting gives a center of interaction located at δ_{D2}, δ_{P2}, and δ_{H2} and hence may be used in a work of adhesion:

$$W_{12}\propto 0.0715(\delta_{D1}\delta_{D2}+a\ \delta_{P1}\delta_{P2}+a\ \delta_{H1}\delta_{H2}) \tag{47}$$

Presumably this should eventually include the correction for molar volume disparity,

$$\Phi=\frac{4(V_1V_2)^{1/3}}{(V_1{}^{1/3}+V_2{}^{1/3})^2} \tag{48}$$

by Good (ref. 37), who prefers to build up his own equivalent of table 2 from other parameters and is very cautious about his ability to predict works of adhesion at solid-liquid interfaces.

Zadumkin (refs. 38 and 39) attempts to simplify the whole problem to essentially electrostatic attraction:

$$W_{12}=B\,\frac{\epsilon-1}{\epsilon+1} \tag{49}$$

where B is a constant for any given metal that is proportional to its contact potential against a hydrocarbon. His supporting evidence on liquid gallium and mercury looks favorable, though some nonconforming data are discarded on the basis of "impure liquids." He probably has justification for this screening, as such impurities taint the whole history of interfacial energies. The writer has shown (ref. 33) that B must vary with temperature to avoid a second-law violation and used equation (49) to explain the formation of multilayers of stearic acid (ref. 41) but has some reservations about describing a liquid with ϵ alone.

Despite the fragmentary state of this phase of the work, it appears that high values of V, δ_D, probably δ_P, and perhaps δ_H will lead to high values of W_{12}. Presumably this will at last quantify lubricity, where this is used as the modern equivalent of oiliness. Other usage of this word implies that chemical reactions are involved (see secs. 4.1.3 and 4.2.4) so still more parameters will be needed to eliminate that controversial word.

Up until recently, it has been taken for granted that high W_{12} values are an unmitigated blessing, but Rounds (refs. 42 and 43) has shown that some additives that enhance boundary lubrication can have adverse effects on ball bearing fatigue. Unfortunately, his tests were conducted without controlling the humidity. High humidity promotes fatigue, presumably through hydrogen embrittlement (ref. 44), so Rounds' case is incomplete, but there is another reason to believe his conclusion is correct. The standard Griffith equation for the minimum force L_0 to propagate a crack of length l in a solid is

$$L_0^2 \propto \frac{E\gamma_2}{l} \tag{50}$$

where E is the Young's modulus and γ_2 the surface free energy of the solid. For submerged solids, $\gamma_{12}(=\gamma_1+\gamma_2-W_{12})$ must replace γ_2, tending to lower L_0. Data on crystalline materials certainly bear this out (ref. 45), while data on glass usually take the opposite trend, quite unexpectedly, since equation (50) was basically derived from glassy concepts. It is to be hoped that some way around this conflict of interest can be found, but for the moment it appears that increasing W_{12} to protect gears, etc., entails some risk of decreasing L_0 on ball bearings in the same housing.

4. CHEMICAL PROPERTIES

In comparison with the abundant work of the materials sciences people, the crop of prediction methods from those studying chemical interactions with the environment seems scanty. However, it must be remembered that there are a limited number of chemical reactions that can be expected from lubricants, except those used in the chemical process industries which are outside the scope of this paper. The reactions which have been sufficiently studied to justify inclusion are thermal and radiation decomposition, hydroperoxide oxidation, oxidative dehydrogenation, flash and explosivity, autogenous ignition, and corrosion. Each of these categories must be subdivided into catalytic and noncatalytic, but not all of these subdivisions can be discussed in any meaningful way.

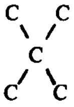
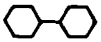
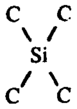
4.1 Thermal Decomposition

As implied in the above list, thermal decomposition will be discussed as it takes place under inert atmospheric conditions. The careless use of the term "thermal stability" to mean "catalytic oxidation and corrosion resistance at elevated temperatures" is a deplorable instance of language pollution. The reaction is basically homogeneous when noncatalytic; the effects when catalyzed are more difficult to classify. Radiation is handled simply as a special case of thermal stability.

4.1.1 Noncatalytic Thermal Stability

This is commonly measured in the isoteniscope, recently standardized as ASTM D 2879. Table 7 shows some typical results. Strictly speaking, only the decomposition point column relates to D 2879, which defines this as

TABLE 7.—*Effect of Chemical Structure on Thermal Stability*

Weakest links	Activation energy, kcal/mol	Decomposition point, °C
CH_2—CH_2	57.6	350
	67.6	330
	65	455
CH_2—CH_2—O—CO—CH_2	45.0	275
CF_2—CF_2—O—CO—CF_2	60	310
	65.7	350

the temperature T_D at which the rate of pressure increase $(\Delta P/\Delta\theta)$ is equivalent to 500 torr in 10 hr.

The activation energy is obtained by continuing the test beyond the decomposition point, as described in the appendix of the ASTM method. The slope of the plot is then converted to an apparent activation energy (E') by the Arrhenius equation

$$\ln \frac{\Delta P}{\Delta\theta} = \ln A' - \frac{E'}{RT} \qquad (51)$$

where A' is proportional to the frequency factor or Arrhenius constant.

Blake (ref. 46) has done a great deal of work to elucidate the effects of various structures on A and E, with the specific objective of designing more thermally stable molecules. A molecule tends to fail at its weakest link, so those containing combinations of the groups shown have the lowest T_D values possible. If two groups fail at nearly the same T_D, the D 2879 result tends to be blurred. Several general rules supplement table 7.

(1) Branched chains tend to be less stable than straight ones, due to steric crowding and the production of relatively stable free radicals.
(2) Aromatic C—H and C—C bonds are strengthened by resonance.
(3) Ordinary esters fail by a special mechanism in which the β-hydrogen of the alcohol attacks the C=O group to form a quasi-6-member ring, which decomposes to olefin and acid. Esters without β-hydro-

gen are not subject to this and show T_D values as high as the corresponding hydrocarbons.

(4) Cyclohexane rings are more stable than alkane chains and may even surpass aromatic rings.
(5) Ether groups decompose to an alkane and an aldehyde or ketone, but unsubstituted aromatic ethers cannot follow this route and so resemble polyphenyls.
(6) Even one methyl group is enough to destabilize the polyphenyl ethers, by about 65° C, and multiple substitutions cause further decrease due to more decomposition sites.
(7) NH groups fail by a low-energy path, but in N—CH_3, etc., this is blocked.

Work by Klaus (ref. 47) added another rule,

(8) Polymers with an all-carbon backbone have a sort of "zipper" structure and revert to monomer or dimer at about 275° C. Oligomers tend to follow the same path, and hydrogenation does not "lock the zipper."

When the 455° C limit of the polyphenyls is passed, lifetime lubrication ceases to be feasible. However, as implied in figure 1, glass molding at 480° C on the mold and 1000° C on the glass is being lubricated. More recently, continuous casting of steel at 200° C on the mold and 1200° C on the steel has been added. These jobs depend upon rapid renewal of the lubricant film, and the fact that the E values are low enough to fit the cycle time. For glass, this is about 1 sec, and the lubricant has a safety factor of 20 or more.

4.1.2 Radiation Stability

The effect of radiation, as briefly mentioned above, resembles a rather special form of thermal decomposition. A high-energy (0.5 to 10×10^6 eV) photon or particle enters the liquid. If a single atom absorbed all this, it would acquire kinetic energy equivalent to about 10^{10} degrees Celsius. Such total absorption is rare, and energy transfers often run about 1 percent per atom struck. The secondary radiation from a primary impact is considerably milder, ranging down to very-short-wavelength ultraviolet. Each impact, according to the Compton principle, tends to produce two photons or electrons of about half the incoming energy so that near the end of the process, the original photon might have generated 10^6 more photons, each of about 1 eV. After that, chemical action ceases and the photons end as entropic heat.

Regardless of the type of molecule involved, the first 10^4 or more impacts will tend to rip out the hydrogen or carbon atom struck, leaving an ionized gap. It makes a great difference which is struck in terms of subsequent events. Hydrogen removal merely creates a free radical and some hydrogen gas, but striking a carbon causes scission if a linear molecule is involved. The two fragments are also radicals; they may cool off to olefin or combine into tar. If air is present, they may initiate autocatalytic oxidation reactions. The products are thus different from those of thermal cracking, which tends to generate one olefin and one saturate.

Cyclic molecules tend to be more resistant, as the two hot ends are kept together and healing can take place. In aromatics, there is additional protection because the ring is elastic enough to store moderate energy long enough to dissipate it without scission.

There is no threshold below which radiation damage is completely healed. In general, the integrated dose in ergs per grams is a true measure of the damage regardless of whether initiated by a high- or low-energy photon or electron. However, the measurability of the damage tends to increase more or less exponentially with the integrated dose. Thus, a linear molecule often shows little or no detectable damage at 10^8 erg/gm and yet is distinctly degraded at 10^9 erg/gm, while an aromatic would show the same effects at about 100 times the dose.

As in a thermal decomposition, the weak parts of a molecule fail first, and alkylated aromatics tend to show the response of the alkyl groups. However, there are no special traps such as the β-hydrogen or zipper polymers to be feared.

4.1.3 Catalytic Thermal Decomposition

Lubricants seldom encounter catalytic cracking in the ordinary sense because oxides and silicates require temperatures of 400° C or more. However, some interactions with metals are now becoming recognized as a factor in lubricant failure, and these fall within the complex discipline known as catalysis. Blake (ref. 46) conducted tests with 52100 steel present and noted a loss of 35° to 60° C in T_D for three esters. Klaus (ref. 47) has done a great deal of this work, using the MIL–H–27601A stainless steel pressure cylinder, with balls of M–10 tool steel, 52100 steel, and naval bronze which have been HCl washed and dried. His work tends to confirm that catalysts decrease T_D for esters but shows little difference from the D 2879 all-glass method on well-refined hydrocarbons.

An interesting further analysis can be made of his data on a more or less homologous series of five superrefined oils of various molecular weights. He analyzed the data on a constant frequency constant A of 10^{13}, but if instead it is analyzed on the basis of a constant E value of 63 000 cal/mol (the mean of the data), A becomes a function of the molar volume V so that

$$\ln \frac{\Delta P}{\Delta \theta} = 49.2 + 0.0014V - \frac{63\,000}{RT} \tag{52}$$

This indicates that frequency of scission per unit volume is the variable, and hence that large molecules are less stable than small ones. This will be further considered in section 4.4.

There is a special feature of the lubrication process that may bring out effects not ordinarily observed. It is the vigorous wiping action that not only exposes fresh surfaces, but goes further and activates them with dislocations. The effect of freshly cut metal is not at all like that of the usual metal specimen that is isolated from the oil by a layer of hydrated oxides.

Two phenomena are known to take place. With aliphatic hydrocarbons, the primary process is dehydrogenation (ref. 48). This may take two, four, or even more hydrogen atoms away from the molecule, leaving a multiradical that tends to polymerize. The hydrogen soaks into the metal; it may contribute to hydrogen embrittlement and fatigue failure, though only on the harder steels (ref. 49). Under some conditions, the dehydrogenation is so complete as to form a cementite (Fe_3C) layer on the metal surface (ref. 50).

Aromatic hydrocarbons follow a different path, according to Goldblatt (ref. 51). The primary process is electron acceptance to form anionic radicals. These may discharge their energy to aliphatic molecules, leading to polymer formation; be quenched by O_2, H_2O, or heteroatom organic impurities, or combine with the metal to form unstable compounds that later dump the metal as semicolloidal wear debris.

Due to the newness of these concepts, no predictions can be made as to the interactions of nonhydrocarbon molecules, except that many of them would fall in the category of quenching agents for the anionic radicals.

The effect of polymer may sometimes be helpful, as discussed below, but it can also, and more often, form harmful deposits (ref. 52). Carbide formation certainly is not beneficial, as Fe_3C is quite brittle and abrasive.

No catalytic effects of metals have been reported in radiation decomposition. This may be partly due to the fact that metals resemble radiation in their effects and even emit electrons similar to β-particles from freshly deformed surfaces. The effects would thus be simply additive rather than catalytic.

4.2 Oxidation Phenomena

As mentioned above, there are several oxidation processes, most of which must be considered from both noncatalytic and catalytic viewpoints. The two processes that take place without flame should be considered separately from the others, as they tend to overlap for a certain temperature interval.

4.2.1 The Hydroperoxide Reaction Without Catalyst

The phenomenon of low-temperature oxidation of aliphatic structures (ref. 53) has been so well studied that only token mention will be made of this process. The typical result of a series of reactions is represented by

$$R\text{—}CH_3+1.5O_2 \rightarrow R\text{—}CH_2OOH+O \rightarrow R\text{—}COOH+H_2O \qquad (53)$$

Side reactions on CH_2 groups produce ketones, and aldehydes may also be formed. The resulting mixture has a fruity odor that is quite characteristic.

4.2.2 The Catalyzed Hydroperoxide Reaction

While thermal stability tests run in inert vessels can usually be correlated with the more realistic catalyzed situations, this is by no means true of oxidation. One reason is that catalysis of thermal decomposition takes place mainly at the metal surface. This heterogeneous catalysis involves only a few steps. Oxidation depends quite heavily on homogeneous catalysis, in which dissolved metal is the main accelerating factor. This type of reaction is basically simpler, but many complications arise in the processes of dissolving the metal and then losing it again into sludge. In a classic paper, Thompson (ref. 54) studied the interaction of copper with transformer oils and air. The results of seven series of increasingly sophisticated experiments could be correlated into one line by a corresponding-test-conditions principle. This is less basic than the corresponding states of section 2, but it served to unify about 80 points, some of which represented means of as many as 36 separate determinations, from several laboratories. Other tests in which he deviated from corresponding conditions fall off the line in the appropriate direction. The correlating equation is

$$\log A_S = 1.15 \log A_I - 0.31 \qquad (54)$$

where A_I is the acidity or sludge due to solid metal catalyst in 164 hr at 100° C and A_S, that due to 5 ppm of dissolved copper in 164 hr or to 5 ppm Cu+5 ppm Fe in 48 hr, at 110° C.

All Thompson's oils were without additives but contained varying amounts of aromatics and heteroatom compounds. It is probably safe to say that his conclusion is generally valid, and hence that the rate of oxidation is directly proportional to the amount of metal in solution at any instant. It should be possible to write a model equation based on rate of solution and rate of loss of metal as sludge, both as functions of the acidity already produced, but that is outside the scope of the paper.

When antioxidants, metal deactivators, and other additives are used, as is almost always the case, except in electrical oils, modelmaking would require more terms and is hardly worth trying. It is probable that the interaction terms would dominate the result, which leads to a very important point: Tests run without appropriate additives and environment are worse than useless.

The ranking of metals as catalysts for this reaction is based on their ability to alternate between two valence states, thus serving as a very active link in a chain reaction. Copper is at the top of the list, by any of the many criteria; cobalt, manganese, iron, and lead follow in about that order, based on equal concentrations in solution. These effects are subject to great variations due both to the lubricant composition and the surface condition of the metal. Alloys may behave as if composed of 100 percent of the catalytic metal in some cases (Cu in monel), or proportionate response (Cu in brass), or totally concealed (Fe in 300 series stainless steel). The responses seem to follow the Gibbs principle of the surface of a mixture presenting the composition that minimizes the free energy of the system. However, there does not seem to have been any detailed study of this. This situation is complicated by the three kinds of freezing noted just above equation (34), metals being especially prone to form addition compounds.

The effects of temperature and pressure are readily predictable if done on an induction period basis. This is illustrated in figure 9, where the behavior of a pure compound, an uninhibited petroleum oil, two oils A and B with antioxidants, and an inhibited oil with catalyst are illustrated at the same temperature T. The induction period θ_i is the vital parameter. The dangerous fallacy of testing to a constant time is shown by oils A and B. If examined at θ_1 or at θ_2, oil A will be given the better rating, but actually oil B is superior if the oxidation level A_1 represents the point at which serious metal damage starts, usually the widely accepted rejection criterion of 2.0 mg KOH per gram of oil neutralization number. Thompson was fortunate that he was using uninhibited oils, as his sampling was too infrequent to give accurate values of either θ_i or the time to reach A_1.

If a suitable test method is used, such as ASTM D 943 (iron and copper

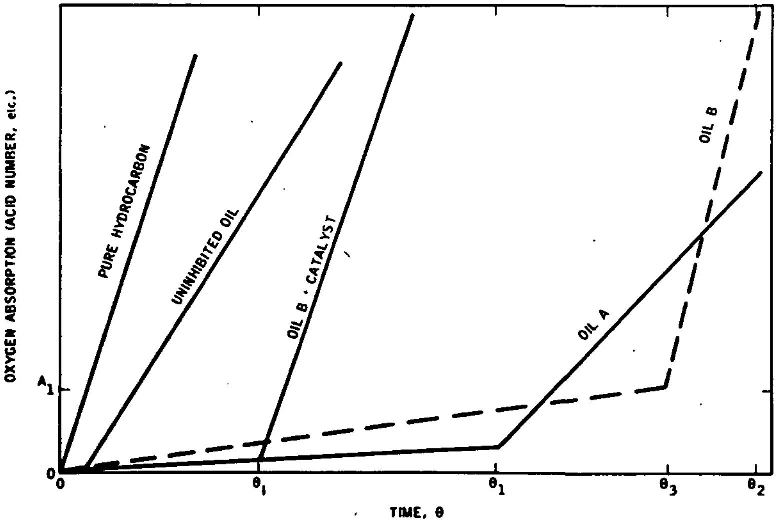


FIGURE 9.—Idealized oxidation models.

catalysts, water, oxygen at 1 atm, and 95° C) or ASTM D 2272 (copper catalyst, water, oxygen at 14.3 atm, and 150° C), θ values are acquired for A_1, which may be taken as an approximation of θ_i. There are a great deal of data, not yet properly assembled, which show that θ_i is inversely proportional to the partial pressure of oxygen and follows an Arrhenius equation, doubling for every 10° C decrease in temperature. Combining these, the induction period at T_2 and P_0 is

$$\theta_i = \theta_0 \frac{0.210}{P_0} \exp\left[-33\,500\left(\frac{1}{RT_1} - \frac{1}{RT_2}\right)\right] \tag{55}$$

where θ_0 is the induction period at T_1 in air and P_0 is the partial pressure of oxygen.

Not much can be offered in the way of correlations with chemical structure. The above discussion was based on typical petroleum lubricants, more or less well refined. There is no distinction among normal, iso, and cycloparaffins in this respect, but aromatics require special attention. Those with one ring must be further subdivided into those that include a hydrogen in the benzylic position and others. The others behave like the aliphatics, but the benzylic groups are extremely difficult to inhibit and tend to poison any mixture in which they constitute even a few percent. The fused-ring aromatics tend to have inhibitive properties, in addition to having inherent oxidation resistance unless heavily alkylated. The heteroatom molecules are so many and complex that they have still not been classified in this way, but it appears that some are oxidation catalysts, others are inhibitors, and many are neither. The same applies to synthetic lubricant molecules, past, present, and future. The chain-linked aromatic hydrocarbons and ethers share many of the properties of the fused-ring type. Perfluoro compounds are, of course, free from the hydroperoxide reaction but have troubles all of their own.

4.2.3 Dehydro-Oxidation Without Catalyst

A second oxidation process competes with the hydroperoxide mechanism. It may be typified by

$$4R-\mathrm{H}+\mathrm{O}_2 = 4R^* + 2\mathrm{H}_2\mathrm{O} = 2R\text{—}R + 2\mathrm{H}_2\mathrm{O} \tag{56}$$

and might be loosely described as a combination of thermal decomposition, with oxygen as the catalyst, followed by prompt oxidation of the hydrogen. The free radicals can discharge their energies in all the usual ways but tend most frequently to end by polymerizing, first to thickened oil, and then to sludge. A great deal can be learned about this reaction from the asphalt industry, where products are customarily thickened by air blowing at 225° C. It is hard to draw any sharp line between the hydroperoxide and this free radical mechanism, but the former may be considered dominant from 25° to 175° C, and the latter above 215° C.

This is not the place to discuss additives, but it should be mentioned that the phenols and aromatic amines that are so effective at lower temperatures often become substantial contributors to high-temperature sludge. These peroxide destroyers seem especially prone to dehydrogenation. The radical-quenching inhibitors are a much more miscellaneous collection of chemicals.

4.2.4 Catalytic Dehydro-Oxidation

Predictably, the metal catalysts tend to reinforce and extend the temperature range of this reaction. When the metal is freshly deformed, this mechanism can prevail even at 25° C. Because the catalysis is heterogeneous, the free radicals tend to deposit on the metal in the form of polymers, just as under inert conditions. However, the process in the presence of oxygen is many times faster than without, and the results are extremely common. On the harmful side is a series of films known as lacquer, varnish, and coke, formed at increasing temperatures. What forms at relatively low temperatures is a material originally known as friction polymer. It was first recognized and named by Hermance and Egan (ref. 55), who found it on noble-metal electrical contacts as a high-resistance deposit. Subsequent work has shown that a related surface resin can be beneficial in lubrication (refs. 33 and 51). Because it forms in the vicinity of wear spots as a thick liquid that subsequently polymerizes to a resin, perhaps "wear oligomer" would have been an appropriate name, but "surface resin" appears quite descriptive. It is believed to alleviate wear by filling in the antiasperities, which causes increased hydrodynamic lift and relieves the load on the asperities. It has long been recognized that successful break-in sometimes involves a sort of "glaze"; this is now believed to be surface resin at its hardest and best.

The composition of this material has been reported by Fein and Kreuz (ref. 56) and confirmed in our laboratory. It contains a substantial amount of oxygen as CO and CO—O groups and up to 3 percent of nitrogen. As the latter must have come from the air, and as even pure aromatics are split into aliphatic chains, it is evident that very high energy is involved.

Time has not permitted an extensive investigation of the effects of changing metallurgy on the beneficial results of surface resin. However, the original data (ref. 55), plus some confirmatory work by Dietrich and Honrath-Barkhausen (ref. 57), have been analyzed. Two steps were taken that may startle the catalyst workers, but which seem justified. Based on some correlations by Bond (ref. 58), it was assumed that the A constant in equation (51) was independent of the metal and that the activation energy E was a function of γ_2, the surface free energy of the metal. The resulting correlation is shown in figure 10 and in the equation

$$\log r = 7.3 \times 10^{-7} \gamma_2 RT - 6.85 \qquad (57)$$

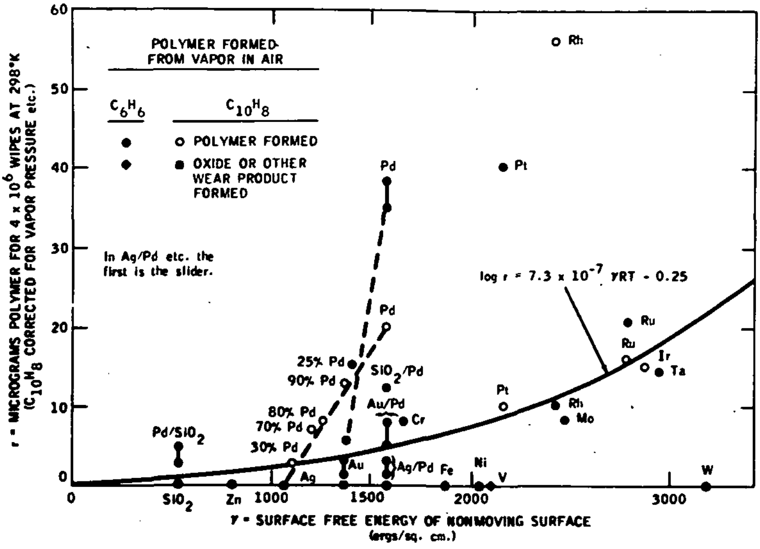


FIGURE 10.—Correlation between polymer formation and surface free energy.

where r is the rate of polymer formation in μg per wipe of the contacts. It is somewhat presumptuous to include T, as all the data were obtained at 25° C, but analogy to the much simpler reactions cataloged by Bond tends to justify this step.

The bulk oil also undergoes polymerization, just as happens without catalyst. While there are many other points of difference, it may be postulated that the clearest postreaction distinction between the hydroperoxide and dehydro reactions is that the main result of the former is acidity, and the latter, viscosity increase. Sludge may arise from secondary reactions in either case. If, as frequently happens, acidity and viscosity increase together, mixed modes are to be suspected.

Structuring to resist catalytic dehydro-oxidation is difficult because all hydrocarbons are subject to it. Perfluorination or the use of free radical trapping additives appear to be the best routes available.

4.2.5 Catalytic Oxidation With Radiation

There is little to add since the previous publication (ref. 1), so figure 11 is reproduced from it without change. The technique was a modification of ASTM D 943, run without water to permit the use of higher temperatures than the standard 95° C. Results from the latter may be entered at the point marked by "+" to estimate the combined effects of temperature and radiation. Two points are made in figure 11, the first being the way that radiation rate and temperature may be interchanged one for the other. The second is that lubricants are insensitive to radiation doses that

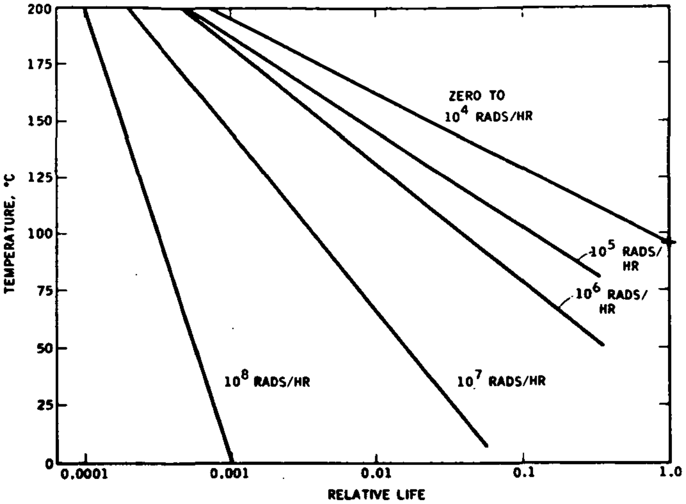


FIGURE 11.—Effects of radiation and temperature on life of turbine oils.

would kill a human in about 30 sec, so in any part of a powerplant visited by personnel special lubricants are not required.

4.2.6 Effects of Water and Humidity

The ubiquitous presence of moisture makes it hard to find cases in which it is absent, especially because it is a primary product of oxidation by both equations (53) and (56). However, it has long been known that there is a difference between dry and liquid H_2O present, especially in the presence of catalytic metals. It may be presumed that water serves several roles, one of which is to facilitate solution of the metal into the homogeneous catalyst situation. Very recently, Vaessen and de Gee (ref. 59) have thrown some light on the intermediate situation by pointing out that each metal has a critical relative humidity (RH) above which it or its corrosion products maintain a film of liquid water. This would help to account for some anomalies that have been only vaguely reported. Much more work is needed in this 50- to 95-percent RH area.

4.3 Flashpoint and Explosivity

Work by Affens (refs. 60 and 61) has shown that the various flashpoints have a rational basis. However, his data are limited to fuels, and no comparable correlations have been published on lubricants. Some years ago, the writer (ref. 62) undertook to establish the relations among the ASTM D 1160 distillation under reduced pressure, the vapor pressure, and the ASTM D 972 evaporation rate. The literature search uncovered work by Dreisbach (ref. 63), who had already correlated the Cleveland open cup flashpoint by ASTM D 92 with vapor pressure for a number of classes of compounds, as shown in table 8. With this encouragement, the writer then proceeded to correlate the D 92 flashpoint T_F and D 1160 temperature for 5 percent distilled at 10-torr pressure T_{b5} on a total of 50 lubricating oil base stocks. Flashpoints ranging from 190° to 580° F were successfully included in the equation

$$T_F = 0.924T_{b5} + 9.62 \tag{58}$$

with a correlation coefficient of 0.996. This gives an equivalent reproducibility of prediction of 26° F, compared with the single-test reproducibility of 30° F (ref. 21). As a result of these three separate studies, a few rules can be laid down with considerable confidence:

(1) The flashpoint (D 92) of lubricating oils comes at the temperature for 5 percent distilled at 10-torr pressure.
(2) This is essentially as predicted by Dreisbach, so his other values in table 8 should apply to lubricants.
(3) Raoult's law blending, as discussed by Affens, gives good predictions for the 10-torr temperature, and hence the flashpoint, for hydrocarbons.
(4) The lower flammability limit F_L and the flashpoint are two expressions of the same phenomenon.

TABLE 8.—*Estimation of Flashpoints*

Family	Formula	Vapor pressure at flashpoint (torrs)	Accuracy
Benzenes with saturated side chains	C_nH_{2n-6}	8	Close
Benzenes with unsaturated side chains	C_nH_{2n-8}		
Alkylchlorobenzenes	$C_nH_{2n-7}Cl$	10	Very close
Dichlorobenzenes	$C_nH_{2n-8}Cl_2$	25	Very close
Monochlorobenzene	$C_nH_{2n-7}Cl$	16	Exact
Naphthalenes	C_nH_{2n-12}	10	Close
Phenylethyl alcohols	$C_nH_{2n-6}O$	13	Close
Phenols	$C_nH_{2n-6}O$	10	Close
Aromatic amines	$C_nH_{2n-5}N$	8	Close
Aliphatic hydrocarbons	C_nH_{2n+2}	6 to 10	Approximate
Aliphatic alcohols (C_1 to C_5)	$C_nH_{2n+2}O$	40	Approximate
Aliphatic alcohols (t–C_5 and C_6)	$C_nH_{2n+2}O$	15	Approximate
Aliphatic ketones	$C_nH_{2n}O$	10	Very close
Aliphatic esters (T_b<80° C)	$C_nH_{2n}O_2$	40	Approximate
Aliphatic esters (T_b=80 to 120° C)	$C_nH_{2n}O_2$	25	Approximate

(5) The fire point by D 92 corresponds to 20 torr at 5 percent evaporated on lubricating oils. There is reason to hope that this correlation is as good as that on flash, allowing for the difference in standard deviations of testing (ref. 21).

(6) The upper flammability limit F_U is estimated, on a similar basis to that used by Affens, to represent 6 percent (volume or mole) of vapor in the space above the liquid. At 1 atm, $P_v = 45$ torr for this condition.

In regard to rule (3), the reader must be warned that any blends not essentially all hydrocarbon may show very marked deviations from Raoult's law. In such cases, both Hildebrand (ref. 2) and Prausnitz (ref. 13) give methods for calculating the fugacities from the V and δ values. However, many of the worst deviations come from blends involving alcohols, where flashpoints up to 15° F below that of the lower component have been observed. Fortunately, alcohols are not often major components in lubricant blends. If they are required, three-parameter equations must be used.

Rule (4) requires some consideration of the four flashpoint methods, because it can strictly be true of only one. Affens gave this matter a great deal of thought and selected the Tag closed cup (ASTM D 56). This is eminently logical and proper, but bad news to the lubrication engineer who thinks only in terms of D 92. As implied in rule (1), D 92 correlates with the vapor pressure at 5 percent off. This is the reason that many years of study have never produced a valid correlation of the closed cup tests D 56 and D 93, with the open cup tests D 92 and D 1310. Pure compounds may generate one correlation line, but mixtures must generate a whole series of lines whose spacing is a function of the initial slope of the distillation curve $dT_b/d\phi$, where ϕ is the volume fraction evaporated. However, since most of the loss takes place in the last few minutes of heating, while P_v is between 0.25 P_F and P_F, the vapor pressure for flashing, and the evaporation rate $d\phi/d\theta$ for a given geometry and ventilation is proportional to $P_v\theta$, the lines should be parallel.

This being the case, the writer has found that inquiries as to P_v and the flammability limits are best handled with dual answers. The questioner is asked to decide between the closed system regime, in which all vapor is retained, and the open system in which 2 to 5 percent of weathering off may be anticipated. Almost all engineers have expressed their need for open system data, though a number have also collected the other just for information. This is gratifying, because most lubricant test methods relate to open system, including the open cup flash and fire tests, ASTM D 972 evaporation and D 1160 distillation. The latter specifically forbids collecting data before 5 percent has distilled and references an article in which initial boiling points by D 1160 were shown to be highly inaccurate. Our problems clearly are different from those of the fuel and solvents people, who seem to need closed system data. The only closed system methods designed to provide both fuel and lubricant data are ASTM D 93 flashpoint by Pensky-Marten closed cup and D 2879, vapor pressure by isoteniscope.

In view of this reference, coupled with the much greater capability of the lubricant makers to supply open system data, the writer decided to limit this discussion to flammability limits as measured by D 92, D 972, D 1160, and D 2878. This is the philosophy expressed in rules (4) and (6), which cover the flammability limits at 1 atm. The effect of changing air pressure can readily be computed. The two vapor pressures are first converted to mole fractions by dividing by 760 torr; the lower limit, $x_L = 0.013$, and the upper limit, $x_U = 0.060$. These are then multiplied by the prevailing pressure to yield the two pressures, P_L and P_U, which are converted to temperatures by equation (20) or, more simply, by a Maxwell chart (ref. 64) that expresses the same facts. The results are shown in figure 12.

These correlations are based on the premise that the lubricant maintains its chemical integrity. If this is not true, due to oxidation or thermal decomposition, other rules apply. When T_D is reached, $F_U \simeq T_D$.

4.4 Autogenous Ignition

Several different ignition phenomena may be grouped under the general term "autogenous," which simply means that no pilot flame is required to touch off a self-sustaining reaction. These phenomena are only related to that extent, as they proceed by very different mechanisms.

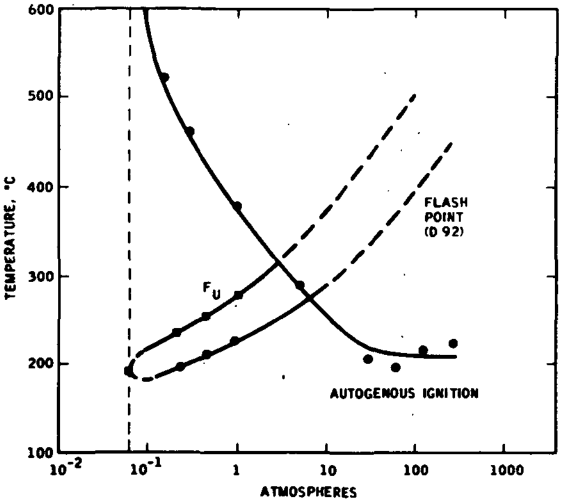


FIGURE 12.—Effect of air pressure on turbine oil.

4.4.1 Spontaneous Combustion

There seems to be some degree of confusion over the old problem of oily rags that, left too long in a heap, have been known to heat up and burst into flame with disastrous results. The problem is real, but much of the concern is not necessary as this reaction is quite specific to paintmaking oils such as tung and linseed, which are characterized by conjugated double bonds. This phenomenon was intensively studied many years ago, and a method developed for measuring the heating tendency. The Mackey test, now out of print, involved soaking a wad of cotton in the suspected oil, wrapping it around a thermometer bulb and passing a stream of oxygen past it. If no spontaneous rise took place from room temperature, the whole apparatus was slowly warmed until it started or 100° C was reached. No oil that would be classed as a lubricant ever failed the Mackey test; but the supposition that rags saturated with lubricants are dangerous certainly contributes to better housekeeping.

4.4.2 Autoignition Temperature

A second phenomenon, which does involve hydrocarbons, is a serious concern to both fuel and lubricant experts. This takes the form of a flame arising, without any source, when an oil is injected into a heated vessel containing air. Affens (ref. 65) did a good deal to elucidate the effects of structure on the autoignition temperature (AIT) of fuels.

His results may be summarized by listing the factors favoring resistance to autoignition: decreasing chain length, addition of methyl groups and branching, alicyclic rather than straight chain, aromatic better than alicyclic, and freedom from side chains on aromatics.

This list has a good deal in common with the results in section 4.1. Except for addition of methyl groups and branching, which clashes with Blake's list but was not found to be important by Klaus, these effects are precisely what one would expect if autoignition is preceded by thermal decomposition. Unfortunately, it is difficult to compare Affens' data on C_6 to C_{10} *n*-alkanes with equation (51); but his increase of 20° to 25° C in AIT over that range of molar volumes is quite in line.

While there are undoubtedly similar structural effects in lubricants, they tend to be mingled in a confusing way in such large molecules. As a general observation, there seems to be a fair degree of correlation with thermal decomposition temperature, so the AIT tends to be about 40° C above the result of ASTM D 2879. This may not be applicable to all types of lubricants, but it would indicate that decomposition is a necessary first step on mineral oil. As a result, the AIT's of most well-refined petroleum lubricants tend to cluster around 375° C. Higher molecular weight oils tend to be a little lower. Synthetics vary so much that discussion of structures and mechanisms will be omitted.

The technique for AIT has long been ASTM D 286, using a small quartz flask. This was replaced by an improved version, D 2155, in 1966. Both of these methods have been criticized because of wall effects, known and suspected, due to the use of small flasks. A new method, D 2883, called the reaction threshold temperature (RTT), was introduced in 1970. It uses a much larger (1000 cm^3) flask, which may be stainless steel to permit running RTT at up to 10 atm. It is too soon to state whether the improvements anticipated will all be realized.

Previous work at pressures other than 1 atm has largely been done by Zabetakis (ref. 66). Some of his data, on a typical steam turbine oil, are shown in figure 12 along with the flammability envelope on the same oil. While Zabetakis drew this particular curve with minimum at about 70 atm and justified this on the basis that *n*-propyl nitrate also shows a minimum (ref. 67), all of his other data show a regular decrease of AIT with increasing pressure.

4.4.3 Impact Sensitivity

A rather specialized oxidation mechanism is associated with aerospace, where liquid oxidizers are commonly handled in equipment, some of which must be lubricated. The test consists of submerging a standard volume of lubricant in the oxidizer and dropping a 20-lb weight on it. The maximum height for no reactions from 20 drops is known as the threshold in ASTM D 2512, originally limited to liquid oxygen, but now extended to include liquid fluorine, nitrogen tetroxide, etc. A different philosophy is expressed in appendix III of D–2—1969, in which the reaction intensity is measured at a standard drop height of 43.3 in.

All hydrocarbons and many other synthetics fail these tests, and little has been learned about structural effects in the perhalogenated lubricants that pass. It is not likely that any correlations with other oxidation tests will be possible.

5. STRETCHING THE ENVIRONMENTAL CAPABILITY OF LIQUID LUBRICANTS

The U.S. Air Force recently sponsored two studies on what factors in lubricants represent the main barriers to further improvements in aircraft (refs. 68 and 69). Both came out with essentially the same conclusions, that the weakness lies in thermal and oxidation stability, with an accompanying need for higher AIT. Both studies point out that this could be alleviated by improvements in thermal conductivity and heat capacity, but no amount of improvement in λ and C_p will help enough to avoid higher engine temperatures. Other physical properties were also subject to improvement, but not in any pressing need of it. On the other hand, improvements in stability that adversely affect thermal properties, vapor pressure, viscosity at low temperatures, or density would be of questionable value. Bulk modulus and gas solubility were not specifically considered. Bearing life and gear load capability had to be considered in terms of overall design plus lubricant improvements; significant results were found, but the current state of lubrication theory made it impossible to assign separate credits.

Thus, it appears that the burden lies largely on the lubricant manufacturer to increase the thermal decomposition temperature, the AIT, and oxidation resistance. The first two were shown above to be intimately related and probably will have a common solution. The third, viewed as primarily high-temperature oxidation by the free radical mechanism, also shows strong symptoms of being initiated by decomposition. This is indicated best by the resistance of aromatics, as well as other lesser evidence. If this is indeed the case, the problem becomes one of maximizing thermal stability without impairing the physical properties. Obviously, this has been tried hundreds of times, but perhaps new insight into what all the effects are that a given change would produce will aid in planning for a minimum of dead ends. A few guidelines might be—

(1) Low molar volume minimizes the exposure to thermal damage but raises the vapor pressure.
(2) Strong dipoles will lower the vapor pressure, but hydrogen bonds will not.
(3) Dipoles may raise the glass transition temperature T_g a little, but if molar volume is kept low, T_g will approach the freezing point T_m.
(4) Low melting point in such a molecule as described calls for an extraordinary amount of ΔS_m because ΔH_m will be raised by the dipoles.
(5) The presence of hydrogen is highly detrimental, and it should be replaced with fluorines, at least in the most vulnerable positions, plus chlorines to provide polarity.
(6) If the resulting liquid fails to lubricate, interdisciplinary work with metallurgists and bearing designers is strongly recommended.

6. CONCLUSION

It is evident that liquids have solved lubrication problems in the past on a trial-and-error basis solely because they had far greater potential than was realized. The present situation marks the end of such good fortune, and further improvements will depend on thorough ability to predict the interactions in figure 3, lest a fortune be spent in half-blind searching. Help must be drawn from the chemical engineers, the paint and adhesive experts, the ceramicists, the metallurgists, and other materials scientists for the time when an uneasy alliance of organic chemists and mechanical engineers could make progress by trial and error is now ended.

ACKNOWLEDGMENT

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DISCUSSIONS

F. T. Barwell (University College of Swansea, Swansea, England)

While sympathizing to some extent with Mr. Beerbower's view that "the time when an uneasy alliance of organic chemists and mechanical engineers could make progress by trial and error is now ended," one must acknowledge a great deal of achievement attributable to those workers who have overstepped the bounds of their initial discipline and have cooperated with men from other fields of study to develop the subject of tribology. If what the author means is that chemists and engineers must themselves acquire the outlook of tribologists, I must agree with him.

In common with other authors in this symposium, Mr. Beerbower has been set a difficult task of dealing with a specific topic, in his case liquid lubricants, which must however be set within the context of the total tribological system, which embraces the complete machine element as affected by the thermal and dynamic duties imposed thereon. In figure 3 he has resolved this problem by taking the lubricant as his standpoint and considered the manner in which it reacts with other elements of the tribological system. In section 4 the importance of specific reactions with the surfaces are illustrated by the case of friction polymers. These may be beneficial by limiting corrosion and facilitating lubrication or they may be harmful as in microelectrical contacts where tarnish films may inhibit proper functioning. Closely allied to the friction polymers are the degradation products that cause lacquering of engine pistons. Similarly, in a study of the temperature limitations of the lubrication of ball bearings with inner-race-located separators, it was observed that failure was due to polymer-type deposits that were similar in appearance to the lacquering of pistons and piston rings and that eventually filled the space between the separator and the locating land on the inner ring leading to failure. In supplementation therefore of his treatment of the crucial problem in the formulation of liquid lubricants, namely, their thermal and oxidation stability, perhaps Mr. Beerbower would indicate the extent to which basic chemical structure can determine the nature of the degradation products. In the last resort it is the nature of the degradation product that may determine whether or not failure of the mechanism will occur. Solid carbon or polymers are disastrous, whereas a substance that degraded to give off a gaseous decomposition product would be entirely acceptable.

Regarding collaboration between different disciplines, the contribution of Professor Lamb, an electrical engineer, at this symposium is worthy of mention. Most chemists and engineers tend to think in terms of steady-state solutions, whereas the electrical engineer has to face up to transient conditions involving both resistance and reactance, two terms governing effects that are related by a 90° phase lag. Therefore in considering what happens in a tribological contact, particularly under concentrated elastohydrodynamic (EHD) conditions where the time scale is exceedingly short, any elastic or Hookean strains will be in quadrature with the viscous or Newtonian deformations. Therefore the electrical engineer's way of thinking is particularly appropriate. Of course, the introduction of phase considerations may have been fortuitous, arising from electrical methods used in excitation of the crystals in the determination of the appropriate properties rather than from forethought. Nevertheless, the result of the intervention of the electrical engineer has been of considerable benefit. Referring to the paper by Professor Cheng, the conditions of the concentrated contact in a fast-running machine element are so specific that it is virtually impossible to reproduce them in any other form of laboratory apparatus. Nevertheless, the vibrational method can approach reality more closely than the conventional viscosity measurement using a capillary tube, which is essentially a steady-state experiment.

Recent computer studies on ball bearings operating under EHD conditions have indicated that variation in the pressure-viscosity index may be of critical importance. Have we any indications as to how this quantity may be determined by chemical structure?

Mr. Beerbower has spoken of pollution of language and in this connection I would like to comment about the tendency to use the word "lubricity" for "oiliness." The difficulty with both these terms is that they imply a specific property of lubricants rather than their tendency, which may differ in different circumstances, to react with surfaces. In any case, the dictionary definition of the word "lubricity" should be sufficient to cause its use to be avoided by anyone seriously interested in good terminology.

Am I correct in concluding from Mr. Beerbower's lecture that the synthesis of viscous liquid lubricants for use at 300° C and above is going to elude us so, if and when we must operate tribological systems at higher temperatures, designers must employ externally or internally pressurized bearings operating on gas or process fluids?

K. L. Berkey (Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, Ohio)

Rather than go into a discussion of the ins and outs of lubricant properties and capabilities, which the author has already accomplished quite nicely, I felt that a short discussion of predicted future military aircraft engine lubrication requirements would be in order. Guidance from the propulsion side of the house has been rather sparse. There have been various studies on future aircraft propulsion needs. However, these have been lamentably lacking in details on lubrication requirements. The two Air Force studies cited by Beerbower have given some guidance, but still fall short of a complete picture. Currently, studies are underway to define lubrication requirements for the next two decades. These studies will also consider fuels, engines, and aircraft requirements to attain high-performance mission profiles.

Figure 13 shows past history and predicts future lubricants based on current knowledge. It looks like esters may take us to 500° F bulk oil temperatures at best. Some people draw this line at 450° F. Polyphenyl ethers can go to 650° F, at least for short-term operation. The perfluorinated materials show promise of up to 700° F operation in aircraft turbines if their corrosion problems can be solved. Above 700° F, materials other than currently known organics will be required. Gases, solid lubricants, and inorganic materials are likely candidates. Let me point out that lubrication capability will be required for most or all temperature plateaus at levels of about 75° F apart. This will be necessitated by the varying mission aircraft that are expected to be developed during the next decade.

I agree with the author that the day of economically solving future lubrication needs by trial and error is past. The capability to design lubricants as well as their applications must be developed. As indicated by the author, great strides are being made toward this end.

D. H. Buckley (NASA Lewis Research Center, Cleveland, Ohio)

The three-sentence conclusion presented in this paper very succinctly and aptly states our present position not only with regard to liquid lubricants, but applies to our position with respect to lubrication in general.

The importance of the elements and the interaction of the elements referred to in figure 3 of the author's paper cannot be overstressed. As indicated by this paper, all too frequently in the past, the organic chemist has

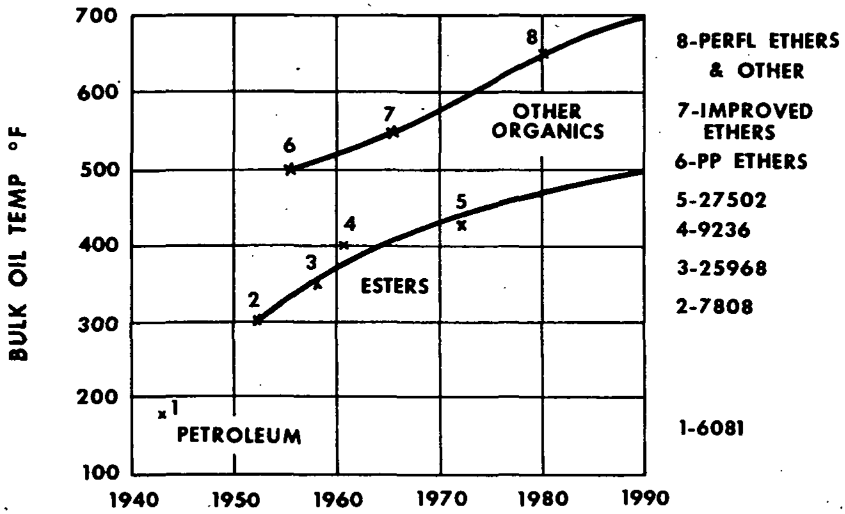

FIGURE 13.—Turbine engine lubricant trends.

been concerned with tailoring molecules to give physical properties of one kind or another that are somehow better than the presently used lubricants. At the same time the mechanical engineer, finding that frequently the organic chemist cannot predict the behavior of a specific lubricant in a particular system, has had to resort to the trial-and-error technique referred to by the author.

For the organic chemist, the mechanical engineer, and the balance of us in the field of tribology to better understand lubricant performance, liquid or otherwise, in a particular system, we must all come to a better understanding of the respective roles played by the elements in figure 3 and their interactions. This is imperative.

We all know that the friction coefficient for a typical bearing steel in air can be reduced from approximately 0.5 to 0.1 when a boundary lubricant is applied to its surface. This is a fivefold reduction in friction. Yet, the interaction of the oxygen from that same air environment with that same steel in the clean state can reduce its friction coefficient from well over 100 to the 0.5 we started to reduce with our liquid lubricant. With Nature's own lubricant, the oxide, the friction coefficient is decreased 200-fold. Even when a liquid lubricant is present on a surface, it contains large quantities of dissolved oxygen and water vapor that can alone or by interaction with other active species present influence friction and wear. Have we ever, outside of vacuum experiments, ruled out the role played by oxygen and water vapor in the lubricating properties we think we are measuring for a particular liquid lubricant?

It would appear that stepwise studies are in order. First, we must come to appreciate the interaction of the environment with the metals we wish to lubricate. Second, we should understand the interaction of the liquid lubricant with the environment. And third, we should study the interaction of all three components. It would appear that this is the way and the only way we will be able to understand the lubrication system.

In the author's discussion of catalytic thermal decomposition and oxidation phenomena, brief mention is made of the role played by the metals being lubricated in these processes. All too often insufficient attention is paid to the surface to be lubricated. The reaction products formed from the interaction of the lubricant or the environment, or both, with the surface to be lubricated can vary markedly with the metal or alloy.

It very frequently happens that when we think of chemical interactions with such materials as copper alloys, we think of reactions with copper, steels, reactions with iron, etc. Even in basic studies, bulk properties are frequently used to predict surface behavior. The surface of a metal or alloy does not have the same properties as the bulk material. The surface may, and frequently does, not even have the same composition as the bulk alloy.

Recent studies in our laboratory indicate, for example, that small concentrations of aluminum in copper can undergo equilibrium segregation to the alloy surface. The segregation can be temperature or strain initiated. With a few atomic percent aluminum in copper, the surface layer consists entirely of aluminum atoms that have popped out onto the surface. The number of aluminum atoms in this outermost layer is one-third that of the total atoms contained in the first subsurface layer (one-third monolayer coverage). With respect to adhesion, the alloy behaves as if it were elemental aluminum rather than copper.

Similar studies with iron-aluminum alloys indicate segregation of aluminum to the surface during sliding friction experiments. In dry sliding this segregation of aluminum to the alloy surface resulted in increased friction and adhesive wear. With stearic acid in hexadecane present on the surface as a lubricant, a lower concentration of stearic acid was needed to achieve effective boundary lubrication than was necessary for iron because of the greater chemical reactivity of the aluminum and its segregation to the surface with sliding.

The segregation of silicon to the surface of iron-cobalt-silicon alloys has also been observed in lubrication studies. These segregation observations all indicate that the true surface of an alloy should be considered in studies of liquid lubricant interaction with metal surfaces. The surfaces may not at all be what we think they are.

Another important interaction from the author's figure 3 and one not touched upon by him is the effect of the liquid lubricant on the mechanical properties of the surface to be lubricated or the Rehbinder effect. Through the years many researchers have made mention of this effect with respect to lubrication. In recent years we have seen the presence of such materials as stearic acid influence the plasticity of lithium fluoride, calcium fluoride, and zinc single-crystal surfaces during sliding. Not only can the lubricant present on a surface influence plastic deformation, but in the case of zinc, it affects the modes as well. The effect of a lubricant in determining whether a metal surface deforms by twinning or slip can be very significant in such observations as fatigue behavior.

The author, in his discussion of wetting, cites the work of Zadumkin with gallium and mercury. Extreme care must be taken with reference to the wetting of surfaces by gallium. Since gallium will react chemically with nearly all metals, and a wide variety of other surfaces as well, any wetting studies with this metal are apt to be relatively meaningless.

In a discussion of hydrogen embrittlement of steels, the author uses the Griffith equation for crack propagation. Griffith originally postulated his equation to predict crack propagation in amorphous glass. It is difficult to see how the equation can be applied to the propagation of cracks in steels during bearing fatigue. Crystallinity, grain boundaries, and inclusions would seem to exert an influence on crack growth and the rate of growth in steels.

The author, with reference to dehydrogenation of aliphatic hydrocarbons, indicates that the hydrogen soaks into the metal, resulting in hydrogen embrittlement. One can understand the dehydrogenation process resulting in the formation of cementite on a ferrous surface because the carbon is a solid and remains on the surface after dehydrogenation. The liberated hydrogen is, however, a gas and would be expected to pass into the environment rather than into the metal. One wonders what the evidence is for it soaking into the metal. It certainly cannot be any measurements involving surface brittleness.

Mention is made to the fact that the resultant carbide formation from dehydrogenation is detrimental. Is this always true? Carburization is frequently employed to improve surface wear resistance.

In concluding, this discusser found that the author attempted to cover many topics, giving each a cursory treatment. While the title and subject of the paper were relatively broad, the author should have selected a few less topics and given those selected for incorporation a more in-depth and thorough treatment. For example, the very important concept of the influence of water and humidity were discussed in only a short paragraph in the paper. This topic could have been expanded at the expense of deleting such topics as seal swelling.

B. W. Hotten (Chevron Research Co., Richmond, Calif.)

The link made by the author between the prooxidative power of metals and their ability to alternate between two valence states reflects conventional opinion, but it is a weak link in the chain of evidence. Everyone who has measured the oxidation rate of lubricating greases gelled with Li^+, Na^+, Ca^{2+}, Ba^{2+}, etc., soaps knows that metals with static valence are also powerful oxidation catalysts (ref. 70). Even when a catalytic metal is potentially varivalent, as Fe^{3+} in Fe^{3+} naphthenate (also in hemoglobin), it probably retains the higher valency under oxidizing conditions. A more general mechanism for metallic oxidation catalysis may be by coordination of O_2 with the metal cation. The most prooxidative of the statovalent metals listed, Li^+ in the alkali metal family and Ca^{2+} in the alkaline earth family, also have the highest charge density and greatest coordinating power for electron donors. The varivalent metals usually studied as oxidation catalysts have even stronger coordinating power through their available *d* orbitals.

G. Salomon (Central Laboratory, TNO, Delft, The Netherlands)

The thermodynamical classification of lubricant properties given by the author will be of great help to physical chemists, who have to deal with lubrication technology. The discusser proposes to extend and slightly modify some of these concepts.

Molecular Interactions.—The discusser applied Langmuir's principle of independent surface action with some success to the interpretation of ring-closure reaction more than 30 years ago (ref. 71). Since that time the discusser and his associates have used the now conventional molecular models in the study of molecular interactions of polymer systems, thus avoiding more complex theories. (See also Zisman, ref. 72.)

Gas-Polymer and Gas-Oil Interactions.—The low gas permeability of polyisobutylene was explained in terms of CED by Van Amerongen (ref. 73). In a recent study the discusser found that the solubility of He, N_2, O_2, and CO_2 in natural rubber (ref. 73) and in the oils compiled and measured by the author (ref. 29) are almost identical. Solubility of the same gases in oils of lower aromaticity, estimated by the discusser, was much higher, in good agreement with predictions (table 3). Diffusion constants for gas-oil and gas-polyisoprene systems are also very similar. Structural comparisons are easier to perform with polymers (ref. 73) than with oils.

For prediction of gas entrainment in and gas transport through oils, actually two sets of data are required: the thermodynamic equilibrium solubilities and diffusivities and the time-dependent stability or instability of finely dispersed gas bubbles. The former depend on the bulk properties of the liquid, the latter on the concentration of surface active impurities. By comparing the ratio of inert gas permeability, for example, He to Ar or H_2 to N_2, in pure gum rubbers and in oils, separation of molecular and surface chemical parameters could be achieved.

Liquid-Polymer Interactions.—Technical service groups of lubricant and paint industries have to cope with a great variety of solubility problems. These involve an almost unlimited combination of liquid-polymer systems. Though extension of the well-founded solubility theory (refs. 11 and 74) as proposed by Hansen (refs. 5 and 35) is based on experiments with dirty surfaces and of questionable (ref. 72) theoretical value, these experiments are certainly useful for rapid interpolation. However, extrapolation to specific systems, such as nitrile rubbers with liquid amines or nitrile rubbers with CX_3H halides, is difficult to perform with either equation (5), (23), or (24). As such combinations can pose a problem, e.g., in seal technology, swelling measurements (refs. 75 and 76) in series of liquids with incrementally changing chemical structures (ref. 71) have been performed.

The Surface of Metals and Lubricity.—The discusser agrees with the author that the work of adhesion is one of the parameters needed in the analysis of the term "lubricity." However, the discusser fails to understand how the extrapolations suggested by Gans (ref. 30) can add to the original conclusions of Bernett and Zisman (ref. 32), more particularly when these are taken in conjunction with other data of high-energy surfaces at 0.6 percent *RH* (ref. 72). The Naval Research Laboratory data describe the γ_c value of a partial monolayer of water. The existence of this layer is also evident from UHV work on the wetting of silica by CH_2I_2 (ref. 77). If the extrapolation in figure 8 has a physical meaning, it describes differences in the ease of removing residual water from metal oxides. The conclusions of Zisman (and not of Gans) are in excellent agreement with those of Groszek, given in his paper presented at this symposium. In many practical cases, differences in the reversible heat of adhesion to metal oxide surfaces will be leveled out by traces of water, as shown by Zisman and by Groszek.

White (ref. 78) has demonstrated that all metal oxide surfaces rapidly adsorb organic vapors. Schrader has produced similar evidence in elaborating the hydrophilic properties of gold (ref. 72) in UHV (ref. 79). Great differences, however, exist in the rate of desorption from the same surfaces (ref. 78).

The combined evidence cited above points to the following parameter, partly determining the quality of physical lubricity: the ratio between reversible and irreversible adhesion to metal surfaces. Lubricity will increase if certain types of chain molecules are adsorbed and then bonded irreversibly to the metal surface.

The Design of Tribological Experiments.—Figures 1 and 2 of the paper should be placed in front of young researchers, planning a career in four-ball chemistry. The author states in his introduction that our competence in dealing with these problems is gradually increasing. The discusser would like to emphasize that the International Research Group on Wear of Engineering Materials under the auspices of OECD is taking part in this process by way of self-education. A test should be built up in steps of increasing chemical effects.

As pointed out already (see my discussion of Mr. Furby's paper), a distinction should be made between isothermal and adiabatic friction testing. While conventionally the transition to severe wear, scuffing, or seizure is explored (a situation of nearly adiabatic heating), merit rating of lubricants under isothermal conditions needs more attention.

The next step should be a comparison performed in neutral and in oxidizing atmospheres. Many researchers hesitate at this point and for good reasons. Surrounding a friction couple with an argon or a helium atmosphere poses leakage problems, which demand designs beyond the means of many testing laboratories. Further, convenient gas-analytical tools are not always at the disposal of mechanical engineers. However, in our experience, even a "dirty" argon atmosphere with about 0.5 to 1 percent air leaking in, can suffice to show great differences between lubricants. Probably the natural esters discussed by the author would show up as even more superior, if compared with mineral oils in a neutral atmosphere. The ease of formation of irreversible adsorbates and of protective films with the metal is probably greater with unsaturated esters than with hydrocarbons. It would be of great help to have merit ratings of the "lubricity" of natural products in a neutral and dry atmosphere.

The third step, already extensively studied by the author and his colleagues, would then be the influence of moisture. In an early phase of our cooperative effort, we found no systematic trends in the presence of moisture when testing "dry" steel on steel (ref. 80). What we did not know, at that time, is that the adsorption properties of iron oxides are leveled out already by small quantities of water, while according to the author, the condensation of a water film on steel takes place only at very high RH (ref. 81).

C. E. Vest (NASA Goddard Space Flight Center, Greenbelt, Md.)

Mr. Beerbower in his lecture has presented information regarding liquid lubricants related to predicting properties of liquid lubricants from their structural formulas, the ability to design liquid lubricants by forecasting the results of changing their structure, and the ability to map out the ultimate limits to which liquid lubricants can cope with extremely hostile environments. He has shown formulas and the reasoning behind each for determining various properties and their relationship to each other.

The lecture is very interesting to a lubrication technologist in the space applications field, and it has made me more aware of several points that have been bothering me in ball bearing work. The author listed and discussed several properties under "Interactions of Liquid Lubricants With Their Environment." I would appreciate comments by the author on the following questions: What is the effect of changing density upon the lubricant's interaction with the environment, especially fresh new surfaces and oxygen? What effect does the bulk modulus have on the operation of a ball bearing? Would the isothermal tangent bulk modulus be more meaningful to ball bearings? Can vapor pressure be related to cohesive energy? I have read that there is a significant difference in the bulk V_p and the V_p of a monomolecular layer of the same liquid lubricant. In ball bearings wherein the film between the ball and race is very thin, which V_p should be of prime consideration? In considering gas solubility, it is implied that some gases are beneficial with regard to oxidization of a fresh surface but nonbeneficial with regard to breakdown and polymerization of the liquid. In space applications, where we are working in a reduced overall pressure and the liquid becomes degassed, what do you feel would happen if someone decided to use a liquid lubricant with no additives? Viscosity was discussed regarding temperature and pressure. Values are available for the viscosity at various temperatures. What would be the change in viscosity of the lube in a ball bearing at the ball-race interface due to the increase in pressure and temperature? Would the change in viscosity be great enough to consider increasing the bulk viscosity for that application?

In the discussion of adhesion to metals, the contact angle of a good lubricant should be 0 on its own monolayer. In space applications in which zero gravity is a part of the environment, would it not be better to have a small contact angle so that creepage would be reduced? Or would it be best to have an autophobic liquid that spreads on its own monolayer?

The author's discussion of noncatalytic and catalytic reactions with the liquid, its gases, and the contacting surfaces is very enlightening and informative. He shows that some reactions could be beneficial and others nonbeneficial. This would be true especially where the lubrication supply is limited. In a case where boundary lubrication is not of primary concern, but is of concern at startups and stops, it may be beneficial for a free radical and a fresh surface to combine and form an organometallic compound at the fresh surface. Would the author comment on this?

Mr. Beerbower has presented helpful information on the manner in which properties can be predicted, on how structural design can be made to forecast specific results, and on how the ultimate limits to which lubricants can be exposed can be mapped out. Mr. Beerbower also knows from his past experiences many applications by which he could illustrate the effects of each of the property changes. It would be greatly appreciated if he would illustrate a few of these for us.

The author has presented guidelines for consideration in research and development of better lubricants. It would be advisable for the researcher to keep these in mind during his work.

Mr. Beerbower is to be congratulated on a very interesting and informative lecture.

LECTURER'S CLOSURE

In reply to Dr. Barwell, the writer did indeed mean that all of us should drop our special labels and work together as a team. Whether we call it tribology or lubrication engineering, each of us is going to need all the help he can get, and soon.

The point that surface resin is a mixed blessing is certainly an important one. The paper stressed its value in journal bearings, but the same amount of resin is known to be very harmful to rolling-element bearings. It is also apt to be the first stage in the notorious series "lacquer→varnish→coke." The goal should be controlled generation of resin, when, as, and if it is needed, by judicious use of appropriate liquids and metals. Ranking the resin-forming tendency of hydrocarbons has been discussed (ref. 33), but it is much more difficult to devise a ranking scheme in which gaseous products are also predicted. The only sure guide to the latter is that the zipper polymer structure (sec. 4.1.1) always breaks down to low-boiling material with essentially no residue; this has been used for the bearings in annealing tunnel carts. At the other extreme, the complex aromatics found in petroleum residua tend to split into hydrogen and asphalts that soon resemble coke.

The point on viscoelastic phenomena is a good one, in that tribology must adopt ideas from electrical engineering. However, this applies especially to oils formulated with polymers, and rheology as discussed in the paper had to be limited essentially to that of base stocks, where this concept is least useful.

It is to be hoped that tables of the reversible and irreversible energies of surface interactions will soon begin to appear, and that "lubricity" can be turned back to the ever-growing science of pornography.

As Dr. Barwell concluded, there is little hope for organic compounds to stand up to continuous service at 300° C. Possible alternates are discussed in reply to Mr. Berkey.

The pressure-viscosity index is very intimately related to the bulk modulus K for flow depends on the free volume in the liquid and any compression leads to a viscosity increase. Thus, high $(d\eta/dP)$ liquids may be obtained by increasing δ_D and δ_P, as shown in equation (15). Specifically, this would lead to aromatics with functional groups such as polyphenyl ethers, etc.

Mr. Berkey raised the same point as Dr. Barwell on the bad prospects for organic lubricants above about 300° C or 650° F. However, this limitation is based on the practice of exposing the bulk of the lubricant to the temperature. As seen in figure 1, glass molding is routinely lubricated at over 500° C. Actually, the mold is at about 450° C and the glass at 900° C, with the lubricant somewhere in between. A similar pattern is found in continuous steel casting, where the mold is at about 200° C and the steel at 1100° C. The secret of such operations is to regard the lubricant as expendable and use it on a once-through basis. Data on glass molding are available (ref. 82) to show that liquid lubricants can be formulated that far exceed the required lifetime of about 0.25 sec. Application to advanced aircraft will require some ingenuity, as once-through lubrication does not provide the cooling power of bulk lubrication. However, it does seem more promising than the relatively unexplored field of liquid inorganics. Liquid metals have not been very satisfactory. While gas bearings and solid films have their uses, they also have some very harsh limitations.

Mr. Buckley raises the question of the role of dissolved oxygen and water vapor in liquid lubrication. He is right to question whether most of the dry, inert atmosphere experiments reported in the literature really are free from such effects. However, techniques are now being used, in a few laboratories, that give results so different from the conventional data as to encourage belief that these contaminants have been rendered negligible.

Though the point was not stressed in the paper, figure 10 does include two demonstrations of the alloy effect. The two dashed lines represent alloys of palladium with silver and gold. The rates of polymer formation correlated excellently with the surface free energies of the alloys as calculated by Hildebrand's equation (ref. 24, p. 408),

$$\gamma_m=\gamma_2-\frac{RT}{V_m^{2/3}}\left[\ln\,(1-x_3)+x_3\exp\frac{(\gamma_2-\gamma_3)\,V_m^{2/3}}{RT}\right]$$

where γ_m is the surface free energy of the alloy, γ_2 is the surface free energy of palladium, γ_3 is the surface free energy of the other metal, V_m is the molar volume of the alloy, and x_3 is the mole fraction of the other metal.

This expresses the general surfactant tendency of low-γ_3 metals, such as the aluminum so ably demonstrated by Mr. Buckley. Related equations that predict the surface composition are also available, but not the rate of attaining this Gibbs equilibrium. It is a great credit to Mr. Buckley that he has shown how rapidly even solid solutions equilibrate and that probably the sliding stress is a factor in this speed.

The point about the Rehbinder effect was touched on briefly in section 3.5, though not by that name, in the attempt to explain Rounds' (refs. 42 and 43) data by equation (50). The loss of free energy in submerging a solid ($\gamma_2 - \gamma_{12}$) should represent the decrease in crack propagating force. As Mr. Buckley points out, this equation does not give accurate predictions in steel, nor in many other situations, but it is still the only mathematical relation available for this problem.

The Zadumkin (refs. 38 and 39) work cited did not relate to the wetting of solids by gallium and mercury, but to the wetting of these liquid metals by organic liquids. He did have to throw out some data because of a change in γ_{12} with time, which he attributed to reaction of gallium with impurities in the liquids. Perhaps the liquids themselves were reacting.

The evidence for hydrogen soaking into steel from a surface reaction is due to Grunberg (ref. 83), who found radioactive hydrogen (tritium) beneath the surface after four-ball tests in the presence of tritiated water. The extension to the hydrogen released from hydrocarbons is by analogy but seems plausible because what is released is not hydrogen gas but hydrogen radical. The latter is well known to cause corrosion embrittlement.

Carbide formation at the surface can be extremely beneficial as casehardening, provided it is not overdone. If carried too far, the case tends to spall away from the soft substrate, and such an effect was intended in the paper.

The author agrees with Mr. Buckley that many topics were given cursory treatment. The intention was to provide a critical review, so that the reader could spend as much time as justified on those references of particular interest to him. This was not done for the effects of humidity and oxygen on lubrication (as opposed to oxidation of the lubricant) because that was considered to be a solid-gas interaction. A review of this interaction is included in the author's recent Army report (ref. 84).

Mr. Hotten certainly has a good point in his statement that statovalent metal soaps definitely accelerate the oxidation of lubricants. The varivalent theory cited is one that has been fairly widely accepted but fails to predict the ranking of even those metals. It would be extremely valuable to have a complete theory that covers both classes of metals, and it is hoped that Mr. Hotten will publish a more complete account of this one.

It seems appropriate at this point to offer an additional reference on the subject of homogeneous versus heterogeneous catalysis. Klaus and Tewksbury (ref. 85) arrived at conclusions similar to those of Thompson (ref. 54) in a much more elegant study.

Dr. Salomon has provided some very interesting light on the relationship of solubilities in the gas-liquid-polymer triad. Having verified that gas-liquid and liquid-polymer solubilities correlate with CED, the author had speculated that gas-polymer interactions would also correlate but lacked the proof that Dr. Salomon provided.

The problems of using the Hansen (ref. 35) surface technique for obtaining thermodynamically useful parameters are as stated by the discusser. A more complete analysis is now available (ref. 84). This also goes into much more detail on the use (and abuse) of the straight-line assumption of Gans (ref. 30) and Bernett (ref. 32) in figure 8. The author's conclusion is essentially the same as that reached by Dr. Salomon, that reversible adsorption is a necessary step in boundary lubrication but does not accomplish much unless irreversible adhesion follows.

As Dr. Salomon states, the contrast of humid air with dry argon is very revealing (ref. 57). We have not found it very difficult to provide special atmospheres, using plastic bags, etc., with enough positive pressure to insure that all leakage is outward. Degassing the lubricant and equipment is more troublesome, but even a modest effort will produce a reasonably inert atmosphere.

Mr. Vest has raised a great many important questions, some of which are beyond the author's ability to answer completely. The following answers are factual as far as is possible, with a minor amount of speculative fill-in.

Density largely controls the solubility of gases, high-density hydrocarbons having low solvency for oxygen but high solvency for water. As a first approximation, high-density liquids have higher works of adhesion on freshly cut metals, but the more important irreversible adhesion is quite dependent on chemistry.

Bulk modulus as such does not affect ball bearing operation, but its tie to pressure-viscosity index might lead to a correlation. Isothermal or adiabatic moduli would be of equal value in this.

Vapor pressure is very strongly related to cohesive energy. As shown in section 2.2.4, it is least responsive to the hydrogen-bonding energy component. The vapor pressure of a monolayer will be greatly dependent on the heat of adsorption ΔH_a from the vapor phase, which must replace ΔH_v in equations (18) and (19):

$$T_{ba} = 25\sqrt{563 + 0.080(2950 + \Delta H_a)} - 593$$

$$d(\ln P_{va})\ dT = \frac{\Delta H_a}{T\,\Delta V_v}$$

On a solid where $\gamma_l > \gamma_c$, $\Delta H_a < \Delta H_v$ and P_{va} is greater than for the liquid, so no monolayer forms. When $\gamma_l < \gamma_c$, the vapor pressure of the monolayer will be less than for the liquid, and the deviation could be computed from figure 8 if a few assumptions are made (ref. 72). This P_{va} should be used for thin films in ball bearings.

Oxygen solubility controls the rate of deactivation of fresh metal surfaces and hence the rate of radical formation, but oxygen availability in the environment controls the rate of polymer formation. Thus, low oxygen atmospheres tend to reduce the usual benefit from antioxidants to the vanishing point.

Viscosity is lowered by temperature and raised by pressure, so the two tend to offset each other. However, good experience shows that the viscosity for a ball bearing lubricant may be selected on a maximum anticipated temperature basis with no regard for pressure.

For adhesion to metals, figure 8 predicts that all lubricants of $\gamma_l < 44$ should spread to a monolayer on all metals. Surely the discusser has a misprint, as autophobic liquids are those which do not spread on their monolayers. Such liquids are rare, as are those of $\gamma_l > 44$, so the use of barrier films of fluorocompounds painted around the races is a more practical solution to the creepage problem.

Catalytic reactions essentially imply the formation, at least temporarily, of an organometallic compound. These can be very beneficial in the situation the discusser describes. Clearly, some care would be required in selecting the metal and lubricant so as to have controlled catalytic reaction, as the cure can be worse than the disease if applied too generously.

The author had planned to include some numerical examples of the design process, but they proved too lengthy for presentation here.

NOMENCLATURE

Latin

A	Arrhenius preexponential constant; Vogel constant (eq. (42))
a	factor in equation (24)
B	bulk modulus (eq. (12)); contact potential function (eq. (49)); Antoine constant (eqs. (20) and (21))
C	molar heat capacity, cal/mol °K; temperature correction (eqs. (20) and (21)); parameter in Roelands equations (38) to (41)
D	parameter in Roelands equation (38)
d	differential of
E	energy, cal; Young's modulus
F	flammability limit
f	fugacity, atm
G	Gibbs free energy, cal
H	enthalpy, cal

K	bulk modulus (eq. (13)), atm
k	term in equation (34)
L	force, gm
l	length, cm
M	molecular weight, g/mol
N	number of
n	refractive index
P	pressure, atm
R	gas constant, cal/mol °K
r	reaction rate
S	entropy, cal/°K
T	temperature, °K (in section 4.3, °F)
t	temperature, °F
V	molar volume, cm^3/mol
W	work, ergs/cm^2
x	mole fraction

Greek

α	expansivity, (°K)$^{-1}$
β	factor in equation (24); second carbon atom in alcohol
γ	surface free energy, ergs/cm^2
Δ	change in
δ	solubility parameter, hildebrands
∂	partial differential of
ϵ	dielectric constant
θ	time, sec; contact angle
λ	thermal conductivity, J/cm sec °K
μ	dipole moment, debyes
η	viscosity, centipoises
Φ	volume disparity factor
ϕ	volume fraction
ρ	density, gm/cm^3
Σ	sum of

Subscripts

A	aromatic carbons (eqs. (39) to (41))
a	absorption
b	at boiling point
b5	at 5 percent boiling point
c	at critical point; carbon atoms (table 5)
D	London force contribution; decomposition
E	extended viscosity index
e	at equilibrium; eutectic mixture
F	at flashpoint
g	at glass point

H	H-bond contribution
I	insoluble
i	position in summation (eq. (6)); induction period (eq. (55))
L	lower
M	of mixing
m	of melting; after equation (33), of melting and transition
N	naphthenic carbons (eqs. (39) to (41))
O	of oxygen
0	at reference condition
P	polar contribution
p	at constant pressure; at the convergence pole (eqs. (39) to (41))
R	reduced property (actual/critical)
r	of transition
S	soluble
s	isentropic
T	isothermal
tr	transition
U	upper
V	at constant volume
v	of vaporization
w	van der Waals (volume)
1	less dense phase (liquid)
2	more dense phase (solid or liquid)

Superscripts

d	London force contribution (eqs. (44), (45), and (46))
G	gas property
j	due to fusion at constant volume
L	property of hypothetical liquefied gas
$^{\circ}$	Bondi's reduced E at $V/V_w = 1.70$
p	polar and H-bond contribution (eqs. (44), (45), and (46))
v	due to change in volume
x	Roelands' temperature exponent (eqs. (38) to (41))
y	Roelands' pressure exponent (eqs. (38) to (41))
$*$	free radical

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Additives

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The objective of this paper is to give the lubrication engineer an insight into the lubricant additive field by describing what additives are chemically and what functions they perform in the lubrication of various kinds of equipment; current theories regarding the mode of action of lubricant additives; how additives have been improved to meet more severe service demands; and areas of the additive field where more research and development activity is needed to help solve existing and anticipated lubrication problems.

Additive groups discussed include all those known to be of commercial importance today: detergents and dispersants; corrosion inhibitors; antioxidants; viscosity index improvers; pour point depressants; extreme-pressure agents; and "fix" additives such as rust inhibitors and antifoam, antistain, antichatter, antisquawk, and antifoulant agents.

FROM A MODEST BEGINNING in the early thirties, the lubricant additive industry has become a major branch of the chemical industry with Western World sales of more than $300 million annually as of 1965 (ref. 1), a market that is believed to have more than doubled since then. Although no estimates appear to be available on the size of the additive industry in certain Eastern European and Asian countries, reports indicate that active research and commercial production programs are being pursued there.

A lubricant additive can be defined as a material that imparts a new and desirable property not originally present in the oil or reinforces a desirable property already possessed in some degree by the oil. Although additives of many diverse types have been developed to meet special lubrication needs, their principal functions are relatively few in number. They are used to reduce the oxidative or thermal degradation of an oil, to lessen the deposition of harmful deposits on lubricated parts, to minimize rust and corrosion, to control frictional properties, to reduce wear, and to prevent destructive metal-to-metal contact. They are also employed to alter purely physical properties of an oil such as viscosity, viscosity-temperature relationship (viscosity index (V.I.)), and a tendency to form stable foams.

Over the years a host of terms has arisen to identify additives and briefly denote their intended functions. Thus, the trade readily recognizes designations such as antioxidant (oxidation inhibitor), corrosion inhibitor, rust inhibitor, extreme-pressure (EP) agent, antistain agent, antifoam agent, antiwear agent, V.I. improver, pour point depressant, detergent, dispersant, antisquawk agent (prevents noise in automatic transmissions), and antichatter agent (prevents noise in limited slip differentials).

The bulk of all additive production finds its way into crankcase, automatic transmission, and rear axle lubricants for automotive vehicles. In addition, additives play an important role in the compounding of lubricants for steam turbines, gas turbines, jet aircraft turbines, railroad and marine diesel engines, aircraft piston engines, stationary piston engines, and relatively low-power two-cycle engines; e.g., outboard engines, small industrial engines, power equipment engines, etc. They are also used in compounding hydraulic oils, industrial gear lubricants, and cutting oils. In the automotive field particularly, many of the engineering advances that contribute to quiet operation, driving ease, improved traction, and extended engine life have been made possible by additive-treated lubricants specifically designed for use in automatic transmissions, limited slip differentials, and high-performance engines with hydraulic valve lifters. Each of the latter automotive components could not be lubricated satisfactorily without the unique performance characteristics conferred by additives.

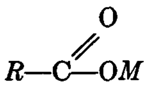
DETERGENT AND DISPERSANT ADDITIVES

Definition of Terms

The term "detergent" as used today refers to an important category of lubricant additives that have the ability to reduce or prevent deposits in internal combustion engines operated at high temperatures. Additives that disperse sludge formed in engines operated at relatively low temperatures (e.g., those prevailing in short-trip, stop-and-go driving conditions) are called dispersants, even though the end result of their use, a clean engine, presumes a detergent or cleansing action. This distinction by function rather than chemical structure is recognized in the industry.

Early Detergent Additives

The first detergent additives employed commercially in the late thirties to reduce ring-sticking and ring-groove carbon in diesel engines were oil-soluble polyvalent metal salts or "soaps" of high-molecular-weight carboxylic acids. These soaps can be represented by the formula



$$R\text{—}\overset{\displaystyle O}{\overset{\displaystyle /\!\!/}{C}}\text{—}OM$$

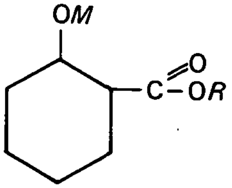
where R is a high-molecular-weight organic radical containing at least 12 carbon atoms and *M* is one equivalent of a polyvalent metal such as barium, calcium, magnesium, or aluminum.

Typical early detergent additives used commercially included (ref. 2) calcium dichlorostearate, calcium phenylstearate, calcium chlorophenylstearate, and aluminum naphthenate.

The first three of these additives were made from substituted stearic acids derived from oleic acid. Dichlorostearic acid was manufactured by the chlorination of oleic acid, phenylstearic acid by the condensation of benzene and oleic acid, and chlorophenylstearic acid by the condensation of chlorobenzene and oleic acid. The last additive, aluminum naphthenate, was derived from petroleum naphthenic acids, the high-molecular-weight carboxylic acids that occur in crude oil and are removed during refining. Processes employed for the conversion of the acids to the desired polyvalent metal salts included direct reaction with a metal base and metathesis of the sodium salt of the acid with a polyvalent metal salt such as calcium chloride, etc.

Although these detergent additives were effective in improving piston cleanliness and extending the service life of diesel engines between overhauls, they acted as active prooxidants and could only be used in engines having corrosion-resistant bearings (white metal or babbitt) without causing unacceptable bearing corrosion. With the advent of hard but corrosion-susceptible bearing metal alloys such as copper-lead, lead bronze, and cadmium-silver, these carboxylate salt detergent additives became obsolete in the early forties.

In the interim between the obsolescence of carboxylate salt additives and the development of detergent additives used today, polyvalent metal phenates of long-chain alkyl esters of salicylic acid found commercial favor. Typical commercial products of this type are represented by the general formula



and include compounds such as magnesium lauryl salicylate (ref. 3).

The manufacture of such additives generally involved the reaction of salicylic acid with a long-chain alcohol to form a salicylate ester and the neutralization of the phenolic group in the ester with a metal base such as magnesium methoxide, calcium oxide, etc.

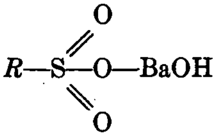
The phenates of salicylate esters were more effective detergents and somewhat less corrosive to sensitive bearing metal alloys than their predecessors, the carboxylate salts. They were costly, however, and were superseded during World War II years by products that, in improved form, are still being used today.

Modern Detergent Additives

The following list is believed to include all families of detergent additives in substantial commercial use at the present time:

(1) Sulfonates, the normal and basic metal salts of petroleum sulfonic ("mahogany") and long-chain alkyl-substituted aromatic sulfonic acids.
(2) Phosphonates and/or thiophosphonates, the normal and basic metal salts of the phosphonic and/or thiophosphonic acids obtained from the reaction of polyolefins such as polyisobutenes with inorganic phosphorus reagents, principally phosphorus pentasulfide.
(3) Phenates, the normal and basic metal salts of alkylphenols, alkylphenol sulfides, and alkylphenol-aldehyde condensation products.
(4) Alkyl-substituted salicylates, the normal and basic metal salts of long-chain alkyl-substituted salicylic acids. These products should not be confused with the metal phenates of salicylate esters discussed earlier.

In this listing, the term "normal" metal salt denotes a salt of an acid that contains the stoichiometric amount of metal required for neutralization of the acidic group present. The term "basic" metal salt denotes a salt of an acid that contains more metal than is required for neutralization of the acidic group present. Such excess metal may be present due to a true basic salt structure, e.g.,



$$R\text{—}\overset{\overset{\displaystyle O}{/\!\!/}}{\underset{\underset{\displaystyle O}{\backslash\!\!\backslash}}{S}}\text{—O—BaOH}$$

as suggested by early investigators (ref. 4). A more likely explanation, supported by electron microscope studies, is that the excess metal is present in the form of colloidally dispersed metal compounds.

Sulfonate Detergents

Normal metal sulfonates derived from mahogany acids (the mahogany-colored petroleum sulfonic acids obtained as a byproduct during white oil manufacture) were first employed as detergent additives in commercial crankcase oils during World War II. Almost without exception, the metal present in such sulfonates was calcium or barium. Petroleum sulfonates were not only superior to the early detergent additives with respect to detergency but were much less corrosive to sensitive bearing metal alloys and responded well to corrosion inhibitors. They can be represented by the general formula

$$R_x\mathrm{ArSO_3}M$$

where R_xAr represents complex alkylaromatic and alkylnaphthene radicals derived from petroleum and M is one equivalent of a polyvalent metal. A detailed review is available on the preparation of petroleum sulfonic acids and the use of their normal salts as lubricant additives (ref. 5).

Supplementing the supply of natural petroleum sulfonates in more recent years are the synthetic sulfonates derived from long-chain alkyl-substituted aromatics (e.g., polydodecyl benzene bottoms) obtained both as primary alkylation products and as byproducts in the manufacture of household detergents. The extent of their use commercially is governed largely by the relative availability and cost of petroleum sulfonates and polyalkylaryl sulfonates on the market.

In the period between the close of World War II and 1950, sulfonate detergent additives were improved by converting them to their basic salts. This was generally accomplished by heating the metal sulfonate with water and an excess of metal base at an elevated temperature. Such basic sulfonates usually contain from 10 to 100 percent more metal than the corresponding normal sulfonates.

In the early fifties, methods were discovered by which one could prepare highly basic sulfonates containing from three to 15 times as much metal as the corresponding normal sulfonates. Called overbased, superbasic, or hyperbasic sulfonates, these products are manufactured by heating a mixture of certain promoters or solvents with a normal sulfonate and a large excess of metal base, carbonation with carbon dioxide frequently being used to convert the metal base to colloidally dispersed metal carbonate. Suitable promoters or solvents for overbasing processes included phenols (ref. 6), thioacids of phosphorus (ref. 7), alcoholates (ref. 8), alcohols (ref. 9), and ketones (ref. 10). Metal bases employed in the preparation of overbased sulfonates are for the most part basic compounds of alkaline earth metals such as calcium, barium, or magnesium.

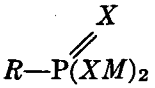
Basic sulfonates, and more particularly overbased sulfonates, possess the ability to neutralize acidic contaminants formed in lubricating oils and thus reduce corrosive wear of engine components such as piston rings and cylinder bores (ref. 11).

Phosphonate and/or Thiophosphonate Detergents

This important family of additives made its appearance during the World War II years, when it was discovered that alkali and alkaline earth metal salts of the acidic products obtained from the reaction of liquid polyolefins such as polyisobutene with phosphorus sulfides were effective as detergents in lubricating oils. The polyolefins used were usually within the molecular-weight range from about 500 to 2000. One of the first products of this type to be used commercially in crankcase oils was a normal potassium salt of the product obtained from the reaction of phosphorus pentasulfide with a liquid polyisobutene having a Saybolt universal (SU) viscosity of about 550 sec at 100° F (ref. 12).

Later commercial products have been alkaline earth metal salts, principally barium salts, and steam treatment of the polyolefin-phosphorus sulfide reaction product before conversion to the desired metal salt has been extensively employed (ref. 13).

Although it had been speculated that the products contain carbon-to-phosphorus-bonded thiophosphonic acids (ref. 14), little definitive evidence to support this hypothesis appeared in the literature until barium salts of thiopyrophosphonic, thiophosponic, and phosphonic acids were found in commercial barium salts of phosphorus pentasulfide-treated polyisobutene (ref. 15). For convenience, the commercial products are generally designated as thiophosphonates or phosphonates of the general formula



$$R\text{—}\overset{X}{\overset{/\!\!/}{\text{P}}}(XM)_2$$

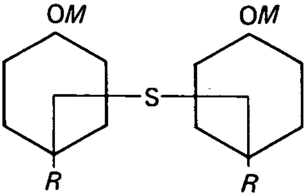
where R is a large aliphatic radical of at least 500 molecular weight, X is oxygen and/or sulfur, and M is one equivalent of a monovalent or polyvalent metal. By steam treatment or prolonged hydrolysis before or during neutralization, a portion or substantially all of the sulfur present in the thiophosphonate group, $\text{—P(S)(S}M)_2$, can be substituted with oxygen to yield a phosphonate.

The history of thiophosphonate and phosphonate detergent additives closely parallels that of sulfonate additives because basic and overbased salts have replaced normal salts in all but a few commercial applications. The processing methods used to make basic and overbased salts of phosphorus sulfide-treated polyolefins are generally quite similar to those employed for the manufacture of their sulfonate analogs. Such processing methods involve the use of promoters or solvents such as phenols or phenol sulfides (ref. 16), alcohols (ref. 17), or acids such as formic, etc. (ref. 18). In many of the foregoing processing methods, carbonation of the reaction mass is carried out to increase the amount of colloidally dispersed metallic base present in the filtered product in the form of metal carbonate.

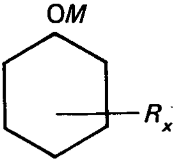
Phenate Detergents

Phenates and phenate sulfides have played an important role as detergent additives ever since their introduction during World War II. Among the earliest additives of this type to gain commercial acceptance were—

(1) Calcium and barium phenates of tertiary-octylphenol sulfide and tertiary-amylphenol sulfide with the general formula (ref. 19)



(2) Calcium phenates of tertiary-amylphenol–formaldehyde condensation products (ref. 20)
(3) Calcium and barium phenates of paraffin wax substituted phenol with the general formula (ref. 21)

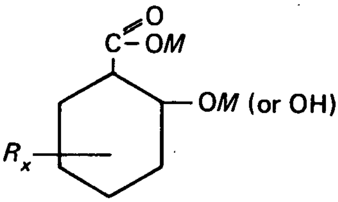


In addition to performing a detergent function, phenates, and more particularly phenate sulfides, exhibit substantial corrosion-inhibiting and antioxidant properties. This fact makes it possible to reduce the amount of corrosion and oxidation inhibitors employed in balanced detergent oil formulations and, in some instances, to eliminate supplementary inhibitors altogether. For example, a mixture of the zinc and magnesium phenates of 18 to 30 carbon atom alkyl-substituted phenols (ref. 22) has been used as the sole additive in aircraft piston engine oils.

Basic phenates proved to be superior to normal phenates in many detergent oil formulations. Substantially all phenates used commercially in crankcase oils are barium or calcium phenates of the basic or overbased variety. Manufacturing techniques are simpler than for basic sulfonates or phosphonates, because the phenol itself acts to catalyze the incorporation of excess metallic base in colloidal form. Carbonation is also widely practiced to incorporate excess metal as colloidal metal carbonate in the finished additive. Details are available on commercial methods used for the production of carbonated basic phenate detergent additives (ref. 23).

Alkyl-Substituted Salicylate Detergents

These additives can be represented by the general formula:



where *R* is an oil-solubilizing organic radical and *M* is one equivalent of a polyvalent metal.

One of the first additives of this type to see commercial use was the zinc carboxylate of diisopropyl salicylic acid. More recently, calcium carboxylates of long-chain alkyl salicylic acid (e.g., isooctyl salicylic acid) have been used. The manufacture of such additives is generally carried out by the Kolbe reaction, which involves carboxylation of a metal phenate with carbon dioxide under elevated pressure (ref. 24). As with the other detergent additives discussed, overbasing techniques have been employed to prepare improved products (ref. 25).

Mode of Action of Detergent Additives

Detergency in aqueous or other ionic media has been shown to be a colloidal phenomenon in which normally insoluble contaminative particles are adsorbed in soap micelles, with the polar portion of the soap molecule extending toward the ionic medium and the nonpolar portion being adjacent to the contaminant.

The mode of action of detergents in nonionic media such as mineral oils is not fully understood. Evidence has been found, however, for the existence of soap micelles in nonionic media (ref. 26). There is reason to believe, then, that detergent oils may act upon contaminant particles in a manner similar to that of aqueous soap solutions. From a theoretical standpoint, the character of the micelles in a detergent oil would be quite different from those in an aqueous system because the polar portion of the detergent additive would be adsorbed on the contaminant and the nonpolar portion would extend toward the oil.

Further evidence of an indirect nature to support this mechanism of detergency is found in the chemical composition of detergent additives themselves. All commercial detergent additives of proven effectiveness possess in common an oleophilic, nonpolar group and an oleophobic, polar group.

Suspension and soiled-cloth-washing techniques employing either carbon black or graphite as the contaminant have long been used to evaluate the detergent power of soaps for aqueous systems. It is hardly surprising, therefore, that early attempts to measure the effectiveness of detergent oils outside of an engine should rely on closely related techniques (ref. 27). More highly specialized bench tests that are contingent on the ability of a detergent additive to retard the separation of asphaltenes from oil (ref. 27) or reduce the buildup of coke or lacquerlike deposits on hot metal panels (ref. 28) have also been proposed.

Another bench best for detergency involves the microscopic examination of a used oil at various elevated temperatures extending from 60° to above 200° C (ref. 29). The resistance of the contaminative particles in the oil to flocculation with increasing temperature is taken as a measure of the detergent power of the oil.

Although such bench tests have shed light on the mode of action of detergent additives, none has yet proved equal to the task of predicting the relative effectiveness of different detergent oils in full-scale engines with a satisfactory degree of accuracy and reproducibility.

As noted earlier (ref. 11), basic and overbased detergent additives also possess the ability to neutralize harmful organic and inorganic acids that accumulate in crankcase lubricants during service.

Dispersant Additives

The term "dispersant" is presently used to designate additives that are capable of dispersing the cold sludge formed in gasoline engines operated for the most part at relatively low cooling jacket temperatures. Such sludge, a complex mixture of fuel combustion products, unburned fuel, carbon, lead antiknock residues, and water, is largely a result of the short-trip, stop-and-go service that characterizes the operation of door-to-door delivery vehicles, taxicabs, and most passenger cars. Unless maintained in fine suspension (i.e., dispersed) in the lubricating oil, this sludge is deposited on engine parts such as oil screens, valve train components, and oil control rings, where it eventually interferes with engine operation.

The petroleum and additive industries had long recognized that detergent additives which performed effectively in diesel engines and gasoline engines operated for extended periods at high speeds under heavy load were of relatively little value in controlling the sludge formed in low-temperature gasoline engine operation. Although research indicated that a very large concentration of basic sulfonate detergent substantially reduced sludge deposition in low-temperature engine service,[1] this approach introduced other operational problems and had little to recommend it from an economic standpoint. Because known metal-containing detergents did not appear to offer a likely solution to the cold sludge problem, many laboratories turned their attention to metal-free organic compounds in the hope that an ashless detergent would provide an answer. The first evidence of significant progress in such research came in 1955 when it was reported that copolymers of lauryl methacrylate and diethylaminoethyl methacrylate greatly reduced cold sludge deposition in passenger car service (ref. 30).

Since that time, many dispersants have been developed, and a number of types have gained commercial acceptance. Among them are—

(1) *N*-substituted long-chain alkenyl succinic derivatives of amines. These products contain the characteristic succinamide, succinimide,

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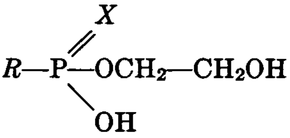
[1] The Lubrizol Corp.: Unpublished research.

or succinamidine groups. Processes for their manufacture usually involve the reaction of alkenyl succinic anhydrides with polyalkylene amines such as triethylene tetramine, tetraethylene pentamine, etc. (ref. 31).

(2) Polybutene of 750 molecular weight treated successively with phosphorus pentasulfide, steam, and ethylene oxide to produce a material with the general structure



$$R\text{—}\underset{\text{OH}}{\overset{\overset{X}{\|}}{\text{P}}}\text{—OCH}_2\text{—CH}_2\text{OH}$$

where X is oxygen or sulfur and R is a polybutenyl group (ref. 32).

(3) High-molecular-weight polymers containing oxygen- or nitrogen-bearing comonomers (ref. 33) such as alkyl methacrylate-dimethylaminoethyl methacrylate copolymers, alkyl methacrylate-*N*-vinyl pyrrolidone copolymers, vinyl acetate-dialkyl fumarate-maleic anhydride copolymers, and alkyl methacrylate-ethylene dimethacrylate copolymers.

The impact of low-cost, effective ashless dispersants on the compounding of passenger car crankcase lubricants has been profound. Since copolymer ashless dispersants can be prepared with substantial V.I.-improving properties, some multigrade lubricants in current use contain only a V.I.-improving dispersant additive, a suitable corrosion or oxidation inhibitor, and sometimes an antiwear agent with no detergent or separate V.I. improver present. Most current formulations, however, contain both detergents and dispersants.

Ashless dispersants are being used in so-called superpremium motor oils currently marketed by a large number of petroleum companies. These formulations have been found quite effective in combating sludge formation under typical stop-and-go driving conditions.

Mode of Action of Dispersant Additives

The role of a dispersant is to retard or prevent the formation and accumulation of harmful deposits on engine parts. Such deposits result from the agglomeration of contaminants in the lubricant such as oil oxidation products, entrained dirt and carbon, residues of incompletely burned fuel, and water. The nature and amount of these deposits is dependent to a large extent on the kind of fuel used, the type of internal combustion engine, and engine service conditions, particularly operating temperatures.

The principal contaminants encountered in diesel engine operation are oxidized lubricating oil fragments, soot or carbon from incompletely burned fuel oil, and sulfur oxides from combustion of the sulfur present in commercially available fuel oils. The sulfur oxides react with entrained water in the lubricant to form corrosive sulfurous and sulfuric acids.

The kinds of deposits encountered in gasoline engines depend for the most part on engine operating temperatures and the quality of the fuel. In engines operated at high temperatures, the main contaminants in the lubricant are products of oil oxidation and degradation. In engines operated at low temperatures such as those prevailing in short-trip, stop-and-go service, the principal contaminants are oxidized fuel products that reach the crankcase by blowby from the combustion chamber. These contaminants, which include lead salts formed from octane number improving agents in the fuel, degrade further in the lubricating oil and deposit on hot engine parts as varnish or mix with oil and water to form oil-insoluble sludge.

The mode of action of dispersants in controlling engine deposits has been the subject of much research (refs. 33 to 36). In summary, it is proposed that oil-insoluble liquid contaminants are solubilized by incorporation in dispersant micelles. Solid contaminants, on the other hand, are peptized into the lubricant by one or more of several postulated mechanisms. The dispersant may be adsorbed on a solid contaminant particle and by steric hindrance prevent its agglomeration to form larger, oil-insoluble masses. The dispersant may be adsorbed on a solid contaminant particle and give it an electrical charge. This charge then prevents agglomeration by electrostatic repulsion. The dispersant may form a protective film around a solid contaminant particle by virtue of hydrogen bonding, which film acts as a physical barrier to agglomeration.

Although studies such as the preceding have contributed to an understanding of the mechanism of dispersancy, it is generally acknowledged that full-scale engine tests in the laboratory and the field are required to assess the effectiveness of dispersant additives in crankcase lubricants (refs. 37 to 39).

CORROSION INHIBITORS

In the additive industry, the term "corrosion inhibitor" is applied to a material that protects corrosion-susceptible nonferrous metal components of an engine, principally bearings, against attack from acidic contaminants in the lubricating oil. A different term, "rust inhibitor," is used to designate materials that protect ferrous metal surfaces against rust.

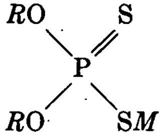
Among the earliest types of corrosion inhibitors to see commercial application in crankcase oils were organic phosphites. Most of these were not pure chemicals, but rather mixtures of monoorgano, diorgano, and triorgano phosphites obtained from the reaction of alcohols or hydroxyesters (e.g., methyl lactate, trimethyl citrate) with phosphorus trichloride (refs. 40 and 41). They can be represented by the general formula

$$(RO)_x\mathrm{P(OH)}_{3-x}$$

where R is an organic radical and x is 1, 2, or 3. Such phosphites were widely used in the so-called premium motor oils of the late thirties and early forties, often in combination with film strength agents such as methyl dichlorostearate and hexachlorodiphenyl ether (ref. 42).

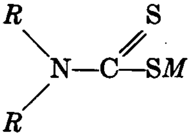
By the midforties, most phosphite inhibitors had been superseded by new sulfur- or phosphorus-containing compounds, prototypes of products that still dominate the commercial scene today. The major classes of corrosion inhibitors in commercial use at the present time are—

(1) Metal diorganodithiophosphates, especially zinc diorganodithiophosphates. They possess the structure



where R is an aliphatic or aromatic radical and M is one equivalent of a polyvalent metal such as zinc or nickel. Their manufacture involves first heating an alcohol or phenol with phosphorus pentasulfide to form diorganodithiophosphoric acid, then neutralizing such acid with a metal base (ref. 43).

(2) Metal diorganodithiocarbamates, especially zinc diorganodithiocarbamates. They are described by the general formula



where R and M are as defined in (1) above. Their manufacture involves the reaction of an organic amine, carbon disulfide, and a metal base (ref. 44).

(3) Sulfurized terpenes, for example, sulfurized dipentene. These products are manufactured by heating elemental sulfur with a terpene hydrocarbon and then optionally washing the crude product with aqueous alkali or alkali metal sulfide to remove dissolved or corrosive sulfur (ref. 45).

(4) Phosphosulfurized terpenes, for example, phosphorus-pentasulfide-treated turpentine. These additives are manufactured by heating phosphorus pentasulfide with a terpene hydrocarbon (ref. 46).

Of the four major classes of corrosion inhibitors listed, metal dithiophosphates, and more specifically, zinc dithiophosphates, have achieved the widest and largest volume use. Virtually every major oil company producing crankcase lubricants offers one or more products which contain zinc-dithiophosphate-type corrosion inhibitors. Although first described in the patent literature (refs. 47 and 48) and used commercially as corrosion inhibitors for crankcase oils as early as 1941, zinc dithiophosphates have remained fundamentally the same products over the years. Recent developments have been concerned with objectives such as lower cost of manufacture (ref. 49), improved thermal stability (ref. 50), lighter color (ref. 51), or improved odor (ref. 52); however, such improved products are still described chemically by the general structure shown in (1) above.

Mode of Action of Corrosion Inhibitors

Corrosion inhibitors function by reacting chemically with the nonferrous metal components of an engine, e.g., copper-lead or lead-bronze bearings, to form thereon a corrosion-resistant, protective film (refs. 53 and 43). This film must adhere tightly to the bearing surface, lest it be removed by dispersants or detergents and expose the underlying bearing metal surface to attack by acidic contaminants in the lubricating oil (ref. 54).

As for the mode of action of zinc dithiophosphates, the most important commercial corrosion inhibitors, it has been shown that these compounds form acid-resistant coatings on vulnerable bearing metal surfaces and also function as antioxidants by reducing peroxides formed in lubricants in service (ref. 55).

ANTIOXIDANTS

In most environments in which a lubricating oil is used, it comes in contact with air, often at high temperatures and in the presence of metals or chemical compounds that promote oxidation of the oil. As a consequence, the oil undergoes a complex series of oxidation reactions, the harmful results of which include principally an increase in viscosity of the lubricant, the formation of acidic contaminants such as petroleum oxyacids (ref. 56), and the development of carbonaceous material.

Antioxidants or oxidation inhibitors are additives that are employed to reduce the harmful effects of oil oxidation. They assist corrosion inhibitors by reducing the amount of acidic contaminants formed in the oil. Among the more effective chemicals employed as commercial antioxidants today are zinc diorganodithiophosphates (also effective, as noted earlier, in the role of corrosion inhibitors); hindered phenols, i.e., phenols in which the hydroxyl group is sterically blocked or "hindered" such as 2,6-di-*t*-butyl-4-methylphenol (refs. 57 and 58), 4,4′-methylene *bis* (2,6-di-*t*-butylphenol) (ref. 59), and 4,4′-thiobis (2-methyl-6-*t*-butylphenol) (ref. 60); and amines such as *N*-phenyl-α-naphthylamine (ref. 61), *N*-phenyl-β-naphthylamine (ref. 62), tetramethyldiaminodiphenylmethane (ref. 63), and phenothiazine and alkylated derivatives (refs. 64 and 65).

Of all these antioxidants, the most widely used in crankcase oils are the zinc diorganodithiophosphates. To reduce the oxidation of steam turbine oils, however, hindered phenols are favored. Phenothiazine and its derivatives have found widespread use as antioxidants for synthetic ester lubricants used in jet aircraft engines.

Antioxidants are probably employed in a wider variety of lubricants than any other type of additive. In addition to their use in crankcase lubricants, steam turbine lubricants, and gas turbine lubricants, they find application in automatic transmission fluids, gear oils, cutting oils, greases, and hydraulic oils.

Mode of Action of Antioxidants

It is generally accepted that the oxidation of a lubricant involves a chain reaction in which initially formed organic peroxides attack unoxidized oil and are subsequently regenerated by oxygen in the air to continue such attack. In accordance with this theory, an effective antioxidant is a material that reduces or otherwise destroys organic peroxides, causing the chain oxidation reaction to cease. An excellent review of the detailed chemistry associated with the peroxide theory of oxidation inhibition is available (ref. 15).

Research efforts over the past 40 years have identified many classes of organic compounds that can reduce organic peroxides and thus retard the oxidation of a lubricant. A list of the more important classes would include sulfides, disulfides, sulfurized unsaturated organic compounds, phosphites, amines, phenols, selenides, and zinc dithiophosphate (ref. 66).

VISCOSITY INDEX IMPROVERS

The V.I. is an arbitrary number calculated from the observed viscosities of a lubricant at 100° and 210° F (ref. 67). V.I. values can range from 0 or negative numbers to numbers of 200 or more. The higher the V.I. of a lubricant, the greater is its ability to resist viscosity change with changes in temperature. In other words, a high V.I. lubricant will resist thickening at low temperatures and thinning at high temperatures.

The ideal lubricant for most applications would be one that maintains the same viscosity at all temperatures encountered in actual service. All lubricants, mineral oils as well as synthetic oils, depart from this ideal, some more than others. For example, lubricating oils derived from highly paraffinic crude oils have higher V.I. values than lubricating oils derived from highly naphthenic crude oils.

The operational advantages offered by a lubricant with a high V.I. include less friction due to viscous drag at low temperatures as well as reduced lubricant loss and lower wear at high temperatures. Precisely how high the V.I. of a lubricant should be depends, as a practical matter, on the intended application. Thus motor oils and automatic transmission fluids will ordinarily have V.I. values somewhere between 85 and 150, whereas certain hydraulic oils and special gear oils may require values of 200 or more (ref. 68).

V.I. improvers are polymeric thickeners that are added to lubricating oils to make them conform more closely to the ideal lubricant; i.e., one whose viscosity remains unaltered by changes in temperature.

All commercially important V.I. improvers belong to polyisobutenes (ref. 69), alkyl methacrylate copolymers (ref. 70), alkyl acrylate copolymers (refs. 71 and 72), and vinyl acetate alkyl fumarate copolymers (ref. 73), all of which are polymers.

Of these, the first three types account for the largest portion of the present commercial market. A new type of styrene-based polyester has been introduced recently, as well as a series of polyolefins based on ethylene and propylene.

As for manufacture, polyisobutene products are prepared by polymerizing isobutene at low temperature in the presence of a Friedel-Crafts catalyst. The last three types are generally prepared by the free-radical-initiated polymerization of the selected unsaturated monomeric esters. Commercial V.I. improvers have molecular weights in the range from about 45 000 to 1 700 000.

The principal use of V.I. improvers is in the formulation of multigrade motor oils; that is, oils that satisfy the viscosity requirements of two or more SAE viscosity grades simultaneously. These V.I.-improver-treated lubricants behave like a light oil at low temperatures and a heavier oil at high temperatures. They permit easier starting of an engine in cold weather, yet at the same time retain sufficient body at higher engine operating temperatures to assure good lubrication and low lubricant consumption.

Until about a decade ago, the demand for V.I. improvers was relatively small and came largely from lubricant formulators who sought to raise the V.I. of lubricant stocks without resorting to costly refining processes. The growing popularity of multigrade oils over the past 10 years or so has changed this picture drastically and has resulted in an unprecedented demand for V.I. improvers. V.I. improvers are also used in automatic transmission fluids and hydraulic fluids to insure satisfactory performance of the associated equipment over a wide range of temperatures.

Mode of Action of Viscosity Index Improvers

V.I. improvers exert a greater thickening effect on oil at high temperatures than they do at relatively lower temperatures. The results of such selective thickening is that the oil suffers less viscosity change with changing temperature. It is believed that the selective thickening occurs because the polymer assumes a compact, curled form in a poor solvent such as cold oil and an uncurled, high-surface-area form in a better solvent such as hot oil (refs. 15 and 74).

Polymers whose solubility in oil changes very little with temperature act as thickeners, but are not effective as V.I. improvers as those polymers whose solubility is poor at low temperatures but good at higher temperatures. V.I. improvers are more effective in increasing the V.I. of low-viscosity oils and become progressively less effective as the viscosity of the base oil increases.

V.I. improvers undergo temporary viscosity reduction under shear because of the alinement of the polymer molecules in the direction of flow. This temporary viscosity reduction has the effect of reducing friction in high shear zones and gives a significant advantage for the V.I.-improver-treated oil over a base oil of the same viscosity on startup. Another advantage is that in low shear zones the viscosity of the treated oil remains high, thus minimizing oil consumption. Polymer-treated oils also exhibit lower bearing wear than their comparable mineral oil counterparts (ref. 33). These factors have been important in the acceptance of multigrade engine oils.

Polymers used as V.I. improvers must be relatively stable to chain scission under high shear rates. Molecular weight is drastically reduced by shearing, thus causing a deterioration of properties improving V.I. The shear stability of a polymer type is dependent on polymer molecular weight and increases with decreasing molecular weight. It can be seen that shear stability and V.I. improvement require divergent molecular weights. The molecular weights of commercial polymers are based on a compromise between these two properties. In many cases, this has resulted in the use of larger amounts of lower-molecular-weight polymers for a given application.

Chemical and thermal stability are important properties of a good V.I. improver. For good stability, it is important that catalyst residues be completely removed during the manufacturing process. Some commercial polymers are formulated with inhibitors to enhance their stability. Several of the commercial V.I. improvers are multifunctional because they are also effective pour point depressants or dispersants when used at normal levels.

POUR POINT DEPRESSANTS

Ever since lubricating oils were prepared from crude oils, refiners have experienced difficulty with congelation of these products at low temperatures. Part of the difficulty arises from a natural stiffening of the hydrocarbons comprising the bulk of the oil, something that can usually be corrected by the use of a solvent such as kerosene to reduce viscosity. The rest of the difficulty, the more serious part, arises from crystallization at low temperatures of the paraffin wax present in almost all lubricating oil fractions. Upon crystallization, this wax tends to form interlocking networks that adsorb oil and form a voluminous gellike mass which restricts the flow, or "pour," of the oil.

Although refining processes known as dewaxing can remove most of the paraffin wax from lubricating oil fractions, small amounts of remaining wax will substantially raise the lowest temperature at which the oil will flow freely as measured by pour point tests such as ASTM D 97–47 (ref. 75).

Pour point depressants are chemicals that modify the wax crystallization process so the oil will pour at low temperatures. Many different kinds of chemicals are effective pour point depressants, but all commercially important products are polymeric materials: alkyl methacrylate polymers and copolymers (refs. 76 and 77), polyacrylamides (ref. 78), vinyl carboxylate-dialkyl fumarate copolymers (refs. 79, 80, and 81), alkylated polystyrene (ref. 82), alpha-olefin polymers and copolymers (ref. 83), Friedel-Crafts condensation products of chlorinated wax and aromatic compounds such as naphthalene or phenol (refs. 84 and 85), and styrene-based polyester.

Some investigators do not class these Friedel-Crafts condensation products as polymers; others maintain that they are relatively low-molecular-weight polymers with a plurality of aromatic rings and paraffin wax radicals.

The molecular-weight range of polymers effective as pour point depressants is generally below that of polymers used as V.I. improvers and is usually in the area of 500 to 10 000.

The largest usage of pour point depressants is in the formulation of crankcase lubricants, gear lubricants, and automatic transmission fluids for automotive vehicles. They also find use in the compounding of hydraulic oils.

Mode of Action of Pour Point Depressants

Although many investigators have studied the mode of action of pour point depressants, two recent papers (refs. 86 and 87) give an excellent description of the crystallization phenomena involved. The authors present convincing evidence that alkylaromatic polymers such as the Friedel-Crafts condensation products are adsorbed on the nascent wax crystal, causing it to grow in new directions and form a compact, multilayer wax crystal that does not impede the flow of the oil at low temperatures. Aliphatic polymers with comblike molecular structures such as alkyl methacrylate polymers and copolymers, polyacrylamides, vinyl carboxylate-dialkyl fumarate copolymers, and alpha-olefin polymers and copolymers are said to modify crystal growth in a similar manner, although here the mechanism is one of cocrystallization with the wax rather than adsorption on the surface of the wax crystal.

EXTREME-PRESSURE ADDITIVES

EP additives, as they are commonly called, are chemicals that are added to lubricants to prevent destructive metal-to-metal contact in the lubrication of relatively moving surfaces. Plain mineral oils provide good lubrication as long as a film of oil is maintained between the relatively moving surfaces. This kind of lubrication, termed "hydrodynamic," is governed by parameters of the lubricant, principally its viscosity. When pressures or rubbing speeds between the moving metal surfaces are such that an intact film of oil is not maintained, however, metal-to-metal contact occurs over a significant portion of the lubricated area. This kind of lubrication, called boundary lubrication, is governed largely by parameters of the contacting surfaces such as surface finish, metal shear strength, and the coefficient of friction between the metals involved. Unless the latter parameters can be chosen to meet expected pressures and rubbing speeds, destructive metal-to-metal contact will take place. Such destructive contact manifests itself in various different forms such as welding, scoring, scuffing, ridging, rippling, and, in some cases, a catastrophic deformation or complete destruction of the lubricated component. It is the role of EP additives to prevent this sort of thing from happening.

Mode of Action of Extreme-Pressure Additives

EP additives function by reacting with relatively moving metal surfaces under boundary lubrication conditions to form an adherent film of metallic salts with lower shear strength than that of the metal surfaces (ref. 88). This film acts as a solid lubricant and takes over the task of lubrication when metal-to-metal contact occurs. With an appropriate EP additive, there is no appreciable formation of such solid lubricant on the metal surface under conditions of hydrodynamic lubrication. It forms only at the elevated temperatures that develop locally between the moving metal surfaces under conditions of boundary lubrication.

Commercial Extreme-Pressure Additives and Their Application

Virtually all commercial EP additives are organic compounds that contain one or more elements or functions, such as sulfur, halogen, phosphorus, carboxyl, or carboxylate salt, which can react chemically with the metal surface under conditions of boundary lubrication. The ease with which an EP additive reacts with the metal surface, i.e., its activity, determines to a large extent whether it would be used in a lubricant such as a cutting oil, a hypoid gear oil, or a steam turbine oil. Likely fields of application of commercial EP additives can be assigned on the basis of their relative activity. High-activity EP additives can be used in straight cutting oils, drawing compounds, metal-forming lubricants, and some hypoid gear oils; moderate- or intermediate-activity additives can be used in hypoid gear oils, e.g., multipurpose gear lubricants, and industrial gear oils, e.g., open gear oils. Mild- or low-activity EP additives can be used in worm gear oils, spiral bevel gear oils, manual gearbox oils, motor oils, steam turbine oils, jet aircraft turbine oils, gas turbine oils, automatic transmission fluids, and hydraulic oils (fire-resistant emulsion types).

Automotive Extreme-Pressure Gear Oils

These oils are used to lubricate the worm, spiral bevel, or hypoid gear drives of automotive vehicles. Because hypoid gears require the greatest measure of EP protection of all commercial gear drives, most additive treatments are designed to give satisfactory performance in this environment.

Several different types of EP additives have been used in hypoid gear service. The earliest successful treatments, ca. 1928, used lead soap, e.g., lead naphthenate, plus an active or corrosive organic sulfur compound. In the late 1930's, chlorine and moderately active sulfur present in the same or different organic molecules were used. During World War II, sulfur, chlorine, and phosphorus in suitable organic carriers were the important types. The most recent types, from 1960 to the present, are sulfur and phosphorus and sulfur, phosphorus, chlorine, and zinc in suitable organic carriers. This information should not be interpreted as indicating that early treatments are obsolete; in fact, all of the indicated treatments are still in commercial use today. The more recently developed additives, however, enjoy most of the market.

A list of commercially important EP additives that can be used to formulate hypoid gear lubricants includes chlorinated paraffin wax (ref. 89), chlornaphtha xanthate (ref. 90), chlorinated paraffin wax sulfides (ref. 91), sulfurized unsaturated esters (ref. 92), alkyl and aryl sulfides (ref. 94), sulfurized and phosphorized fatty oils (ref. 94), esters of phosphorous and phosphoric acids (ref. 95), lead naphthenate (ref. 96), and metal salts of diorganodithiophosphoric acids (ref. 97).

An evaluation of the practical effectiveness of a hypoid gear lubricant must be carried out in full-scale equipment in the laboratory and in the field. Bench test rigs have not been able to perform this task, although they are useful in screening likely candidates for full-scale evaluation.

In full-scale tests, the phenomenon of performance incompatibility can be observed. Performance incompatibility means that one or more of the additives present in the total treatment contributes to performance in one kind of service, high torque or high speed, but negates or reduces the effectiveness of another additive in the other type of service. Table 1 shows the performance characteristics of a number of classes of organic compounds in full-scale laboratory gear tests.[2] Although there are exceptions to the generalizations noted in the table because, obviously, not all the members of each class could be tested, the results are believed to be indicative. The performance incompatibility of certain classes of compounds is evident. This should not be construed to mean that members of such classes are not useful; it does indicate, however, that care must be

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[2] Research conducted in the laboratories of the Lubrizol Corp.

TABLE 1.—*Performance Characteristics of Classes of Organic Compounds in Full-Scale Laboratory Gear Tests*

Classes of compounds	Use in hypoid gear service	
	High speed	High torque
Chlorine bearing	+	0 to (+)
Active sulfur in noncarboxylic compound	+	−
Relatively inactive sulfur in noncarboxylic compound	+	(−)
Relatively inactive sulfur in carboxylic ester	(−) to (+)	+
Relatively inactive sulfur in carboxylic acid	+	+
Carboxylic esters	−	+
Carboxylic acids	(−) to −	+
Oxyphosphite acid esters	+	+
Oxyphosphite neutral esters	0	0
Oxyphosphate neutral esters	0	0
Thiophosphate neutral esters	+	+

+ = definitely effective
(+) = slightly effective
0 = ineffective, but not harmful
(−) = slightly harmful
− = definitely harmful

taken in the amounts and proportions of such additives used in the total treatment.

Extreme-Pressure Additives for Motor Oils

The advent of high-performance engines for passenger cars posed new lubrication problems. Engine inspection began to reveal unmistakable evidence of excessive wear and scuffing of valve train components; high rotational speeds and increasing pressures between cams and lifter foot surfaces had apparently combined to shift lubrication requirements into the boundary region. The first and perhaps most effective EP additive for controlling or eliminating wear and scuffing in the valve train area was found to be that versatile additive, zinc dialkyldithiophosphate (ref. 98).

Other additives found useful for the control of steel-on-steel wear in valve trains include tricresyl phosphate, dilauryl phosphate, didodecyl phosphite, sulfurized terpenes, sulfurized sperm oil, chlorinated compounds, and zinc dialkyl dithiocarbamate (ref. 99). EP additives used for controlling valve train wear have become known in the industry as antiwear or antiscuffing agents.

In a related development, certain organotin compounds, believed to be trimeric dialkyl tin sulfides, have been reported to be of value in reducing piston scuffing in two-stroke-cycle engines (ref. 100).

MISCELLANEOUS ADDITIVES

Frequently an additive-treated lubricant will be quite satisfactory in many performance areas in its intended field of application, but exhibit certain deficiencies that mar that performance and detract from the salability of the product.

For example, an otherwise satisfactory lubricant may tend to cause rust, promote foaming, form stains on copper or copper-alloy parts, cause spark plugs to become fouled, or permit an objectionable noise, e.g., a squawk or chatter, to come from a lubricated component. Although efforts to eliminate the source of the difficulty occasionally require a major reformulation of the additive treatment, more often they involve the simple addition of a corrective additive or "fix" to the lubricant. In curing the difficulty, the fix must not adversely affect, of course, the performance of the lubricant in any other respect. Some of the more important additives of this type are described in table 2.

NEEDED RESEARCH AND DEVELOPMENT IN THE AREAS OF ADDITIVES AND ADDITIVE-BASE-STOCK INTERACTION

Trends in automotive equipment, already well underway, point toward substantially higher temperatures in virtually all environments in which lubricants are used. Thus, the entire spectrum of additives, detergents, dispersants, antioxidants, corrosion inhibitors, EP agents, etc., will need to be improved to carry out intended additive functions at these higher temperatures.

For example, there is need for the development of improved ashless dispersants that will perform well at high temperatures. Presently available ashless dispersants are effective in normal gasoline engine service, e.g., stop-and-go operations, home-to-work driving, etc., but fail to maintain satisfactory cleanliness in high-output diesel engines where temperatures of 500° to 600° F prevail in the ring belt area.

In the latter case, ash-containing detergent additives (organometallic compounds) are currently required and used by lubricant formulators to control harmful piston deposits. Lubricants formulated with high levels of ash have been reported to cause problems in some diesel engines. These problems could be avoided if an ashless dispersant that is effective at high temperatures were available.

Then, too, it has been observed that present antioxidants for crankcase oils, principally zinc dithiophosphates, tend to lose their effectiveness prematurely at the high temperatures encountered; for example, in diesel engines and in high-horsepower gasoline engines used in trailer-towing service. Under such conditions, the oil is subject to severe oxidation and thickens rapidly. It is possible to increase the amount of antioxidant used and thereby extend the useful life of the oil, but the best answer to the

TABLE 2.—*Additives Employed as Fixes*

Commercial designation	Typical chemicals used	Principal field of application
Rust inhibitor	Alkenylsuccinic acids and derivatives (ref. 101) Alkylthio-acetic acids and derivatives (ref. 102) Substituted imidazolines (ref. 103) Amine phosphates (ref. 104) Metal and amine sulfonates	All types of lubricants
Antifoam	Silicones (ref. 105) Organic copolymers (ref. 106)	All types of lubricants
Antistain	Substituted thiadiazole Dibenzothiazole	Gear oils
Antichatter	Amine salt-azomethine combinations Amine dithiophosphates (ref. 107)	Gear oils for limited slip differentials
Antisquawk	*N*-acylsarcosines and derivatives (ref. 108) Sulfurized fatty acids and esters (ref. 109) Organophosphorus acid-fatty acid combinations (ref. 110) Esters of dimerized fatty acids (ref. 111)	Automatic transmission fluids
Antifoulant	Chlorinated hydrocarbons (ref. 112)	2-stroke engine oils

problem would be the development of an antioxidant that is inherently more stable and long lived.

The cited need for improved dispersants and antioxidants is but illustrative of the overall demand for additives that can cope with higher temperatures. Similar cases could be established for improved EP agents to be used in lubricants for hypoid gears and automatic transmissions, where operating temperatures are also on the rise.

New refining techniques for base stock production such as hydrocracking, hydrofining, and hydrotreating, coupled with the phasing out of leaded gasoline and the development of new, lead-free fuels, have already changed additive requirements and promise to do so to an even greater extent in the future.

For example, there is reason to believe that tomorrow's cars will run on unleaded gasoline and be equipped with devices such as catalytic mufflers, thermal reactors, or afterburners to control harmful exhaust emissions. Additives used in the crankcase oil of such cars may affect the durability and efficiency of these exhaust control devices. Research will be necessary, therefore, to single out additives that not only are effective but also neither reduce the efficiency nor shorten the life of the control devices. This research must, of course, await decisions by automakers as to which type or types of emission control systems will be employed to meet Federal exhaust emission standards in the years ahead.

As for additive-base-stock interactions, no one has yet been able to select the additive combination best suited for a given base stock without actual experiment in trial-and-error fashion.

It has been found, for example, that hydrocracked oils of high V.I. respond much better to antioxidants than do solvent-extracted, high-V.I. oils from the same crude, but what chemical differences between the oils are responsible for this behavior remain unknown. Similarly, oils containing 0.5 to 1 percent naturally occurring sulfur have been found to be much more oxidation resistant than oils containing 0.1 to 0.3 percent sulfur. Whether the different sulfur content is wholly responsible for the observed behavior or whether other chemical differences between the oils are important remains unanswered.

Although a knowledge of crude source and refining process is helpful in choosing candidate additive treatments, such knowledge falls far short of a complete characterization of a base stock that, hopefully, would enable the lubricant formulator to predict the best additive system with confidence.

DISCUSSIONS

E. D. Edwards (Burmah-Castrol Co., Bracknell, England)

As Mr. Smalheer points out, the whole purpose of adding an additive to a lubricant base stock is to improve performance.

In a simple case where an antioxidant is added, the time to runaway oxidation is put off; in other words, the induction period is prolonged. One way of demonstrating this effect is by means of an oxygen-absorption test from which emerge the results shown in figure 1.

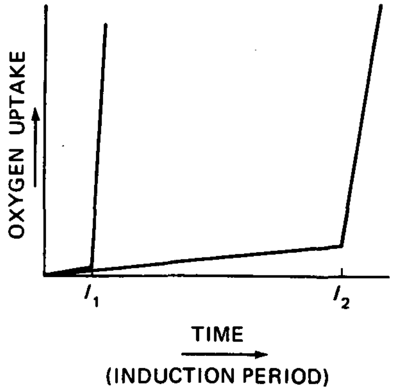

FIGURE 1.—Oxygen uptake versus time plot.

This is all very fine until awkward questions get asked. For example, if figure 1 applies at 150° C, what happens at 180° C? The answer may well be that $I_2 = I_1$, a polite way of saying the antioxidant does not work at that temperature. The situation may be worse than this—the antioxidant may itself break down and actually increase the problems by, for example, depositing sludge. Such things have happened. Therefore, one limitation is the effective temperature range of an antioxidant. However, even within the effective temperature range this is not all. In synthetic lubricants for jet engines, e.g., diesters of sebacic and azelaic acids, it was common to employ phenothiazine as an antioxidant. During the oxidation process this is converted to phenothiazine sulfoxide, which is insoluble and flops out as a black powder. The centrifuging action of bearings leads to this byproduct building up and eventually blocking lubricant flow.

This can result in bearing seizure and then engine failure. Modification of phenothiazine has led to a product that avoids this problem entirely, as the oxidation byproduct is soluble and no longer appears as a sludge. Here, then, is another limitation, the insolubility of the byproducts of an antioxidant. Obviously, this is solvent dependent. Hence it is necessary to consider the additive in the system concerned and not just by itself. It is also evident that automotive engine piston temperatures will rise yet further, and this will make the need for better high-temperature antioxidants and detergents all the more urgent. For a variety of reasons, ashless antioxidants would be preferred, but it is not at all easy to provide wholly satisfactory substitutes for the ash-containing zinc dithiophosphates. The need for antioxidants with improved high-temperature capability is very general. It arises not only in automotive lubricants but also in synthetic ester-type lubricants; e.g., for the Concorde aircraft. If the aim is to push back boundaries in lubrication technology, then what is needed are antioxidants of improved temperature range that do not give insoluble byproducts. This can be done by modification of existing chemical structures, as already indicated. Chemical guidelines are known and can be used, but we are approaching the limits of our knowledge. A much better understanding of how antioxidants act, why one is better than another, and how improvements can be made is plainly needed. It is not so much the academic answer as the practical means for the improvement of antioxidants that is called for.

Experience also shows an analogous problem with what Mr. Smalheer refers to as dispersants. These were designed to cope with stop-and-go driving conditions where, for example, the rocker-box cover may never get really warm and hence fuel byproducts and water build up in the oil as a voluminous cold sludge. While present dispersants are effective in dealing with this problem, they must also survive hot conditions. So the dispersant must not interfere with the job of work that the detergent is doing. Nor must it contribute to deposit problems, e.g., varnish, under such conditions. It is odd that two different types of compounds are needed to do these two jobs. Why not only one additive to do both types of work? The answer is not easy to get. Notice that effective temperature range might appear to be the reason but probably is not because (up to a point) dispersants will work at high temperatures and, as Mr. Smalheer remarks, large doses of detergent will work to some extent with cold sludge. Detergents are effective with dry sludge at both high and low temperatures. Actual breakdown of the dispersant molecule at high temperatures may well be a significant cause. Yet, is it not possible that it acts as a coagulant?

It seems likely that partial exhaust gas recirculation (EGR) via the inlet manifold will be adopted as a means of reducing NO_x emissions. Of course, the presence of combustion byproducts and partly burnt fuel in the lubricant is common, but EGR will dramatically increase the problems that arise from this cause and will put heavier demands on the sump oil with respect to oxidation, rusting, and general corrosion resistance. This illustrates the way in which the lubricant additive technologist sometimes has wholly unexpected problems descend upon him. To minimize a fuel combustion problem, EGR has been favored, but one wonders if the impact on the lubricant was really considered.

If we turn to EP additives for gear oils, there is much technology available to enable the expert to select a suitable additive (or combination of additives) that will work in the application concerned whether it be at high or low temperature, in mineral oil or synthetic base stocks, or for low friction or low wear. All this is on the basis of experience. It is exceedingly difficult to give specific parameters that exactly define, for example, frictional characteristics or load-carrying ability. Usually, definition is only in terms of the application. Experience, then, counts for much in this area, and a lot of protective bunk is talked for this reason. Thus, it is said that you cannot develop a new oil without using a selection of gear rigs before field testing in the actual gear. I know of a hypoid gear oil developed using a four-ball machine that proved absolutely satisfactory in the particularly nasty back-axle unit concerned. Experience was what counted in this case, not gear rigs, which proliferate and answer only the question of whether this oil will lubricate this gear rig.

The presence of water in brake fluids (which are generally synthetic oils) gives rise to trouble; for example, reduction of boiling point and hence loss of braking efficiency, even to the point of total failure. To reduce this problem, brake fluid compositions of low moisture avidity have been successfully employed, but now fluids that entirely avoid the problem have been developed. Here the additive technologist has been hard put to come up with the solution.

B. W. Hotten (Chevron Research Co., Richmond, Calif.)

Mr. Smalheer's review of lubricant additives gives little justification for contradiction or addition, but further discussion of some environmental challenges facing additive research may be of interest. We are fighting against pollution and toxicity and even lending a hand in wildlife conservation and fire prevention. I propose the term "sociotropic" for such research to emphasize that its products go beyond the immediate needs of the consumer to meet needs of society at large.

Pollution Control.—The leading challenge here, as noted by Mr. Smalheer, is to develop lubricants for engines burning lead-free gasoline. Such gasoline will help minimize emissions to the atmosphere but may produce more engine varnish (ref. 113). Oil used with it will need better dispersancy, but succinimide dispersants may be difficult to surpass. The new polybuteneamine detergent dispersants in gasoline will help maintain overall engine cleanliness. We may have to eliminate metal-containing additives from the oil to prevent metals from being carried through to catalytic mufflers and deactivating them. Metal salts in engine oils also contribute to spark-plug fouling, preignition, and exhaust emissions. Fortunately, when lead goes, its scavengers will go with it. The overbased sulfonates and phenoxides now needed to neutralize hydrohalic acids formed by lead scavengers may be unnecessary. Zinc dithiophosphates have several functions and may require several additives for replacement.

Two other effects of pollution control on additives come to mind. Base oils are changing, partly to reduce pollution. Acid treating of oils, which produces SO_2 and acid sludge, is being replaced by hydrotreating, as described by Mr. Furby; additive response will change as a result. Finally, the manufacturing process for some additives is changing: reduced aromatic contents and better recovery of the solvents used are making the air more breathable.

Toxicity Control.—The ideal food machinery lubricant would be as edible as any food that it might accidentally contact. The development of a food machinery grease based on white oil illustrates some problems that arise. A complex aluminum soap solved the gelling agent problem because of its high melting temperature, good water resistance, and low toxicity. The fatty acid portion even added a little nourishment. The problem of finding a rust inhibitor was solved by the convergence of two desirable traits in sodium benzoate: it had served to inhibit rust in radiators and had been used safely in food products (mold inhibitor). It unexpectedly improved the heat stability of this grease also (ref. 114). Other examples of additives suitable for food-grade lubricants are 2,6-di-*t*-butyl-*p*-cresol, called BHT when used in foods, dilauryl thiodiproprionate, and lecithin.

Certain antiwear and EP agents are interesting from the mechanistic viewpoint as well as for being free of such unsavory side effects as toxicity, bad odor, or corrosivity in typical Cl-S-P-Pb compounds. The examples in table 3 defy classification in the usual trimodal system of hydrodynamic, boundary, and chemical EP. Despite their chemical diversity, they may

TABLE 3.—*Test Results for 4 Antiwear and EP Agents*

Additive	Test	Result	
		Without	With
Calcium acetate in complex soap greases.	Timken	10 lb	60 lb
Borax	Wire drawing		
Polyethylene in greases	Shackle machine	50 percent	5 percent[a]
Glycerol in greases	Falex	1500 lb	4000 lb

[a] Area of metal damage in automotive shackles.

share a common mechanism. They may all form highly viscous films on the metal surface, calcium acetate (ref. 115) and borax (ref. 116) by coalescence into glassy layers, polyethylene (ref. 117) by sintering, and glycerol by decomposition and polymerization. Such lubrication should be considered a fourth mode and named "vitridynamic" (ref. 118) because of its relationship to lubrication with molten glass, which was discussed by Dr. Lansdown.

Wildlife Conservation.—Sulfidized glycerides such as lard oil had been used as antiwear and EP agents in gear lubricants for many years when Smith (ref. 119) discovered that their replacement with sulfidized sperm whale oil (a mixture of monoesters of mostly olefinic C_{16}–C_{18} alcohols and carboxylic acids) increased the stability of the gear lubricants. Unfortunately, it decreased the stability of the whale population. The recent U.S. Government ban on sperm whale oil imports makes a replacement necessary. Sperm whale oil would be easy to match synthetically except for the high cost of olefinic C_{16}–C_{18} alcohols. Several potential replacements are surfacing: modified glycerides, methyl esters, and higher alkyl esters.

Fire Prevention.—The fourth group of products that qualify for inclusion under the sociotropic heading reduce the hazard of fires that have occurred in hydraulic systems on naval ships and in mines. Three types of fire-resistant hydraulic fluids are in use. The phosphate esters discussed by Dr. Hatton lubricate well and resist combustion. But, because they are esters of a strong acid, they require special inhibitors against pyrolysis, hydrolysis, and corrosion. Emulsions of water in petroleum oil and solutions of polyethers in water suffer from wear and rust problems and need better additives to accomplish their important mission.

G. Salomon (Central Laboratory, TNO, Delft, The Netherlands)

The author states that EP additives form a low-shear-strength adherent film only at elevated temperature. It would seem that this definition of protective film formation is too narrow.

Since Groszek and Cameron proved the presence of polymeric oxidation products in white oil, we have repeated their work and found such compounds even in medicinal white oil as received. The composition of these impurities differs from that found in the used oil. It is at least probable that such polar compounds contribute to film formation and to boundary lubrication in the absence of EP additives. Further, the work of Landen (ref. 120) and the comments on it made by Kelley (ref. 121) make clear that such films can be formed by nonreactive oils. Rounds (ref. 122), in continuation of his earlier work (ref. 99), has illustrated the tremendous complexity of film formation from interactions between additives and nonhydrocarbons in the oil.

Recently, Bartel in Germany (ref. 123) has pointed out the analytical significance of colored lubricant films. He was able to distinguish between colors due to metal oxides, colors caused by metal-additive interactions, colors of solid lubricants, and colors caused by metal-solid lubricant interactions. Bartel gave also a classification of functional properties of such films into protective, harmless, and damaging.

The discusser believes that a more systematic approach to film properties would be of great help to the production and the maintenance engineer. Bartel has shown already that visual observation (combined with scratching) can be of analytical value. The paint and lacquer technologists have developed many methods suitable for scratch-hardness testing on a microscale. Contact angle measurements with small drops of nonwetting liquids can be performed with simple tools. Such data would yield information on the nature of the film, if combined with the semiempirical solubility theory discussed at this symposium by Beerbower and by Groszek. It might then become possible to intentionally catalyze the formation of protective films, even from nonreactive oils, more in particular in combination with nonferrous metals, where EP additives are unlikely to have a useful function.

T. Salomon (OMER, Israel)

Mr. Smalheer states that "there is reason to believe . . . that detergent oils may act upon contaminant particles in a manner similar to that of aqueous soap solutions." This statement does not reflect the main action of the detergent agents through formation of a complex compound with the blowby products. This complex compound undergoes immediately a thermolysis at about 300° C with formation of solid carbonaceous material. The carbonaceous material produced by thermolysis may become even more important than that due to an incomplete combustion of the fuel. This depends on the operating conditions of the engine. This thesis has been verified when filtered used engine oils were heated up to about

300° C under CO_2 to avoid any oil oxidation. The quantity of detergent destroyed by this thermolysis was in direct ratio to the quantity of carbon produced.

A correct appraisal of the dispersancy of new engine oils cannot be performed with carbon black or graphite. Engine sludge that has been obtained with the same base oil and the same fuel in the same engine has to be used.

The author states that "hydrocracked oils of high V.I. respond much better to antioxidants than do solvent-extracted, high-V.I. oils from the same crude, but what chemical differences between the oils are responsible for this behavior remain unknown." Is this difference not due to the lower content of chemical impurities in the hydrocracked oil?

Regarding the outlook for the future, dispersants need a good ground for action like fertilizers, which do not act in a sterile earth. Such a good ground is given, for instance, by the minor constituents of the base oil (not hydrocarbon material), or the degradation products (resins) of the fuel used. This thesis may explain why two fuels of various composition may produce different results with the same base oil in the same engine; the detrimental effect of organic nitrogen compounds, even as traces, in the base oil; why white oils are not good base stocks for engine oils; and why gaseous fuels, like hydrogen or methane, do not give rise to problems of sludge or oil contamination.

C. Staley (Ciba-Geigy Ltd., Manchester, England)

First of all, I would like to congratulate the author for his excellent review of such a vast field as this. It is quite clearly impossible to discuss in great depth any particular topics in this type of paper, and Mr. Smalheer has, in my opinion, done an exceptionally fine job in compiling an entirely readable and understandable summary covering all the more important types of additives used both previously and currently.

At the same time such a paper is very difficult to discuss, because no real areas of controversy are raised, and yet, at the same time, questions of detail could be raised in just about every section.

Lacking Mr. Smalheer's breadth of experience in the field of lubricant additives generally, I would therefore like to restrict my comments to the form of a discussion in a little more detail of the area with which I am most familiar, that of additives for synthetic lubricants, in particular for organic ester-based gas turbine engine lubricants.

As one might expect with such premium-grade lubricants, many of the types of additives mentioned by Mr. Smalheer are used. These include antioxidants, corrosion inhibitors, antiwear and EP agents, and antifoam additives. You will notice that detergent additives are not mentioned in this list. These are not required in gas turbine lubricants because contamination with combustion byproducts from the fuel does not occur. It is, however, relatively common for the lubricant to include a small quantity of an ashless dispersant to solubilize any solid material arising from lubricant breakdown. As a general rule, additives used in gas turbine lubricants are almost always ashless because of the need for clean, non-deposit-forming, non-coke-forming products.

A second class of additives only rarely used in these lubricants are V.I. improvers. Because of the high inherent V.I. of the ester base stocks used, there is no real need for such products, which, in any case, may introduce adverse side effects such as viscosity changes due to shear, reduced oxidation stability, etc. Similarly, the excellent low-temperature fluidity of ester base stocks eliminates the need for pour point depressants. It is believed, however, that the tendency of the polymethacrylate type of additive to break down to lower-molecular-weight components on heating, with consequent viscosity reduction, has in the past been put to good, if slightly questionable, use. Paper specifications for aircraft gas turbine lubricants normally include an oxidation corrosion test, with limits on the viscosity increase. It has been suggested that polymethacrylates have been used to compensate for an otherwise excessive viscosity increase of the lubricant.

One type of polymer that has been used extensively in ester-based lubricants and that some people may regard as a V.I. improver is the polyalkyleneglycol or polyglycolether type. It is, however, probably more correct to consider these simply as thickeners rather than V.I. improvers. They generally have much lower molecular weights and are shear stable. They are used in the production of the more viscous type of lubricant, which is required for turbopropeller engines to provide the greater load-carrying properties demanded by the reduction gearbox employed in these engines.

Rush inhibitors are also only occasionally used in gas turbine lubricants. Such products, particularly the metal sulfonates, do, however, find use in other types of synthetic lubricant. They are included, for example, in ester-based fine mechanism lubricants, such as those used in aircraft instruments and in wide-temperature-range greases. *N*-acyl sarcosines also find use, for example, in polyglycol-based worm gear oils. Alkenylsuccinic anhydrides and amine phosphate types are used in phosphate ester lubricants and hydraulic fluids. A rust-inhibited gas turbine lubricant may eventually be required by the U.S. Navy, which has been working on a sea-water corrosion-preventive version of their MIL–L–23699 lubricant for some time. A provisional specification XAS–2354 with a sea-water corrosion test has been published, while King and Glassman (ref. 124) have reported promising results with a combination of Lubrizol 859 (alkenyl succinic anhydride), Ciba-Geigy NPA (nonylphenoxy acetic acid), and Polyglycol 1200 (polypropylene glycol).

Undoubtedly the most critical additives used in formulating gas turbine lubricants are the antioxidants, antiwear and EP additives, and possibly to a lesser extent, corrosion inhibitors and metal passivators. These are now discussed separately.

Antioxidants.—As Mr. Smalheer has indicated, phenothiazine and its derivatives are widely used in jet aircraft engine lubricants. Indeed, up to about 1959, phenothiazine was just about the only antioxidant used. However, increased engine operating temperatures have since created a demand for much better performance than that provided by phenothiazine and nowadays most, if not all, jet engine lubricants contain at least two antioxidants that together provide a synergistic effect in reducing oil oxidation. Even so, there are still relatively few products in widespread use. Almost all are of the secondary aromatic amine types. These have lower volatility and are more effective at high temperatures than the hindered phenolic type of antioxidant used in many other kinds of lubricant. The zinc dialkyl dithiophosphate type of product does not find use in this application because of its inadequate thermal stability and ash-forming tendencies and because ester response to this type of antioxidant is not very good.

As mentioned above, phenothiazine has been particularly widely used for this application, initially quite satisfactorily. However, it was found that during service at higher operating temperatures, this product gave rise to heavy sludge deposits. It is probable that these resulted from oxidation of the phenothiazine and subsequent polymerization with the ultimate production of insoluble, oxygenated polymeric compounds.

This problem of phenothiazine dirtiness was largely overcome by the substitution of alkyl groups in the phenyl rings (ref. 125). This appears to have the effects of, first, blocking positions most liable to oxidation and, second, of solubilizing oxidation products that do form. These dialkyl phenothiazines are a considerably less efficient antioxidant than the parent compound, even after allowance has been made for their higher molecular weight, but greatly improved all-round performance is obtained when they are used in conjunction with a second aromatic amine antioxidant acting as a synergist (ref. 126). Table 4 shows this effect quite clearly in the results from oxidation-corrosion tests carried out at 347° F (72 hr with an airflow of 5 liter/hr) (ref. 125).

In addition to the dialkyl phenothiazines exemplified above, other phenothiazine materials that have found commercial use include *N*-substituted derivatives (ref. 127).

Although phenothiazine has been particularly associated with the problems of deposit formation in gas turbine lubricants, other secondary aromatic amines, such as diphenylamine and the phenylnaphthylamines, give rise to similar problems. In these cases also, alkylated derivatives have proved to be much cleaner. *p,p*-di-*t*-octyldiphenylamine (DODP), for example, is an exceptionally clean antioxidant, and this product has now replaced phenothiazine as the staple antioxidant in aerogas turbine engine

TABLE 4.—*MIL-L-7808 Oxidation-Corrosion Tests*

Antioxidant	Increase in viscosity at 100° F, percent	Increase in acid value, mg KOH/g	Insolubles in petroleum ether, percent
0.5 percent phenothiazine	3.1	1.93	0.50
2.0 percent dialkylphenothiazine	6.7	11.1	.20
2.0 percent aromatic amine B	14.0	2.0	.17
1.5 percent dialkylphenothiazine 0.5 percent aromatic amine B	4.9	1.57	Nil
0.5 percent dialkylphenothiazine 1.5 percent aromatic amine B	6.7	1.57	Nil

Note.—72 hr at 347° F; base fluid: di-(2-ethylhexyl)sebacate.

TABLE 5.—*Oxidation-Corrosion Tests*

Additive	Increase in viscosity at 100° F, percent	Increase in acid value, mg KOH/g	Insoluble matter, mg
None	Too sludgy to measure	21.5	4000
4 percent DODP	52.4	2.6	0
2 percent PAN	32.2	4.5	24
1 percent DODP 1 percent PAN	14.4	.0	6

Note.—48 hr at 425° F; base fluid: Trimethylol propane tripelargonate.

lubricant formulations. As in the case of the alkylated phenothiazines, the efficiency of DODP is less than that of diphenylamine itself and again the use of synergists with this product is common. Combinations with dialkyl phenothiazines, as mentioned above for instance, and mixtures with other phenothiazine derivatives as well as phenothiazine itself are used (ref. 128). A second well-known mixture is that of DODP and phenyl α-naphthylamine (PAN) (refs. 129 and 130). A further synergist for DODP that has been widely studied but has not, to my knowledge, found commercial use because of the very high cost is 5-ethyl 10,10-diphenyl phenazasilane (commonly known as 5-10-10). The latter additive also forms highly effective combinations with PAN (ref. 131). Table 5 illustrates the improvements obtained when PAN is added to DODP.

A fairly recent innovation has been the introduction of alkylated derivatives of phenyl α-naphthylamine and phenyl β-naphthylamine (ref. 132).

TABLE 6.—*Panel Coker Tests*

Additive (all+1 percent DODP)	Coke, mg
1 percent phenyl-β-naphthylamine	71
1.5 percent mono-*t*-octylphenyl-β-naphthylamine	2.4
1 percent phenyl-α-naphthylamine	65
1.5 percent mono-*t*-octylphenyl-α-naphthylamine	1.4

Base fluid: Pentaerythritol esters, 5 cs at 210° F.

These have the usual advantage of improved cleanliness over their nonalkylated parent compounds. Again, antioxidant efficiency is slightly reduced, and this also applies to their combinations with DODP. However such combinations show very marked advantages in terms of coke- and lacquer-forming tendencies. These improvements show up very clearly in the Roxana panel coker test in which lubricant is splashed against an aluminum test panel heated to 600° F. Test duration is 8 hr, after which deposits on the test panel are weighed. Typical results from this test are shown in table 6.

In addition to the above types of additives, small amounts of phenolic antioxidants, such as di-*t*-butyl *p*-cresol or 2,6-di-*t*-butyl-α-dimethylamino-*p*-cresol, are often used as low-temperature stabilizers; e.g., to provide good storage stability. In general, however, there is a very limited number of antioxidants currently used in ester-based gas turbine lubricants, and a lot depends on the skillful selection of antioxidant combinations. In this respect, three component antioxidant systems have been developed comprising a phenothiazine, a second aromatic amine, and a phosphorus compound; e.g., a triarylphosphorothionate (ref. 133) or a phosphoramidate (ref. 134). It seems almost certain, however, that further improvements in the high-temperature stability of these lubricants in the immediate future will come from advances in antioxidant technology rather than from radical changes in base stock types.

Anti-wear/Extreme-Pressure Additives.—The load-carrying requirements of gas turbine engine lubricants in the past have not been particularly onerous, except for the case of turbopropeller engines where a higher load-carrying capacity was specified to adequately lubricate the reduction gearboxes. As mentioned previously, this aspect was taken care of by the use of a more viscous lubricant (7.5 cs at 210° F compared with 3 cs for pure turbojet lubricants). In the vast majority of lubricants, therefore, additives having only mild EP properties have proved quite satisfactory, and tricresyl phosphate in particular has found very wide use. Other phosphate ester variants which have found use include triphenyl phosphorothionate (ref. 135) and di-*o*-chlorphenyl phenyl phosphate (ref. 136) while phosphonates, aminophosphonates (refs. 137 and 138), phosphoramidates, and phosphites are other phosphorus compounds that have found past use. Di-iso-propyl phosphite today finds use as an EP additive in diester-based lubricants for other applications; e.g., MIL–L–46000.

Apart from the phosphorus-containing compounds that tend to dominate this field, other products that have been used include chlorinated diphenyls, diaryl thioethers (ref. 139), amides of hydrogenated dimer acids (ref. 140), and even small amounts of dicarboxylic acids (ref. 141), such as sebacic acid and azelaic acid.

Tricresyl phosphate is still widely used in the modern, so-called type 2 lubricants based on esters of trimethylolpropane and pentaerythritol. However, more demanding load-carrying requirements are being presented by engines such as the Olympus 593 of the Concorde (ref. 142). The Olympus specification calls for a 5-cs oil with load-carrying properties equivalent to those of 7.5-cs lubricants. Much activity therefore currently centers around the development of new and more effective additives. The main difficulty is that the more active load-carrying additives, such as the sulfur- and chlorine-containing products, normally have a serious adverse effect on oil stability and tend to be corrosive at high temperatures. As with antioxidants, answers have been found in the development of highly synergistic additive combinations. These may, for instance, consist of the relatively stable tricresylphosphate type together with a small amount of a second, much less stable additive that activates the tricresyl phosphate. These combinations are proprietary secrets, and I can only quote the following examples from the patent literature:

(1) Neutral triorganophosphate plus a neutral salt of dialkyl hydrogen phosphate (ref. 143).
(2) Neutral triorganophosphate and dialkyl hydrogen phosphite (ref. 144).
(3) Trihydrocarbylphosphate plus a salt of an alkylamine, a monohalo alkyl phosphonic acid, and a dicarboxylic acid (ref. 145).

Corrosion Inhibitors/Metal Passivators.—The term "corrosion inhibitors" refers to the protection of nonferrous metals and is distinguished from the term "rust inhibitors," which are exclusively associated with ferrous metal protection.

The corrosion of nonferrous metals is quite frequently a disadvantage of otherwise excellent lubricant formulations. Copper and magnesium are particularly vulnerable metals, and problems can also occur with silver, cadmium, and lead. The corrosion is usually brought about by lubricant breakdown products or is caused by certain additives in the lubricant; for example, phenothiazines can cause copper corrosion while DODP is often aggressive toward magnesium. The more active types of load-carrying additive can also prove highly corrosive. Sometimes the problem can only be overcome by the removal of the offending additive or by a complete revamp of the additive package where no single additive appears to be responsible. This is probably particularly true in the case of magnesium. Frequently, however, a solution can be found in the use of a corrosion inhibitor.

Most of the successful inhibitors for copper are nitrogen-containing products, very often heterocyclic compounds. Among the most widely used products are benzotriazole (and derivatives) (refs. 146 and 147), substituted 1,2,4-triazoles (ref. 148), imidazoles, pyrazoles, and salts of salicylal amino-guanidine (ref. 129). Sulfur-containing compounds such as mercaptobenzothiazoles and thiodiazoles have found little, if any, use.

Many of these copper inhibitors have a valuable secondary effect (some might call it the major effect) in passivating copper surfaces. Copper, of course, is a potent oxidation catalyst, and by forming a complex on the metal surface the inhibitor effectively reduces the catalytic action. The result is an overall improvement in oxidation stability of the lubricant, and the inhibitor-passivator can legitimately be considered as a component of the stabilizer system. Benzotriazoles are particularly effective from this point of view. This is illustrated in the results of oxidation-corrosion tests shown in table 7.

As far as the other metals mentioned are concerned, the choice of inhibitors is not so good, although some of the compounds mentioned do provide some protection to silver and cadmium as well as copper. Dibasic acids, such as sebacic acid, are used for the protection of lead, in addition to contributing some load-carrying properties, while certain partial esters of these acids have been claimed to offer similar performance with the advantage of improved oil solubility (ref. 149). Quinizarin is also used as a passivator for lead and magnesium. A real need does, however, still exist for an effective magnesium inhibitor-passivator.

TABLE 7.—*Oxidation-Corrosion Tests*

Copper inhibitor	Increase in viscosity at 100° F, percent	Increase in acid value, mg KOH/g	Copper corrosion, weight change, mg/cm^2
None	24.7	2.1	−1.38
0.1 percent benzotriazole	17.6	1.1	.02
0.01 percent 5,5′-methylene-*bis*-benzotriazole	20.1	.9	−.05

Note.—48 hr at 425° F; base fluid: pentaerythritol ester, 5 cs at 210° F; antioxidant: 3 percent mono-*t*-octylphenyl-β-naphthlyamine.

Questions.—I would now like to end with two questions that appear to me to be relevant to both Mr. Smalheer's paper and to the subject of my contribution.

I have been talking mainly about the formulation of lubricants based on esters. Dr. Hatton has previously indicated that synthetic lubricants are unlikely to replace mineral oil in crankcase lubricants, and I would agree with him, at least as far as the bulk markets are concerned. I wonder, however, whether Mr. Smalheer could comment on the possible use of esters as additives for crankcase lubricants, at levels of about 20 to 25 percent, where they might be expected to contribute advantages in terms of inherently good V.I., good shear stability (because of the need to use less V.I. improver), easy low-temperature starting, and, perhaps, improved engine cleanliness. In Europe crankcase lubricants containing smaller amounts of ester are commercially available, but the quality of these particular products appears relatively ordinary. I believe there exists a West German crankcase lubricant specification with low-temperature viscosity limits that necessitate the incorporation of a quantity of ester.

We all know of the increasing controls that are being applied on vehicle exhaust emissions in terms of maximum permissible amounts of hydrocarbon, carbon monoxide, nitrogen oxides, and particulate matter. What, in Mr. Smalheer's opinion, is likely to be the effect, if any, of such legislation on crankcase lubricant formulation? Will there, for example, be more emphasis on the use of ashless additives along the lines of those currently used in gas turbine lubricants?

LECTURER'S CLOSURE

The main direction of Dr. Edwards' discussion is that temperatures are on the rise in most environments in which lubricants are employed, and that as a result some additives no longer perform satisfactorily. The additive industry is aware of this trend, and, as pointed out in the section of my paper on needed research and development, work is underway to develop antioxidants, detergents, dispersants, corrosion inhibitors, and EP agents that can "carry out intended additive functions at these higher temperatures." Some of this research has already borne fruit; for example, the development of improved antioxidants for use in automotive crankcase lubricants designed for high-temperature service.

As Dr. Hotten emphasizes in his discussion, the additive industry must share in the battle against pollution, the preservation of endangered animal species, and the reduction of fire hazards.

Part of the answer to the first-named problem lies in finding better methods for the collection and disposal of used lubricants. The recent decline of the lubricant re-refining industry, due largely to unfavorable economic factors, has unfortunately resulted in more used oil finding its way into the environment as a pollutant. Some of the measures proposed to alleviate the problem include enforced collection and clean disposal of used oils, perhaps supported by a tax on the original oil, lower cost methods of re-refining, and employment of fuel oil and used lubricating oil mixtures as boiler fuels.

Happily, the additive industry uses few or no raw materials, other than the sperm whale oil cited by Dr. Hotten, which depend upon the destruction of wildlife. In fact, the industry is already using synthetic replacements in whole or in part for sperm whale oil, thereby cooperating in the campaign to preserve the sperm whale.

Dr. G. Salomon suggests that my contention that EP additives form low-shear-strength, adherent films only at elevated temperatures is too narrow. I am fully aware that protective films can form on metal surfaces at ordinary temperatures, as Dr. Salomon rightly points out, and I did not intend to deny the existence or value of such films. My purpose, rather, was to describe the role of an appropriate EP additive that would form a solid lubricant on the metal surface only at elevated temperatures. An inappropriate EP additive, for example, a very highly active sulfur compound, will form a ferrous sulfide film on iron or steel surfaces at ambient temperature. But such an additive is not desirable in a gear lubricant because of its corrosive nature, and I sought to exclude it by my definition.

Prof. T. Salomon notes that early methods for evaluating lube oil detergent performance based on washing or carbon-black-suspension techniques are deficient because they do not contemplate the use of actual engine deposits or sludge. I fully agree with his comments on this matter. I cited such methods largely for their historical value in the overall development of improved testing techniques. Indeed, I closed this particular section of my paper by stating that "although such bench tests have shed light on the mode of action of detergent additives, none has yet proved equal to the task of predicting the relative effectiveness of different detergent oils in full-scale engines with a satisfactory degree of accuracy and reproducibility."

Professor Salomon suggests that the response of hydrocracked oils of high V.I. to antioxidants is better than that of solvent-extracted high V.I. oils because of the lower content of chemical impurities in the hydrocracked oil. Although the observed difference in behavior of the two kinds of oils has not yet been explained definitively, it could be as he suggests. Another possibility is that hydrocracking, in some manner as yet unknown, either preserves or enhances certain naturally occurring inhibitors present in the original oil.

I should like to thank Mr. Staley for his welcome contribution to the role of additives in formulating lubricants for gas turbines, an area that was touched upon only lightly in my paper.

He also asks whether I believe that crankcase lubricants containing high levels, about 20 to 25 percent of synthetic esters are a likely possibility.

The chief value of such synthetic ester and mineral oil blends would appear to be in the area of easier low-temperature starting, but this objective, in my opinion, can be achieved at lower cost by the use of appropriate amounts of V.I. improver. Barring substantial cost reductions in the now high-priced synthetic esters, I do not foresee their wide-scale use in automotive crankcase lubricants.

As for legislative controls on vehicle exhaust emissions and the effect of such controls on crankcase lubricant formulation, it is too early to say whether or not this will place a greater emphasis on ashless additives. The answer must ultimately depend on the types of devices adopted by automakers to satisfy emission standards. Already, EGR techniques have been found to increase the severity of engine operation, necessitating an upgrading of the additive treatment. Catalytic converters, if adopted, could also influence the additive treatment of crankcase oils. Ashless additives might prove to be superior to ash-containing types with respect to catalyst life, but at present this is only speculation.

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Role of Adsorption in Liquid Lubrication

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Changes at solid-liquid interfaces caused by adsorption from solution are discussed paying attention to the following aspects:

(1) Stability of adsorbed films and the structure of metal–additive-film–liquid interface. Effect of adsorbate orientation.
(2) Chemical versus physical adsorption.
(3) Heat of adsorption.
(4) Adsorption of additives.
(5) Activated adsorption, effect of activating adsorbates.
(6) Displacement phenomena at solid-liquid interfaces.
(7) Competition of antiwear additives, their solvents, and water.
(8) Effect of adsorption on the orientation of liquid in the interfacial region.
(9) Relation between the chemical nature of solid surfaces and their interaction with liquid lubricants.

The relevance of the above adsorption phenomena to lubrication is discussed, referring where possible to specific examples.

CHANGES IN THE STRUCTURE of liquids in the proximity of solid surfaces have long excited an interest among physical chemists and lubrication technologists. Adsorption of surface-active components of solutions was often considered to constitute a phenomenon closely connected with their function in the improvement of lubrication by the solvents.

It was recognized that simple organic liquids fail to provide effective lubrication at elevated temperatures (ref. 1); it became equally firmly established that the same liquids containing adsorbable compounds, additives, may become effective at the high temperatures. A simple qualitative explanation of this fact was that as long as the surface-active component remained attached to the surface and lowered its energy, adhesion between the surfaces would not take place and wear would be minimized.

A dramatic illustration of this effect was supplied by Zisman who investigated the durability of monolayers of fatty amines adsorbed onto glass (ref. 2). Sliding of a hemisphere on the film-covered surface under a pressure of about 7500 kg/cm^2 gave no visible wear and greatly reduced friction. A more recent example of a slightly different kind, but illustrating the same effect, was reported by Buckley, who has been investigating the effect of close-packed monolayers of sulfur atoms adsorbed on 011 surface of iron on its adhesion to another iron surface (ref. 3). It was found that the adhesion force was minimal for the surface covered with the close-packed sulfur film. In contrast, very strong adhesion forces existed between the clean iron surfaces.

Why should an adsorbed film have a beneficial effect on lubrication? A traditional explanation depends on one basic principle: the adsorbed molecules can drastically decrease the surface energy of solids to a value that precludes material transfer from the surface under the adsorbed film, i.e., the material from the film substrate, whenever the solid surfaces come into repeated contacts. The films effective in lubrication must have one side strongly bound to the solid surface (substrate), the other side forming a low-energy surface. An example is a close-packed film of *n*-octadecylamine on a metal surface.

In a practical situation, one is interested in two surfaces in rolling or sliding contact immersed in a liquid which, as a rule, is a multicomponent mixture. The solid surfaces in an ideal case would be constituted by well-defined crystal faces with no surface impurities and immersed in a pure liquid as shown in figure 1. In practice, however, the solid surfaces are polycrystalline, contain impurities that diffuse to the surface from the bulk of the solid (refs. 3 and 4), and are covered with adsorbed water and components of air (refs. 5 and 6). Immersion of such surfaces in liquids may lead to displacement of some of the adsorbed impurities and substitution by the surface-active components of the liquid. The surface of the adsorbed film, which may not necessarily be a monolayer, would then be in contact with the bulk liquid. The situation is represented diagrammatically in figure 2(*a*).

The region between the adsorbed film and bulk liquid is not clearly defined and should be considered as a diffuse layer in which the orientation

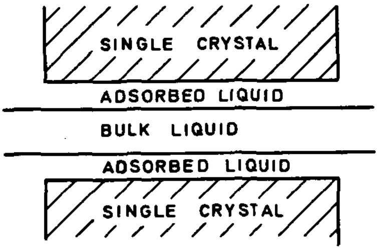

FIGURE 1.—Single-crystal surfaces separated by a pure liquid.

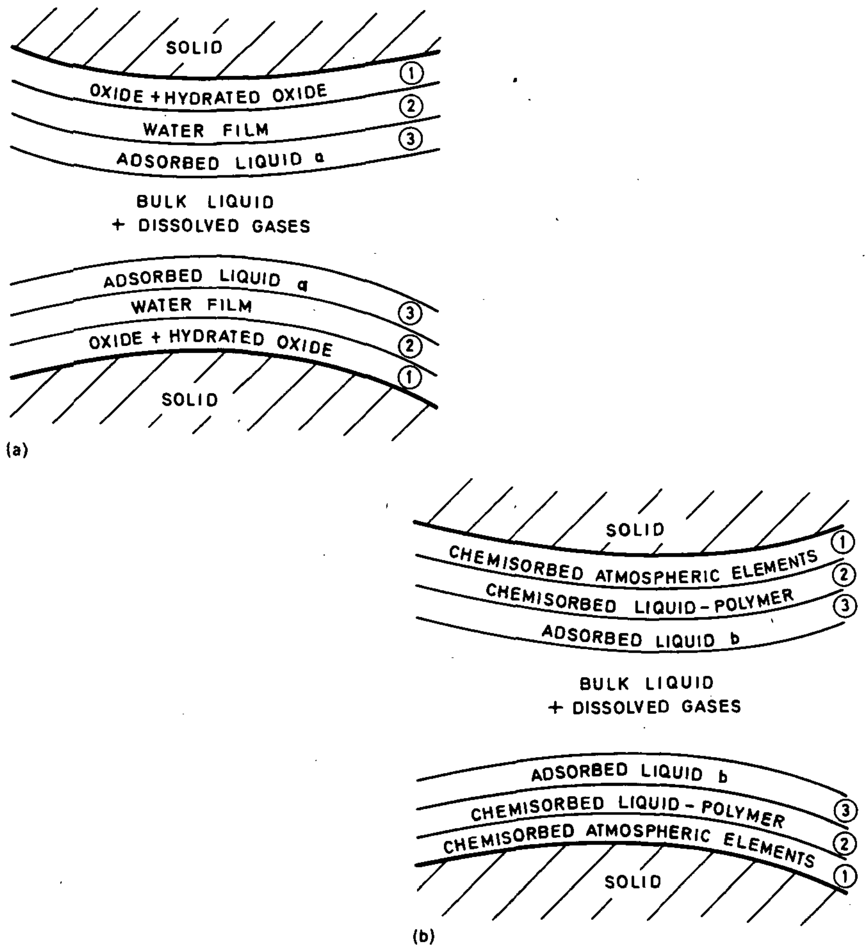

FIGURE 2.—Impure solid surfaces separated by liquids. (*a*) Undisturbed surfaces. (*b*) Run-in surfaces.

existing in the film gradually gives way to the more random structure of the bulk liquid.

Case (*a*) in figure 2 corresponds to a situation in which the solid surfaces in relative motion have never come into direct contact; i.e., the contacts forming when the low-surface-energy films are destroyed or desorbed at high temperatures caused by rubbing and deformation. In such a case, the bulk liquid has never been in contact with the active high-energy solid surface but has been in contact with the layers of oxides covered with adsorbed water.

A different situation arises when all the adsorbed films are destroyed and the bulk liquid comes into contact with the high-energy solid surfaces activated by mechanical deformation. This invariably takes place during running-in processes or during sliding motion in which wear takes place. In such an event, the bulk liquid is subjected to chemical action leading to formation of active molecular species and products resulting from their interaction with and chemical adsorption on the high-energy surface. The state of the surface after completion of these processes is represented schematically in figure 2(*b*), in which the polycrystalline solid surface 1 is covered with the reaction products resulting from the breakdown of the liquid lubricant. These include, of course, polymers, the formation of which has been reported by several authors (refs. 7 and 8). The new interfacial layer formed during the running-in process may radically change the composition of layers 1, 2, and 3 in figure 2(*a*), which cover the surface of the "undisturbed" solid before wear takes place and exposes an active surface causing chemical changes in the components of the bulk liquid. This is important because the new solid surface, as represented by film 3 in figure 2(*b*), may have a much greater affinity for the liquid lubricant than the surface of the water film 2 shown in figure 2(*a*).

To examine the role of adsorption in lubrication, full account must be taken of the complex situation represented by the polycrystalline solids immersed in liquid mixtures before and after running in. We are still a long way from properly understanding the nature of lubrication in such complex systems. Superficially, however, certain factors can be considered in isolation, and tentative deductions can be made from experiments in which one component of the multilayer structure is changed, thus modifying the lubrication of the surfaces in question. An example of such an experiment is a change in the composition of adsorbed film 3*a* and the effect this has on the lubricating effectiveness of the bulk liquid from which the adsorption takes place.

Lubrication of different metals with the same liquid provides another example. Thus clean polycrystalline iron, titanium, and graphite could be immersed in the same liquid, and the lubricating action of the liquid could then be studied in relation to the nature of the solid surfaces.

The present paper analyzes certain model situations that have been studied and makes an assessment of the degree to which these studies explain the role of adsorption in liquid lubrication. At the same time recent progress in the studies of the structure of liquids in contact with well-defined solids is considered, and a possible relevance of such studies to lubrication is discussed.

THEORETICAL BASIS FOR THE STUDY OF ADSORPTION FROM SOLUTION

Separation of individual components of liquid mixtures at solid-liquid interfaces is clearly of fundamental importance to the development of structure of the liquid in the vicinity of the surface and must be related, therefore, to the lubricating action of the liquid. It is now recognized that in the adsorption from solution, at least two components are involved and the role of both components must be taken into account. Over the whole range of concentration for a completely miscible pair of components, neither can really be called the solute or the solvent. However, for systems in which one of the components is very much more strongly adsorbed than the other, adsorption from dilute solutions can be studied. It is often found, in fact, that under these conditions the adsorbent becomes completely saturated by the strongly adsorbed component. The adsorption isotherms for such systems differ in principle from typical gas isotherms by the liquid isotherm's being one of apparent adsorption only. These systems have been treated in detail by Everett (refs. 9 and 10).

Thus if a solution before adsorption contained y moles of component 2 and $(1-y)$ moles of component 1, on addition of an adsorbent which adsorbs x moles of component 2 and z moles of component 1, the solution remaining would contain $(y-x)$ moles of component 2 and $(1-y-z)$ moles of component 1.

The mole fraction of component 2 in the new solution is not $(y-x)$, but

$$N_2=\frac{y-x}{1-x-z} \tag{1}$$

where $(1-x-z)$ is the total number of moles of both components. In a similar manner the concentration of component 1 will be

$$1-N_2=\frac{1-y-z}{1-x-z} \tag{2}$$

Both y and $(1-N_2)$ can be determined experimentally.

To evaluate x and z, an additional factor has to be considered.

Because the adsorbed hydrocarbons are in equilibrium with the solution and it is assumed that the total adsorption n^s is always constant, we have

$$x+z=n^s \tag{3}$$

Substituting this into equation (1),

$$x=y-N_2+n^sN_2 \tag{4}$$

or

$$y-N_2=n^s\left(\frac{x}{n^s}-N_2\right) \tag{5}$$

In equation (5), the apparent adsorption $(y-N_2)$, or surface excess Γ_2, is equal to the difference between the molar fraction of component 2 in the surface phase and in the solution, multiplied by the total number n^s of adsorbate molecules.

The equilibrium constant K, or the separation factor, can be determined from the ratios of component 2 to component 1 in the two phases. Thus

$$\frac{x/n^s}{1-x/n^s}=K\frac{N_2}{1-N_2} \tag{6}$$

Solving for x/n^s,

$$\frac{x}{n^s}=N_2\frac{K}{1+(K-1)N_2} \tag{7}$$

Substituting equation (7) into equation (5),

$$x=n^s\frac{(K-1)(1-N_2)N_2}{1+(K-1)N_2} \tag{8}$$

Equation (8) is related to an adsorption process in which the solvent and the solute molecules are equal in size.

For dilute solution, $(1-N_2)$ is close to unity and the activity coefficients of the solute can be assumed to be very close to unity. Consequently equation (8) can be written in a form that is essentially the same as the Langmuir equation

$$\frac{N_2}{x}=\frac{1}{n^s(K-1)}+\frac{1}{n^s}N_2 \tag{9}$$

The graph relating N_2/x and N_2 should be a straight line if the system conforms to equation (9).

If the graph is a straight line, the total number of adsorbed moles n^s and the equilibrium constant K can be calculated from the slope and the intercept of the line. Furthermore, the standard free-energy change $-\Delta G°$ can be calculated from the equilibrium constant using the equation

$$\ln K=\frac{-\Delta G°}{RT} \tag{10}$$

where R is the gas constant and T the absolute temperature.

From the differential heats and free energies of adsorption for the preferentially adsorbed component, the standard entropies of adsorption can be calculated from the relation

$$RT\ln K=T\,\Delta S°-\Delta H° \tag{11}$$

where $\Delta H°$ and $\Delta S°$ are the standard enthalpy and entropy of adsorption, respectively, and K is the constant defined by equation (10).

For the systems in which one of the components is preferentially adsorbed and completely displaces the other component from the interface, a convenient standard state for the surface phase is that of the pure adsorbed component in a solid or liquid phase. The corresponding standard state for the same component in solution is that for its concentration at which saturation of the adsorbent surface takes place.

For systems in which the molecules of the two components occupy different areas a_2 and a_1 on the surface, the exchange process is more complicated and conforms to the following equation (ref. 10)

$$\frac{1-x/n^s}{1-N_2}\left(\frac{N_2}{x/n^s}\right)^{1/r}=K \tag{12}$$

where $r=a_2/a_1$.

It must be stressed that all the above equations relate to systems for which the adsorption is completely reversible. The adsorption phenomena relevant to lubrication by liquid mixtures are frequently partly chemical and partly physical in nature. Consequently, theoretical models for the mechanism of lubricating action of liquids or their individual components based only on equilibrium physical adsorption must be treated with caution. For example, in Rowe's pioneering work concerned with the role of additive adsorption in the mitigation of wear (ref. 11), it cannot be assumed that equilibrium conditions are achieved when the nascent surface comes into contact with the liquid mixture, and, furthermore, chemisorption cannot be excluded. Nevertheless, the fact that in Rowe's work good agreement is obtained between the experimental values and theory derived for the systems studied strongly suggests the physical adsorption is an important factor in the protection of steel surfaces against wear. In this connection equations (9), (10), and (11) could be used to evaluate the free energy and entropy of the physisorbed additive film, which would characterize its stability and, therefore, effectiveness in lubrication.

Rowe's analysis is perhaps the most comprehensive attempt made so far to evolve a rational picture of wear taking place in liquid lubrication, unlike the unlubricated wear, which received much more attention (ref. 12). It is to be hoped that this first attempt to analyze wear under liquid lubrication conditions would be extended to a larger number of metal couples operating under different conditions of temperature, pressure, and liquid environment.

CALORIMETRIC MEASUREMENTS IN THE STUDY OF ADSORPTION FROM SOLUTION AND SOLID-LIQUID INTERACTIONS

Enthalpy of adsorbates at the solid-liquid interface is a function of their strength of attachment to the solid surface as well as structure. Both these properties are important when the role of adsorption in lubrication is considered, for the adsorbed films that are effective in lubrication must adhere strongly to the surfaces in contact and resist disruption by shearing forces.

Immersion in Pure Liquids

When outgassed solid is immersed in a pure liquid, heat is evolved; i.e., the enthalpy change is negative. The enthalpy change per unit area of solid in this process is given by

$$h_{i(SL)}=h_{SL}-h_S-n^s h_{LV} \tag{13}$$

where h_{SL} is the enthalpy of the solid-liquid interface, h_S is the enthalpy of the solid-vacuum interface, n^s is the number of moles of liquid adsorbed, and h_{LV} is the enthalpy of liquid.

The term $n^s h_{LV}$ is related to the loss of enthalpy in the bulk liquid when the adsorbed molecules are transferred to the interface on adsorption.

The enthalpy of the solid-liquid interface h_{SL} is composed of the two terms h_a, the enthalpy of the adsorbed layer when in equilibrium with saturated vapor of the liquid, and h_L, the enthalpy of formation of the interface between the adsorbed layer and bulk liquid. This is assumed to be equivalent to the enthalpy of the liquid-vapor interface as given by

$$h_L = \gamma_{LV} - T \frac{\partial \gamma_{LV}}{\partial T} \tag{14}$$

where γ_{LV} is the surface tension of the liquid and T is the absolute temperature. Therefore

$$h_{SL} = h_a + \gamma_{LV} - T \frac{\partial \gamma_{LV}}{\partial T} \tag{15}$$

and combining equations (13) and (15)

$$h_{i(SL)} = h_a + \gamma_{LV} - T \frac{\partial \gamma_{LV}}{\partial T} - h_S - n^s h_{LV} \tag{16}$$

The immersion of solid surface equilibrated with the vapor of the liquid giving a surface enthalpy identical to that of the pure liquid gives enthalpy of adsorption

$$h_{ads} = h_{i(SL)} - \left(\gamma_{LV} - T \frac{d\gamma_{LV}}{dT} \right) \tag{17}$$

The enthalpy of adsorption h_{ads} is the integral heat of adsorption that can be obtained from the heats of immersion and surface-tension data. Similarly, the heats of immersion in liquids are integral heats of adsorption, and it can be expected that in general they would be different from the differential heats obtained either calorimetrically or from the variation of equilibrium constant with temperature.

The integral heats of adsorption are seldom determined directly, which is unfortunate because their values should indicate whether the films adsorbed from vapor are monolayers or are duplex films (multilayers). The question of film thickness at solid-vapor interfaces is, of course, a subject of considerable scientific investigation, and it is well known that for many systems the film thickness exceeds considerably the monolayer values at high pressures.

In the case of the heats of immersion, the situation may be somewhat different because the adsorbate is in equilibrium with liquid and not its vapor. Nevertheless, some recent work by Robert (ref. 14), Everett et al. (ref. 15), and Clint et al. (ref. 16) indicates that pure liquid hydrocarbons form thick adsorbed films on graphite surfaces, the surface apparently exerting influence extending over a depth equivalent to several molecular diameters. Similar indications of the structures of liquid near the solid surface have been obtained for the system silica-water (ref. 17). This is perhaps one of the most exciting developments in the study of interactions at solid-liquid interfaces, and work in this field continues in a number of laboratories investigating surface phenomena.

Immersion in Solutions

For a solid immersed in a solution, it must be accepted that all components of the solution may be present at the interface, albeit in proportions different from those existing in the solution. For imperfect mixtures, changes in concentration due to adsorption cause heat-of-mixing effects. For a binary mixture, in which one of the components is preferentially adsorbed, the total heat changes on immersion h_T is equal to (h_i+h_D), where h_D is the heat of dilution of the solution phase and h_i is the heat of immersion.

However, in the case of adsorption from dilute solutions, h_D is small and may be neglected. The heat of immersion in such a solution is given by

$$h_{iSS}=h_{SS}-h_S-n_1{}^s h_{1(LV)}-n_2{}^s h_{2(LV)} \tag{18}$$

where h_{iSS} may be considered as being equivalent to the integral heat of adsorption $h_{(\mathrm{ads})}$ and h_{SS} is the enthalpy of solid-solution interface.

Equation (18) has been used by Goodman et al. (ref. 18) to give information on the nature of the adsorption process in terms of molecular orientation.

Everett (ref. 9) has analyzed the case of the perfect liquid mixture and, assuming monolayer adsorption, shows that the heat of immersion may be expressed as

$$h_{1(SS)}=x_1{}^s h_{1(SL)}+x_2{}^s h_{2(SL)} \tag{19}$$

where $h_{1(SL)}$ and $h_{2(SL)}$ are the heats of immersion of the solid in pure components 1 and 2, respectively. Equation (19) shows good agreement with the heats of immersion for the charcoal-benzene-cyclohexane system (ref. 19).

According to Parfitt (ref. 20), the validity of assuming monolayer adsorption is uncertain. There is now evidence that even for a simple system, graphon-heptane-hexadecane, more than one layer of adsorbed molecules is affected by the underlying surface (refs. 21 and 22). These observations are, of course, of fundamental importance to the studies of lubrication of solids by liquids.

Flow Microcalorimetry

This technique has been introduced by Groszek (refs. 23 and 24) and constitutes a sensitive method of detecting and studying adsorptions from solution at solid-liquid interfaces.

In this calorimeter the solid is first immersed in one pure component of a binary mixture. Subsequently the second component is introduced in small concentration steps until, eventually, the solid is completely saturated with component 2.

We have, therefore, as in equation (17) above,

$$h_{1(\text{ads})} = h_{1(SL)} - \left(\gamma_{1(LV)} - T\,\frac{\partial \gamma_{1LV}}{\partial T}\right) \tag{20}$$

$$h_{2(\text{ads})} = h_{2(SL)} - \left(\gamma_{2(LV)} - T\,\frac{\partial \gamma_{2LV}}{\partial T}\right) \tag{21}$$

For a complete displacement of component 1 by component 2, we have

$$h_{\text{ads}} = h_{2(\text{ads})} - h_{1(\text{ads})} = h_{2(SL)} - h_{1(SL)} \tag{2}$$

The above equation applies to displacement (preferential adsorption) processes in which the changes in concentration are sufficiently small to minimize the terms in parentheses in equations (20 and 21). The magnitude of permissible increments in concentration would vary for different mixtures depending on their ideality (magnitude of heats of mixing). For solutions of polar compounds in nonpolar solvents, the heats of mixing are relatively large and the concentration changes must be below 1 mole percent to make heat of mixing terms negligibly small.

An important feature of flow calorimetry is that both differential and integral heats of adsorption can be measured and that a measure of the rates of adsorption obtained from the rate at which heat is evolved after immersion of the solid in a given solution can be made. Another valuable feature is the possibility of determining heats of desorption as well as the heats of adsorption, which gives information on the reversibility of the adsorption processes under investigation.

For physical adsorption from dilute solutions conforming to equation (9), the differential heats of adsorption of solute can be considered to be proportional to the amounts of adsorption. Consequently, Allen and Patel (ref. 25) used a modified Langmuir equation (essentially equivalent to eq. (9))

$$\frac{C}{q} = \frac{1}{q_m K_1} + \frac{C}{q_m} \tag{23}$$

in which q and q_m are the differential and integral heats of adsorption, respectively, measured in the flow microcalorimeter. The heats are obtained by saturating the adsorbent with solutions containing gradually increasing concentrations of solute until saturation of the surface is achieved. The summed differential heats represent the integral heat of adsorption q_m corresponding to n^s in equation (9).

Allen found that the heats of adsorption from a large number of solutions obey equation (23), which could then be used for the calculation of the equilibrium constant K for the adsorption and the free energy of adsorption. This was found to be a much more rapid way of determining these quantities than the method depending on the determination of adsorption isotherms. The calorimetric method is, of course, ideally suited to the determination of the heats of adsorption of active components of liquid mixtures onto solid surfaces important in lubrication.

SOME ADSORPTION PHENOMENA ON IRON AND IRON OXIDES RELEVANT TO THEIR LUBRICATION

Iron Oxides

Steel probably represents the most common surface requiring lubrication, and therefore adsorption onto steel surfaces is of great practical interest. Attempts to connect adsorption phenomena at liquid-steel interfaces with their lubrication have always been difficult because the chemical nature of the steel surface is not well defined.

An assumption frequently made in the past was that the uppermost surface in steel is composed predominantly of water adsorbed on iron oxides (refs. 6 and 23). Much work has been done therefore on the adsorption of model solutes, known to be effective in boundary lubrication, onto iron oxides equilibrated with atmospheric moisture. The rationale behind this work was that the knowledge of the structure and stability of the adsorbed films on iron oxides would assist in the understanding of the role played by the films in lubrication prior to destruction of the oxide surfaces and their replacement by complex reaction products, as shown in figure 2(*b*).

The most common liquids used in the lubrication of steel are hydrocarbons containing minor proportions on nonhydrocarbon compounds (added or existing naturally) having a strong affinity for metal oxides (refs. 26, 27, and 28). It was of interest therefore to select certain pure hydrocarbons as solvents for the boundary additives for the study of their adsorption. The liquid in such a case is a two-component mixture that simplifies the analysis of the adsorption isotherms so that equation (9) can be used to evaluate the equilibrium constant and free energy of adsorption of the solute.

Solvents used frequently for the adsorption studies are liquid *n*-paraffins (refs. 2, 23, 25, and 29), cyclohexane, and benzene or toluene (ref. 30). These served as models of saturated and aromatic hydrocarbons forming the bulk of mineral oils.

Certain generalizations are possible as a result of the work reported by Groszek (refs. 23 and 24) and Allen and Patel (refs. 25 and 31), who have examined the adsorption of short- and long-chain fatty alcohols and acids onto iron and iron oxides at a wide range of concentrations. Short-chain polar compounds such as *n*-butanol dissolved in *n*-heptane are adsorbed strongly, albeit reversibly, onto the surfaces of iron oxides saturated with atmospheric moisture, with the formation of distinct plateaus in the adsorption isotherms. The equilibrium constants for these adsorptions are of the order of 2000 (ref. 31).

Curves relating the heat of displacement of *n*-heptane by *n*-butanol and its concentration in *n*-heptane are shown in figure 3. Similar curves are obtained for the amounts of *n*-butanol adsorbed, the plateaus being reached at the same solute concentrations and corresponding to close-packed monolayers, in which the cross-section area per adsorbed molecule is 21 Å^2 (ref. 31). The results show clearly that the surfaces of iron oxides are saturated with short-chain alcohols at very low concentrations and that monolayers are formed with the terminal methyl group of the alcohols forming a low-energy surface in contact with liquid *n*-heptane. All the adsorption isotherms obey equation (9), and straight-line plots are obtained for all the alcohols examined to date (ref. 31). The straight lines strongly suggest that the adsorption occurs on a surface that is energetically homogeneous vis-a-vis the OH group of the adsorbed solute and that the heats of the adsorption remain constant with coverage, a necessary condition for conformity with the Langmuir equation. It would appear therefore that water adsorbed onto the surfaces of the different iron oxides makes the surfaces similar to each other and essentially equivalent to the surface of water. The constancy of the heat of adsorption of alcohols onto such surfaces is therefore not difficult to understand.

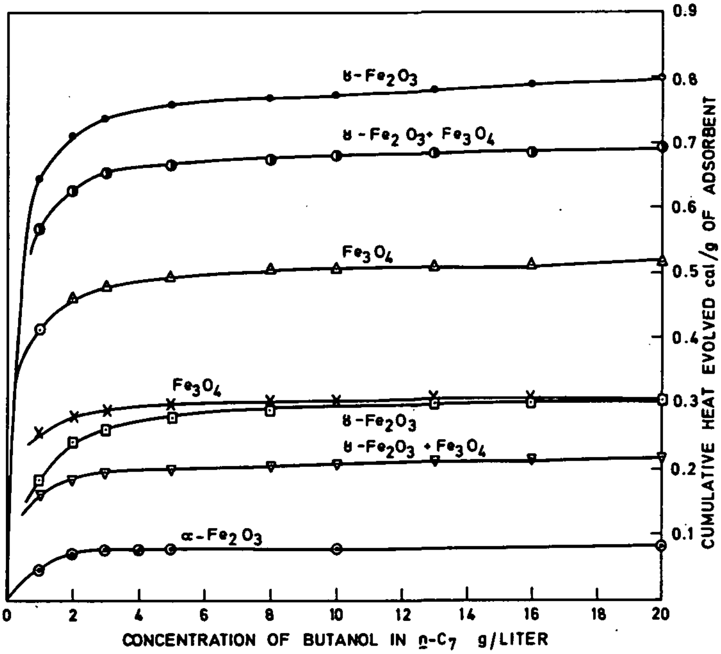

FIGURE 3.—Cumulative heats of adsorption of *n*-butanol from *n*-heptane onto iron oxides, prepared by various methods.

The adsorption of long-chain alcohols onto iron oxides shows some striking features as shown in figures 4 and 5. A sharp upturn occurs in the amount of adsorption and the heat of adsorption as the concentration of octadecanol is increased from 1 to 3 g of octadecanol per liter of *n*-heptane, which strongly suggests that long-chain *n*-alcohols undergo a change of orientation at the interface or a phase change confined to the adsorbed layer leading to a higher degree of ordering of the adsorbate. The effect can be explained by *n*-octadecanol molecules forming a close-packed, vertically oriented monolayer at the higher concentrations. The sharp increase in the amount of heat evolution at the critical range of *n*-octadecanol concentrations (fig. 5) could be due not only to the increase in the amount of adsorption, but also to a sharp decrease of entropy of the adsorbate, on formation of an ordered array of molecules composed of closely packed long-chain methylene chains resembling the arrangement in solid *n*-octadecanol. The marked decrease of entropy on formation of such a film is in line with the high heat of crystallization of *n*-octadecanol, which exceeds 34 kJ-mol^{-1} (ref. 32).

Adsorption of *n*-butanol and *n*-octadecanol from *n*-hexadecane shows some interesting differences from the adsorptions from the shorter chain *n*-heptane. Studies of the heats of adsorption of *n*-octadecanol from *n*-hexadecane onto γ-Fe_2O_3 show that the heats are much higher at concentrations ranging from 0.5 g/liter to 2 g/liter compared with the heats of

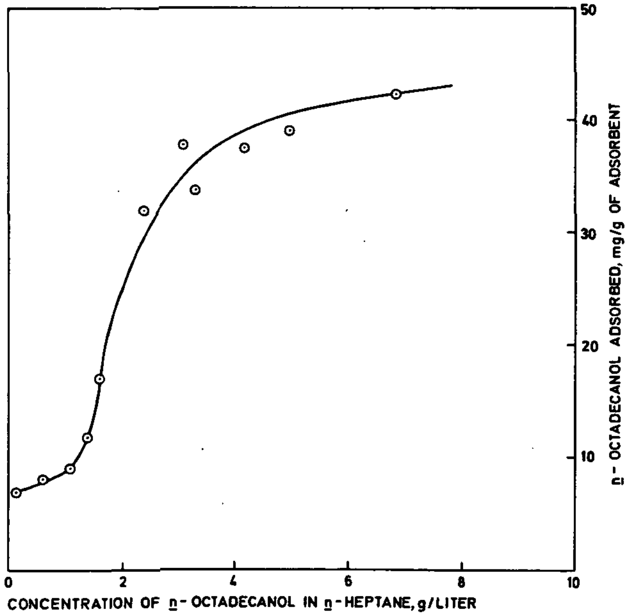

FIGURE 4.—Adsorption of *n*-octadecanol onto γ-Fe_2O_3-Fe_3O_4 from *n*-heptane.

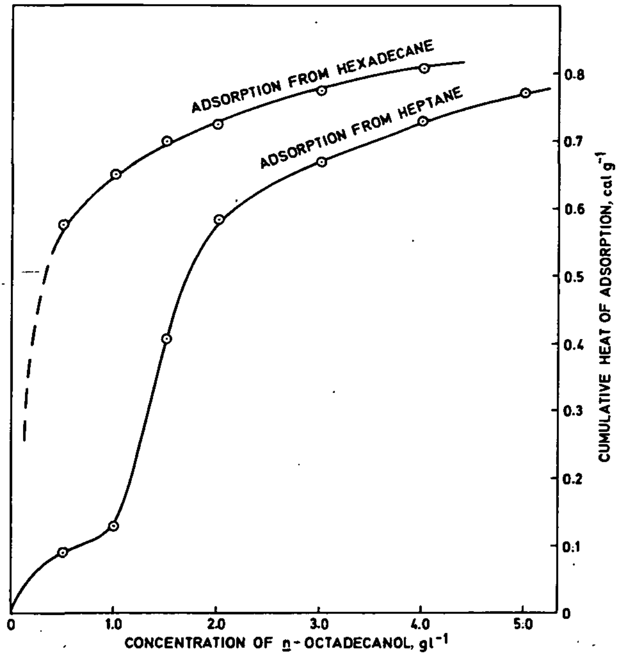

FIGURE 5.—Adsorption of *n*-octadecanol from *n*-paraffins onto γ-Fe_2O_3.

adsorption from *n*-heptane shown in figure 5. However, for the adsorption of *n*-butanol, the difference between the heats of adsorptions is reversed, as shown in figure 6. Presumably, in this case, the similarity in chain length between *n*-butanol and *n*-heptane has an influence on the heats of adsorption. A similar effect has been recently demonstrated by Allen and Patel for the mixtures of *n*-hexanol and *n*-heptane (ref. 25).

The results demonstrate the importance of matching the solvent chain length to that of the solute and suggest that the adsorbed films of *n*-octadecanol formed from *n*-hexadecane should be much more stable than those formed from *n*-heptane solution. This is in line with the work of Askwith, Cameron, and Crouch who reported that the chain matching between the solvent and solute gives improved lubrication (ref. 1). It must be remembered, however, that the adsorption isotherms for the iron oxides indicate that the maximum amounts of adsorption correspond to formation of close-packed monolayers, suggesting that the matching effects are confined to a monolayer. The propensity of *n*-octadecanol and *n*-hexadecanol to form vertically oriented films on the surface of iron oxides may be related to an undoubted superiority of the longer chain alcohols in the reduction of wear in the four-ball machine (tables 1 and 2). The results shown in table 1 illustrate the difference between 1 percent solutions of *n*-butanol and *n*-octadecanol in hexadecane. The table also shows differ-

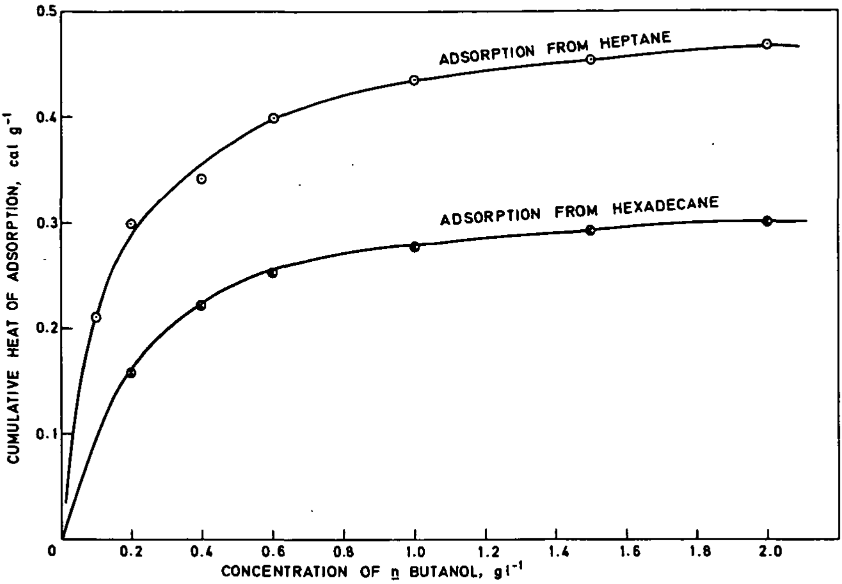

FIGURE 6.—Adsorption of *n*-butanol from *n*-paraffins onto γ-Fe_2O_3.

TABLE 1.—*4-Ball Results for 1-Percent-Weight Solutions of Alcohols and Acids in Hexadecane*

Alcohol added to cetane	Wear scar diameter, mm			
	10 kg	15 kg	20 kg	30 kg
Nil	Seizure	Seizure	----------	
n-Octadecanol	0.63	0.66	0.70	0.78
n-Butanol	0.74	Seizure	Seizure	Seizure
n-Octadecanoic acid	0.42	0.47	0.52	0.78
n-Butyric acid	0.57	Seizure	Seizure	

Note.—Test duration, 60 min.

ences in the wear scar for the fatty acids, which appear to follow the same trend. What must be remembered here is that the forces binding the polar solutes to the surfaces of iron oxides are likely to be very similar irrespective of the chain length of the solute because in both cases the polar functional group is likely to be adsorbed onto a layer of water (ref. 6). Thus the differences in the lubricating performance of the solutions are most

TABLE 2.—*4-Ball Results for 18.5-mmol Solutions of Octadecanol and Octadecanoic Acid in Liquid Paraffin at 15-kg Applied Load*

Additive	Wear scar diameter, mm		
	½ hr	¾ hr	1 hr
n-Octadecyl alcohol	0.39	0.40	.47
n-Octadecanoic acid (stearic acid)	.29	.28	.29

TABLE 3.—*Integral Heats of Adsorption of Octadecanoic Acid Onto Iron Oxides and Ground Iron From* n-*Heptane and* n-*Hexadecane Solutions*

Adsorbent	Heat of adsorption, J-m^{-2} [a]	
	From *n*-heptane	From *n*-hexadecane
γ-Fe_2O_3 (1)	0.042	0.222
γ-Fe_2O_3-Fe_3O_4 (4)	.158	.126
α-Fe_2O_3	.113	.158
Ground iron	.276	.251

[a] Adsorption from solution containing 1 g/liter octadecanoic acid.

probably connected with the orientation of the nonpolar moiety of the solute molecules.

Fatty acids present interesting adsorptional features that include a degree of chemisorption and strong dependence on chain length and great sensitivity to structure of solvent molecules (refs. 9 and 33). The heats of preferential adsorption of stearic (octadecanoic) acid obtained for three different iron oxides and for an iron powder comminuted in liquid heptane (in the absence of free air) are shown in table 3. The acid saturates the oxides at a concentration of 1 g/liter; i.e., the concentration at which the integral heats of adsorption shown in the table were obtained.

Perhaps the most striking result was obtained for γ-Fe_2O_3, for which the heat of adsorption from *n*-C_{16} was considerably greater than that taking place on adsorption from *n*-heptane. The result can be explained by a substantial orientation of *n*-hexadecane taking place near the surface saturated with stearic acid or perhaps by several layers of mixed film forming near the surface.

It is, of course, very striking that the high heat of adsorption is obtained only for one of the three iron oxides examined and that there is only a small difference in the heats for ground iron, which emphasizes the importance of the nature of the surface in these adsorption experiments.

The effect of the chain length of fatty acids on the heat of adsorption was also obtained for the adsorption of small amounts of fatty alcohols and acids from hexadecane onto α-Fe_2O_3 at low surface coverage as shown in table 4. As can be seen, the C_{16} acid produces a very much greater heat effect than C_6 acid, although an almost identical number of moles was adsorbed in both cases.

TABLE 4.—*Pulse Adsorption of Normal Alcohols and Carboxylic Acids Onto* α-Fe_2O_3 *From* n-*Heptane and* n-*Hexadecane*

Adsorbate	Heat of adsorption, kJ-mol^{-1}	
	From *n*-heptane	From *n*-hexadecane
Acetic acid	<0.8	<0.8
Hexoic acid	18.2	9.6
Hexadecanoic acid	50.2	77.0
Octadecanoic acid	59.2	86.0
Butyl alcohol	12.1	4.2
Hexyl alcohol	21.0	11.3
Hexadecyl alcohol	42.7	60.7
Octadecyl alcohol	67.0	75.0

What still remains undecided is whether the high heat of adsorption, attesting to vertical orientation of hexadecane and stearic acid, is confined to a close-packed monolayer or several more loosely packed layers extending into the bulk of the liquid. The fact that the amount of stearic acid adsorbed from n-C_7 and n-C_{16} onto α-Fe_2O_3 is the same in spite of the difference in the heats of adsorption suggests that the orientation is not confined to the monolayer.

The adsorption of the lower fatty acids appears to follow Langmuir isotherm similarly to the adsorption of alcohols giving equilibrium constants ranging from about 1200 to 7100 (ref. 31). Jaycock et al. (ref. 33) reported, however, that the adsorption on α-Fe_2O_3 is partly chemical and that the chemisorbed molecules of the acid displace at least some of the water adsorbed on the oxide surface. Characteristically, adsorption of stearic acid gave rise to heat evolution followed in a few minutes by heat absorption. The negative heat effect decreased with decreasing humidity of the atmosphere with which α-Fe_2O_3 was equilibrated before adsorption, thus strongly suggesting that the heat absorption is due to displacement of water from the interface. However, the results obtained with *n*-heptane and *n*-butanol indicate that neither of these materials is able to displace water.

The adsorption isotherm for stearic acid on α-Fe_2O_3 gave a very distinct plateau corresponding to a fractional coverage of 0.6, assuming a value of 20.5 $Å^2$ for the cross section of stearic acid. This is not dissimilar to the maximum fractional coverages reported by Patel (ref. 31) also for α-Fe_2O_3 and by Erman et al. (ref. 34) for the adsorption of stearic acid on rutile. The situation, however, appears different for alumina for which complete vertically oriented monolayers have been reported (ref. 35).

To what extent water is required for the chemisorption of fatty acids onto iron oxides is a little uncertain, as to date few, if any, adsorption experiments have been carried out on surfaces completely free from adsorbed and chemisorbed water. It may well be, however, that water is essential for chemisorption to occur as suggested by the work of Schrader and Molinsky (ref. 36) and Lancaster (refs. 37 and 38).

It is clear from the foregoing that adsorption of fatty acids onto iron oxides involves at least three processes occurring simultaneously; namely, physical and chemical adsorption, desorption of water, and displacement of hydrocarbon solvent. Physisorption can be equated to that part of the acid that is desorbable by washing the adsorbent with the solvent as described by Hackerman et al. (refs. 39 and 40). This part of the adsorption is probably very similar to that studied at water-oil interfaces using film balance techniques, as well as the study of factors involved in the stability of water in oil emulsions (ref. 41). A point of great importance that emerged from these studies is that metal ions present in water, including iron ions, drastically increase the rigidity of the fatty acid films adsorbed on water. It is likely that the water film adsorbed on iron oxides contains iron ions that would make fatty acid films more stable and rigid compared with the films adsorbed on the metal surfaces freed from water. It is also possible that the relative effectiveness in lubrication of the long-chain fatty acid films adsorbed on reactive metals, such as iron covered with adsorbed water, is due to the films becoming very rigid and stable under the influence of the metal ions present in the interfacial region.

The interaction of fatty acids with metals, including iron and iron oxides, and its relevancy to boundary lubrication has been studied extensively and was reviewed recently by Pilpel (ref. 42). It appears that to date most of the attempts to correlate adsorption of surface-active agents onto metals with their lubricating properties suffer from the fact that both lubrication and adsorption studies have been carried out on poorly characterized surfaces and surfaces that are likely to be contaminated by the cleaning procedures. Cases in point are the cleaning of metal surfaces by washing with volatile organic solvents (ref. 43) and rubbing with abrasives followed by washing with water and drying in a current of air (refs. 44 and 45).

The effect of contaminants on the thickness of liquid film separating the solid surfaces may have misled Deriagin (ref. 46) and Fuks (ref. 44) into thinking that multilayers form between surfaces immersed in solutions of fatty acids in *n*-alkanes. In fact, the cleaning methods used by the above investigators involved polishing and buffing procedures, which may have produced thick films of soaps or soap complexes on the surfaces similar to those described by Smith and Cameron (ref. 47) on the evaporated metal films, whereby it was found that stearic acid and hexadecane can form mixed soap-liquid films having a thickness ranging from 2000 to 10 000 Å. Ideally the work by Deriagin should be repeated on inert single-crystal surfaces, freed from contaminants by efficient techniques, such as, for example, glow discharge (ref. 48).

The formation of multilayers of fatty acids in contact with dilute solutions of the acids in liquid *n*-alkanes has been seriously considered by Allen and Drauglis (ref. 49), who proposed a model for the structure of the films on the assumption that it is similar to the structures found in smectic mesophases; i.e., the molecules arranged in layers with the long axis of each molecule perpendicular to the plane of the layers. This model would explain the results reported by Fuks (ref. 44) and its possible reality is supported by the heat of adsorption measurements of stearic acid on certain types of γ-Fe_2O_3 (ref. 23). The adsorption on many other metal oxides, however, suggests only the formation of monolayers. There is no doubt therefore that much more effort is needed to resolve the question of the existence of oriented multilayers in solutions close to the surfaces of metals and metal oxides. The effect of pressure on the structure of adsorbed films is especially important in this connection and, so far, appears to be largely ignored.

A source of "contamination" of solid surfaces that may lead to a formation of thick films could also be due to polymerization of liquid lubricant on freshly formed solid surfaces. When the surface of the adsorbed polymer is covered with a liquid, a new interfacial region is formed, the energy of which depends on the amount and nature of the polymer. It is, of course, of interest to consider how the adsorbed polymers may affect the interaction of the polymer-covered surface with liquids.

Interesting aspects of this situation have been discussed by Clayfield and Lumb (ref. 50). They considered adsorbed polymers that settle down flat on the surface and others that are only terminally adsorbed with their nonpolar chains extending out from the surface in a fluctuating, randomly coiled configuration. The latter form of adsorption may prevent adhesion to another surface containing the same adsorbed polymer, the phenomenon being called entropic repulsion; i.e., the repulsion due to specific configuration of polymer chains. This is known to be important in the stability of dispersions of solid particles in nonaqueous media but may also be of importance in the case of the lubrication of concentrated contacts. Certainly long-polymer chains extending away from the surface into the bulk of the liquid must affect the viscosity of liquid within the reach of the chains, which should influence the load-carrying capacity of the bulk lubricant. Clearly the degree to which the adsorbed polymer is solvated and can form a structure with the solvent molecules would affect the rheology of the interfacial region. Changes in viscous drag may also be affected by the adsorbed polymers.

The above considerations are undoubtedly important for polycrystalline metal surfaces lubricated by mineral oils. Such oils invariably contain polymeric, strongly surface-active constituents that are preferentially adsorbed onto fresh metal oxides and metal surfaces with the formation of a relatively loose structure (ref. 26). Addition of such surface-active materials to purified mineral oils exerts a powerful effect on their load-carrying capacity (ref. 1). Formation of a thick layer composed of the surfactant and the associated oil molecules may well be responsible for the improvement in the load-carrying capacity and may have an effect on traction and viscous drag properties of mineral oils.

FRESH IRON SURFACES EXPOSED TO LIQUID LUBRICANTS AND ADDITIVES

Recent work by Buckley (ref. 51) on single crystals of iron and Morecroft (ref. 52), following the work of Roberts (ref. 53) on polycrystalline metal surfaces, indicates that hydrocarbons and fatty acids are chemisorbed and may be decomposed on clean iron surfaces at the interface. It can be assumed therefore that whenever fresh iron surfaces are formed in the presence of liquid hydrocarbons, reactions will take place at the interface leading to formation of chemisorbed films. In many machines used in the investigation of the lubricating properties of liquid mixtures, wear of the sliding components takes place continuously with the consequent formation of fresh metal surfaces. The four-ball machine is a case in point; liquid lubricants are tested in this machine under conditions of continuous wear, which may be more or less intensive depending on the relative speeds, pressures between contacts, temperatures, duration of the test, and the atmosphere in which the test is carried out.

Strictly speaking, direct correlation of adsorption onto the stressed surfaces with the role of the adsorbate in their lubrication can only be attempted satisfactorily if the adsorption could be studied in situ; i.e., on the surface within the stressed contact. Adsorption on the wear debris forming between the contacts may also be relevant to the lubrication mechanism within the stressed zone. Unfortunately, studies of adsorption from liquids onto the surfaces of wear debris are difficult because of the very small specific areas available on such surfaces.

The use of metal powders subjected to comminution in pure hydrocarbon liquids, or any component of liquid mixtures used for lubrication, resolves this difficulty. Metal powders can be comminuted in controlled liquid environments to give large amounts of finely divided powders eminently suitable for studies of adsorption of any components of liquid mixtures used for lubrication. The surface of the powder usually contains a layer of solvent used in the comminution, adsorbed on top of chemisorbed fragments of the solvent molecules attached directly to the metal. For the iron comminuted in *n*-heptane, heating to about 200° C under vacuum removes the adsorbed hydrocarbon, whereupon exposure to atmospheric air oxidizes the surfaces rapidly to iron oxides (ref. 54). Fragments desorbed at 200° C and above include heptenes and lower olefins, which are presumably formed during reaction of *n*-heptane with fresh iron surfaces produced during comminution.

Groszek employed iron comminuted in liquid *n*-heptane in the absence of free air for the study of adsorption of alcohols and fatty acids from solution in *n*-heptane (ref. 23). The adsorption of alcohols suggested that, in contrast with the adsorption onto iron oxides, the chain length of the alcohol does not *influence its orientation at the solid-liquid interface*. Thus the heats of adsorption of *n*-butanol and *n*-octadecanol onto the milled iron powder were very similar, unlike the corresponding heats of adsorption on iron oxides. The adsorption of stearic acid on the powder is very strong, much stronger than the adsorption of the alcohols (this is not so evident for the adsorption onto iron oxides) and shows no evidence of any displacement of water similar to that observed by Jaycock et al. on α-Fe_2O_3 (ref. 33). There is no difference in the heats of adsorption from *n*-heptane and *n*-hexadecane, in contrast to the adsorption on γ-Fe_2O_3 and α-Fe_2O_3, for which the heat of adsorption of stearic acid from *n*-hexadecane is markedly higher than the heat of adsorption from *n*-heptane. It would appear therefore that the affinity of stearic acid for the activated iron surface is so high that solvents are completely displaced from the solid-liquid interface and are prevented from the formation of any mixed film at the surface.

The heats of adsorption obtained during saturation of ground iron with *n*-octadecyl alcohol and stearic acid are shown in the form of peaks in figure 7. The peaks are the actual records of the heats of adsorption measured by the flow calorimeter and show that only a partial desorption of stearic acid can be achieved by percolation of *n*-heptane as evidenced by the relatively low heat of desorption of the acid followed by a low heat of its re-adsorption. This is a typical behavior of a partly chemisorbed solute. It is very interesting, however, that the heat of adsorption of *n*-octadecyl alcohol remains virtually the same irrespective of whether the adsorption occurs before or after the adsorption of the acid. This suggests that the alcohol is adsorbed only onto the sites occupied by physisorbed stearic acid.

A further point of interest in the properties of comminuted iron powder is the pronounced surface-activating effect exerted by a minor proportion

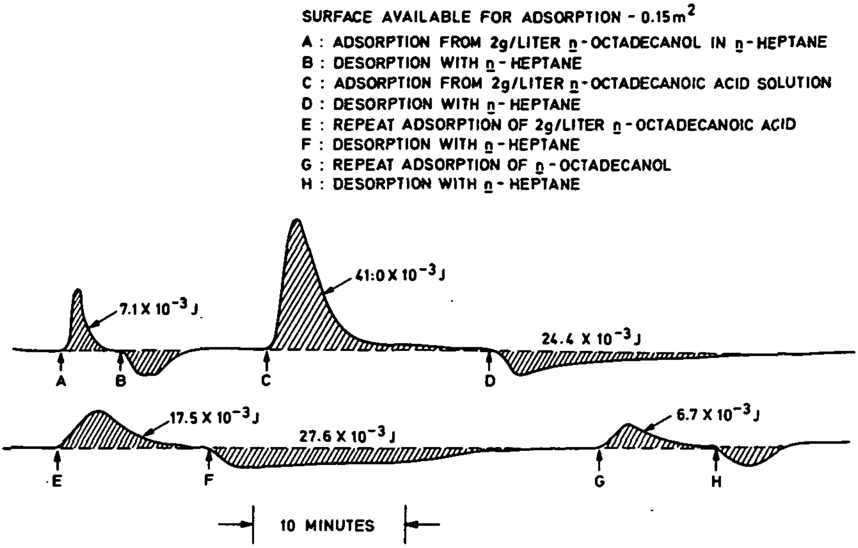

FIGURE 7.—Heat effects produced by adsorption of *n*-octadecanol and *n*-octadecanoic acid onto ground iron from *n*-heptane.

of stearic acid dissolved in the solvent in which the comminution takes place (ref. 54). As shown in figure 8, the surface of iron milled in 1 percent stearic acid solution in *n*-heptane undergoes an intense chemical reaction with dilute solution of *n*-butanol, in contrast to the iron comminuted in pure *n*-heptane on which only physical adsorption of *n*-butanol takes place. Thus it is highly probable that the surfaces of steel lubricated by solution of stearic acid become active toward any other oxygen-containing compound present in the liquid lubricant, including dissolved oxygen, which may lead to increased wear. The increase of fatigue pitting reported by Rounds for the solution containing stearic acid (ref. 55) may be a case in point. Otherwise, in a reasonably sealed system, it might be expected that stearic acid would be a much more effective additive than the corresponding alcohols. This is in fact shown by the wear tests obtained in the four-ball machine and listed in tables 1 and 2.

An excellent correlation between the adsorption of sulfur-containing additives onto comminuted iron and their antiwear performance in the four-ball machine has been obtained recently by Forbes and Reid (ref. 56). It was found that alkyl and aryl disulfides are strongly adsorbed on the surface of the comminuted iron powder at room temperature and react with the surface at 100° C and more elevated temperatures to form sulfur-containing inorganic layers. Extreme-pressure (EP) effectiveness of the disulfides was found to be strongly related to their rates of reaction with the ground iron powder leading to the formation of the protective sulfide layers at the iron surface. These results could only be obtained by study-

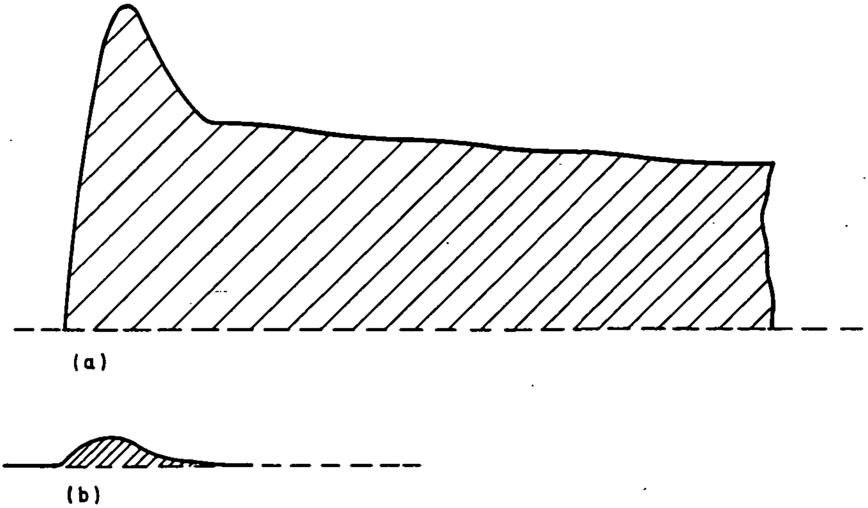

FIGURE 8.—Heat evolution on percolation of 2 g/liter *n*-butanol solution through iron comminuted in liquid heptane with and without addition of stearic acid. (*a*) 35 mg of iron ground in *n*-heptane and 1 percent stearic acid; heat evolved in 30 min: 0.963 J. (*b*) 250 mg of iron ground in *n*-heptane; total heat evolved: 0.011 J.

ing adsorption on the comminuted iron powder, which was substantially free from oxygen and adsorbed water. Ordinary oxidized iron powders and iron oxides did not give the reactions observed for the ground iron powder and were unsuitable for establishing the correlations between the additive adsorption and their antiwear action.

Further interesting use of the ground iron powder is described by Forbes et al. in connection with his studies on the mechanism of action of tricresylphosphate (TCP) as a load-carrying additive (ref. 45). It was found that TCP dissolved in *n*-tetradecane reacts with the ground iron powder at 130° C and that the reaction rate is considerably increased for the hydrolyzed TCP. This suggested that the hydrolyzed TCP containing monocresyl or dicresyl acid phosphates should have a more pronounced antiwear action than the neutral material, which was fully borne out by the results of tests in the four-ball machine. It was also found that the presence of aromatic compounds in the solvent interferes with the adsorption of TCP on the iron, and this was supported by the inferior lubricating performances of the dilute solution of TCP in solvents containing aromatic compounds, compared with the solutions in aromatic-free liquid paraffin.

The work of Forbes et al. serves to illustrate an important function of adsorption in liquid lubrication; namely, provision of films at the stressed interfaces that are rich in elements capable of chemically interacting with the solid surface at high temperatures before the disruption of the original adsorbed films occurs.

RELATION BETWEEN THE CHEMICAL NATURE OF SOLID SURFACES AND THEIR INTERACTION WITH LIQUID HYDROCARBONS—THE CONCEPT OF OLEOPHILIC SURFACE

Surfaces can be classified according to the forces that contribute to their energy. A useful treatment in this connection has been developed by Fowkes following the work of Good and Grifalco (refs. 57 and 58).

According to Fowke's scheme, the total surface energy is composed of several different types of forces such as metallic bond, hydrogen bond, covalent bond due to electron pairs, ionic forces, and the forces created by electric dipoles. However, a component of surface energy present universally in all surfaces is that due to London dispersion forces, which exist in all types of matter and are always attractive. The forces arise from the interaction of fluctuating dipoles, which induce dipoles in neighboring atoms or molecules.

Thus, for example, the total surface tension γ of a metal surface may be equal to $\gamma^d+\gamma^p+\gamma^m$, measuring components of surface tension due to dispersion forces, dipole forces, and metallic bond forces, respectively. It has been estimated that for metals such as mercury, the dispersion component can be surprisingly high and may amount to 200 erg-cm^{-2} (ref. 57). Water, on the other hand, has one of the smallest dispersion components in its surface tension amounting to 22 erg-cm^{-2} (refs. 57 and 58). The surfaces of pure liquid and solid paraffins are characterized only by dispersion forces and in this case their total surface tension γ is equal to γ^d. Such surfaces are hydrophobic because water has a small dispersion force component in its surface energy and prefers to adhere to itself rather than to form an interface with a surface displaying only dispersion forces. Oxidized paraffin surfaces would show, of course, a degree of affinity for water. A simple quantitative way to express this is to use the following term for the interfacial tension (ref. 59)

$$\gamma_{12}=\gamma_1+\gamma_2-2\sqrt{\gamma_1{}^d\gamma_2{}^d} \tag{24}$$

and relate this to works of adhesion $2\gamma_1$ and $2\gamma_2$ for water and the paraffin, respectively.

The work of adhesion between different surfaces can be expressed in terms of individual components of surface energy as follows:

$$W_{AB}{}^i=2(\gamma_A{}^i\gamma_B{}^i)^{\frac{1}{2}} \tag{25}$$

where $\gamma_A{}^i$ and $\gamma_B{}^i$ are the surface-energy terms related to specific types of surface forces and $W_{AB}{}^i$ is the contribution to total work of adhesion made by their forces. The total work of adhesion would be the sum of such individual contributions. The above expression leads to interesting consequences for the work of adhesion between surfaces that may be characterized only by one type of intermolecular forces. For example, the work of adhesion between the basal plane surface of graphite and water can be expressed as

$$W^d = 2\sqrt{21 \times 110} \text{ erg-cm}^{-2} \approx 106 \text{ erg-cm}^{-2}$$

where 21 erg-cm^{-2} and 110 erg-cm^{-2} are the dispersion components of surface energy for water and graphite, respectively. There are no other components in this work of adhesion because for the graphite surface, components other than those due to dispersion forces are nil. The total work of adhesion for this interface is therefore 106 erg-cm^{-2}. This is a rather lower figure than that obtained by inserting the total surface energy of water into equation (24), which would then give the work of adhesion of 179 erg-cm^{-2}, a rather unrealistic result, as it is higher than the work of cohesion of water and would predict wetting of graphite by water, which, of course, does not take place.

The heats of immersion of solids in liquids have also been divided into separate components (ref. 57) to give

$$h_{SL} = h_{SL}{}^d + h_{SL}{}^\alpha + h_{SL}{}^M \tag{26}$$

where h^d, h^α, and h^M are the heats contributed by dispersion forces, polarization forces, and permanent dipole forces, respectively.

Determinations of the heats of immersion of solids in liquids having different proportions of individual surface-energy components can provide therefore a practical means of evaluating the nature of forces characterizing solid surfaces.

Furthermore, determinations of preferential adsorption (heats of displacement) of various solutes can give information on the lowering of enthalpy within the solid-liquid interface occurring on adsorption. This reduction of surface enthalpy may occur only on individual surface sites depending on the nature of the solid surface and the structure of adsorbate molecules. Thus, for example, liquid alkanes can easily displace water from the basal plane surface of graphite and MoS_2, giving a substantial reduction of surface enthalpy. Such a reduction constitutes a measure of the proportion of the basal plane surface in graphite and MoS_2 samples.

The basal planes of graphite represent a surface of special interest in surface science and in lubrication. The energy of this surface in graphite crystals has been estimated to be 110 erg-cm^{-2} (ref. 59), and its special feature is the absence of other components in its surface energy apart from those due to dispersion forces. This low surface energy is considered to be related to very low friction obtained on sliding of other solids on the basal planes of graphite crystals as reported recently by Skinner, Gane, and Tabor (ref. 59). They found that sliding a tungsten stylus on the basal plane of graphite gives a friction coefficient of about 0.01 compared with 0.3 for the sliding on the polar edge surface of the crystal.

The dispersion forces emanating from the basal plane of graphite are much more intense than those operating above the surfaces of liquid and solid hydrocarbons, which accounts for the fact that such substances adhere more strongly to the basal plane surface of graphite than to their own surfaces. It can be said therefore that the basal plane surface of graphite is truly oleophilic, if the prefix "oleo" describes the surfaces of hydrocarbons formed from arrays of methylene or methyl groups and also aromatic rings. On the other hand, all that one can say about a surface of a solid paraffinic hydrocarbon is that it is hydrophobic for it would not necessarily be expected to display a greater affinity for another paraffinic surface than it has for its own surface. In fact, certain types of hydrocarbon surface can be distinctly oleophobic as shown by Zisman (ref. 2).

MoS_2 also shows the surface behavior of the basal plane of graphite as shown by Groszek (refs. 60 and 61), which again is confined to the basal plane surface formed from closely packed sulfur atoms (ref. 62).

The basal planes of graphite and MoS_2 are considered of importance in lubrication science not only because their properties are relevant to the performance of solid lubricants but also because they constitute the surfaces of many practical machine components constructed from metals. Thus the surface of cast iron after running in is covered by a thick film of graphite as shown by Montgomery (ref. 62). Furthermore, the steel surface annealed under conditions that lead to surface decomposition of cementite may be covered by patches of graphite (ref. 63). Finally, interaction of hydrocarbons with iron and other transition-metal surfaces at temperatures ranging from 500° to 1000° C leads to formation of graphite at the sites covered by adsorbed hydrocarbons as shown by recent LEED studies (refs. 64 and 65).

Thus, certain running-in processes may produce a graphite film on steel surfaces that would then dominate the adsorption of liquid lubricant in contact with such a surface. Returning to the surfaces composed of close-packed sulfur atoms, such as the basal plane surfaces of MoS_2, it might be expected that similar surfaces may be formed when sulfur-containing compounds interact with clean iron surfaces, as shown by Buckley (ref. 3). Such films would be expected to display an affinity to liquid hydrocarbons similar to that shown by the MoS_2 surface.

Adsorption of paraffinic hydrocarbons onto the surface of graphite shows interesting features that are believed to be important in lubrication. Groszek established recently that long-chain n-paraffins are adsorbed very strongly from solutions in various volatile solvents onto the basal plane surface of graphite. For all the graphites investigated, the long-chain n-paraffins saturate the basal planes at low solution concentration, ranging from about 0.001 mole percent for n-C_{32} and 10 percent for n-C_{16}, with the formation of very distinct plateau regions (ref. 66). From the amount of adsorption of n-C_{32}, it was calculated that the n-paraffin molecules lie flat on the basal plane surface. The data indicate that the n-C_{32} molecules are closely packed so that each hydrogen atom in a methylene group in con-

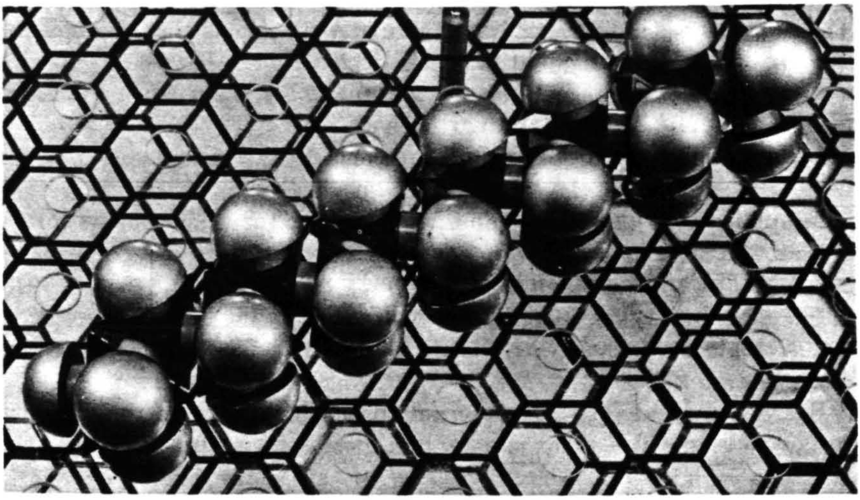

FIGURE 9.—Photograph of the *n*-paraffin model (n-C_{13}) adsorbed on the basal plane surface of graphite.

tact with the surface occupies one carbon hexagon or 5.6 Å^2. The proposed arrangement is shown in figure 9.

The heat of displacement of *n*-heptane by *n*-hexadecane suggested strongly that at a mole fraction of about 0.1, *n*-hexadecane forms a monolayer composed of molecules lying flat on the basal planes as indicated by Tideswell (ref. 21). The heats subsequently increase, unlike the amount of adsorption, to the value agreeing with the high heat of immersion of graphon in *n*-heptane.

It must be stressed that the strong preferential adsorption of *n*-paraffins is very characteristic for graphite and has not been observed for solids having polar surfaces. For example, the high heats of immersion are not observed for silica gel and carbon black (ref. 14).

It was thought that *n*-paraffin molecules form several layers of molecules oriented parallel to the graphite surface. The packing of *n*-paraffins in such multilayers is believed to contribute to the heat of adsorption in the same way as in the film composed of vertically oriented molecules.

Another important observation is the difference in the heat of wetting of graphite in *n*-heptane and *n*-hexadecane. This has been determined with the use of the flow calorimeter for graphon and other graphites by displacing *n*-heptane gradually with *n*-hexadecane and summing up all the heats of preferential adsorption so obtained (refs. 21 and 22). The difference obtained for a sample of graphon in these experiments amounted to 93 erg-cm^2, but for a more perfect graphite composed of thin flakes having a thickness of about 100 Å, the difference was much higher at 130 erg-cm^2.

The important point arising from these experiments is that the heat of wetting of graphite in liquid paraffins depends on the type of graphite used and that the ordering of *n*-hexadecane is increased when the basal plane in graphite becomes more extensive.

As far as mineral lubricating oils are concerned, it was found that the heat of adsorption of the oils increases markedly with their viscosities. This applied to both graphite and MoS_2 (refs. 27 and 67). Oils with molecular weights above 600 were adsorbed very strongly and partly irreversibly. These results paralleled the work with *n*-paraffinic solutes with different chain lengths, in which it was found that the heat of adsorption increased almost linearly with the number of carbon atoms in the paraffin molecule (ref. 27).

Bearing in mind that *n*-hexadecane forms thick films on the graphite surface, it seems likely that mineral oils, most of which have much higher molecular weight than *n*-hexadecane, would also form multilayers at the graphite-oil interface. The presence of such films would generally change the viscosity of the oil in the interfacial region and should therefore have a marked effect on the load-carrying capacity of the oils. It is thought therefore that the well-known relationships established between the viscosity of commercial mineral oils and their load-carrying capacity greatly depend on the thickness of adsorbed layers increasing with the average molecular weight of the oils rather than their viscosities. For example, the heats of adsorption of mineral oil N+P fraction onto cast iron increase greatly with the molecular weight of the oils in line with their load-carrying capacity (ref. 27). On the other hand, thermal diffusion fractions with widely differing viscosities but the same average molecular weights were found to have very similar load-carrying capacity by tests in the four-ball machine (ref. 28). This indicates that viscosity, per se, is insufficient to insure a high load-carrying capacity for mineral oils. Beneficial factors in this connection are believed to be high molecular weight and linear structure of constituent molecules of the oils, which would cause the molecules to be strongly adsorbed on surfaces characterized by strong dispersion forces.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Most of the evidence available to date indicates that the main role of adsorption in lubrication is to reduce the energy and adhesive forces of the solid surfaces in contact. This leads to reduction in friction and wear. The adsorption process in liquid lubrication is one of preferential adsorption onto the surfaces immersed in liquid lubricant; i.e., displacement of relatively weakly adsorbed solvent (major component) by the more surface-active minor components.

The preferential adsorption of the surfactants from relatively inert liquids may result in—

(1) Further reduction of surface energy and forces of adhesion between

the solid surfaces in contact, over and above the reduction that occurs initially when the surfaces are immersed in the liquid free from surface-active agents.

(2) Provision of adsorbed films that are more stable, i.e., capable of maintaining the reduction in surface energy at higher temperatures, than the films of the liquid from which the adsorption takes place. This effect is probably much more important than the small reduction in surface energy that may occur on preferential adsorption. (An important parameter characterizing the stability of adsorbed films is the heat of adsorption.)

(3) Provision of a reservoir of active elements that could chemically react with highly stressed spots of surfaces and thus maintain the protection of the surfaces against wear before the adsorbed films break down or are desorbed.

Adsorption from solution has been a relatively neglected branch of surface science, and therefore the understanding of the connection between the adsorptional phenomena and liquid lubrication is still very incomplete. There are, however, encouraging developments taking place in the theory underlying the adsorption from multicomponent liquid mixtures, and clearly more attention is now being paid to the structure of adsorbate and its dependence on the nature of solvents from which the adsorption takes place. Recent calorimetric work strongly suggests that even for simple systems such as graphite-liquid hydrocarbon, formation of multimolecular layers occurs, which is presumably due to the strong affinity that the graphite surface exerts for liquid hydrocarbons. This is, of course, of considerable importance to liquid lubrication because the adsorbed layers are likely to have markedly higher viscosity and resistance to mechanical deformation than the bulk liquid beyond the influence of surface forces.

It is very likely that liquids filling the space between solid surfaces separated by distances below about 100 Å have a structure that is much more rigid than that of the bulk liquid, the structure and its depth depending critically on the nature of the solid surfaces. Much more work is required in this area, and calorimetric methods are perhaps best suited for the detection of the existence of such films and a study of their structure and stability.

The work must be extended, of course, to investigations of the effect of temperature and pressure on the structure of the adsorbate; the effect of pressure on adsorption from solution seems to be particularly neglected by surface scientists, although it is likely to be an important factor in the behavior of liquid and liquid mixtures at solid-liquid interfaces.

Chemisorption of certain boundary additives onto metals and the formation of polymers is now considered to be a possible cause of the existence of very thick films at metal-liquid interface, extending perhaps to a depth of a few micrometers. These phenomena are still not well understood, and much work remains to be done to elucidate the mechanism of formation of such mixed films.

It seems that at the present time the correlation between adsorption at solid-liquid interfaces and the lubricating effectiveness of adsorbed films can only be made on the basis of unproven assumptions concerning the chemical nature of the solid surfaces. Ideally the role of adsorption in the lubrication should be investigated on the surfaces of single crystals subjected to controlled oxidation or other treatments, producing a surface that could be analyzed by low-energy electron diffraction and Auger electron spectroscopy. This could be complemented by studies of adsorption on clean surfaces of polycrystalline solids and the surfaces of solids freshly formed (and therefore containing dislocations) under pure liquids. The surfaces could then be covered by vapors of liquid lubricants, immersed in pure liquids, and immersed in liquid solutions containing adsorbable molecular species. If the nature of adsorbate were known in each case and if the lubrication of the surfaces in contact with the adsorbates could then be investigated, valid correlation would be established between the physicochemical nature of adsorbed films and their role in lubrication.

ACKNOWLEDGMENT

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DISCUSSIONS

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Mr. Groszek envisages the possibility that solid surfaces separated by distances below about 100 Å have a structure that is more rigid than the bulk liquid. It is difficult to picture a model surface involving separations of this magnitude, and figures 1 and 2 attempt to present models of surface interaction without specifically involving asperity interaction.

Similarly, in figure 2 of his paper, Dr. Rowe [1] presents the usual picture of asperity interaction in adhesive wear. The discusser finds neither of these pictures at all convincing as a description of surface interaction and considers that there is a great need for some generalized concept whereby we can discuss surface nature and action in realistic terms.

Any tribological system is too complex to be comprehended as a whole because of numerous interaction or feedback effects, and one is compelled to consider restricted aspects or specific situations and configurations. A number of statements may be made of which the following are examples:

(1) Friction force is not directly correlated with rate of wear.

(2) There is not necessarily a unique mechanism of friction.

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[1] See the lecture "Wear—Corrosion and Erosion" by C. N. Rowe, which follows this lecture. (Editor's note.)

(3) The coefficient of friction is nothing more than a partial regression coefficient relating tangential force to normal force.

(4) Wear may take many forms and is not necessarily a continuous process.

(5) Surfaces are rough on the atomic scale, so contact is randomly dispersed between asperities.

(6) Even where lubricant is not deliberately introduced, the interlaminary material differs in properties from bulk materials.

(7) Asperity interaction has, since the time of Bowden, been regarded as the key to the frictional process.

(8) A shearing or rotational action must take place, either within interacting asperities as they pass by each other or within any lubricating film that may exist to separate them.

(9) When the thickness of such a film exceeds the combined effective height of the asperities on both surfaces, the film is sheared and the situation is governed by the rheological properties of the substance. For this situation to exist indefinitely, some pressure-generating mechanism must exist.

(10) When these properties are Newtonian or near Newtonian and a pressure-generating mechanism exists, lubrication is said to be hydrodynamic.

(11) A characteristic of hydrodynamic lubrication is that velocity, load, and viscosity can be varied, performance being governed by nondimensional parameter $\eta U/P$.

(12) Wear may follow three modes of progression, wearing in, steady wear, and catastrophic wear, i.e., $W = Ke^{\alpha t}$, with α negative, zero, or positive, respectively.

   (a) If wear is of a nature to roughen the one or both of the surfaces so as to render them more aggressive, α will be positive, wear rate will increase indefinitely and lead rapidly to disaster; e.g., scuffing. A similar unstable thermal situation operates here, and thermal factors operate except at the slowest of speeds. Indeed, the limit to the exponential increase in wear rate may occur when one or other of the surfaces reaches melting point (ref. 68).

   (b) If wear is nonexistent or takes place at a constant rate, α is zero. This is thought to be confined to relatively mild conditions because it implies that, although material is removed from a surface, the behavior of that surface remains unchanged. It is within this region that the laws of wear propounded by Hirst are expected to be applied (ref. 69).

   (c) Where a smoothing action occurs, i.e., α is negative, the well-known running-in action occurs. Then, α can be regarded as a feedback effect, either positive or negative.

(13) Resistance to deformation, i.e., hardness, may vary throughout the tribological system, particularly within the interfacial area. As pointed out by Kragelski (ref. 70), if a gradient exists that has a minimum at the interface, deformation will be concentrated within the interfacial region and will therefore take place within the minimum volume that may be expected to yield the minimum wear rate; i.e., $\alpha < 0$. If, however, the hardness diminishes with distance from the interface, cleavage will take place on a plane remote therefrom and not necessarily parallel to direction of motion. Serious damage will take place, described by Kragelski as tearing in depth and by Hirst as severe wear.

(14) A particular case of this is that instanced by Bowden and Tabor (ref. 71) where the asperity tips are regarded as being welded together. Due to work hardening or other factors causing the weld to be reinforced, failure will occur by a particle being torn out from one surface but remaining firmly adherent to the other. Grunberg (ref. 72) suggests that only a proportion of the wear particles produced in lubricated sliding under boundary conditions remain firmly adherent to one or other of the surfaces.

(15) So far nothing has been said that will cause disagreement with other workers in the field. However, if we apply the Bowden and Tabor relationship between flow stress of asperities and yield strength in shear of isotropic materials, we calculate a coefficient of friction of 1/6 for clean, unlubricated metals. Experiments with clean metal, i.e., unlubricated and with most oxide removed presumably with some residual memory of the initial interface, give coefficients of friction of about unity.

(16) The argument of Bowden and Tabor is probably incomplete because, while they predict correctly the area of asperity contact from normal approach taking into account the supporting action of the substrate, which gives a flow stress approximately three times the value of yield in compression, this support is not available for tangential displacement. The difference in viewpoint is not great insomuch as these authors speak of junction growth as occurring in practice.

(17) If we consider a fully grown junction or follow the discusser's view (ref. 73) that shearing of isotropic material takes place on a plane inclined at approximately 45° to the direction of principal stress, the result is a coefficient of friction of unity.

(18) Lower coefficients than this are always recorded in the case of lubricated sliding. Sometimes higher coefficients are measured. It is believed that these are associated with bulk welding; i.e., loss of the original interface as a plane of weakness or other forms of tearing in depth.

(19) Lower coefficients of friction than unity can be explained either by putting forward two mechanisms operating in parallel, one giving a coefficient of unity and one giving a lower value, or by a mechanism differing in some important respect from the one outlined above; i.e., shearing of an anisotropic material. Thus, graphite has been exploited as a lubricant and is thought to act because the shearing strength parallel to the laminations is much lower than the compression strength perpendicular thereto.

(20) A mixture theory can account for most experience, i.e., a proportion β of the normal load is carried directly by asperities and $(1-\beta)$ is supported by some other, perhaps hydrodynamic fluid pressure generated support.

(21) Bowers and Zisman's results for pressure dependence of shear strength (ref. 74) are not inconsistent with the view that shear takes place at 45°.

(22) If load-carrying capacity is dependent on a mixture of asperity interaction and hydrostatic fluid pressure, assumptions of plastic flow of solids and Newtonian flow of fluids present too simple a picture. Full rheological data are required not only for lubricants but for the surfaces involved in the total tribological system.

Finally, we may conclude that it is necessary to regard any tribological system as a dynamic one involving random effects, and, while it is essential to decouple certain facets for conceptual purposes, a full analysis must be statistical in format and would only seem to be possible by a very large computer program.

R. S. Fein (Texaco Research Center, Beacon, N.Y.)

Mr. Groszek's careful review emphasizes the physical adsorption of surface-active molecules on metal oxide surfaces and the role in the adsorption process of the solvent for the molecules being adsorbed. The review concludes that "correlation between adsorption at solid-liquid interfaces and the lubricating effectiveness of adsorbed films can only be made on the basis of unproven assumptions concerning the chemical nature of the solid surfaces." This discussion is addressed to the question of whether any general correlation will be possible, even when the nature of the solid surfaces is known.

Essentially, adsorption is one of many processes involved in determining lubrication effectiveness. To illustrate the role of adsorption in some of these processes and the complexity of the process interactions, consider the following.

Electron diffraction examination after sliding with an adsorbed monolayer on the asperities of one of the surfaces showed multilayer accumulation on the asperities (ref. 75). Apparently, at least in this one case, the adsorption process does not provide the functional boundary film but rather provides a reservoir of boundary lubricant for displacement to the areas where needed.

Infrared (IR) and radiotracer examination of carboxylic acid adsorption on clean metal showed strong monolayer adsorption in the absence of oxygen and water (refs. 8 and 76); but lubrication is ineffective (ref. 78). Thus, adsorption per se apparently is not sufficient to provide for effective boundary lubrication.

Lubrication transition temperatures for copper-on-copper lubricated with dilute solutions of stearic acid in various solvents were shown to coincide with the critical solution temperatures (i.e., Krafft point) for cupric stearate in the solvents (ref. 78). This indicates that the desorption, i.e., solubilization, of reaction products formed from chemisorbed additive molecules is directly connected to lubricating effectiveness; this desorption process depended on bulk solution rather than surface properties.

Oleic acid treatment of abrasive particles added to a lubricating oil inhibited sedimentation of the particles and reduced wear in a hydraulic pump test (ref. 79). This suggests that adsorption can provide antiwear action by keeping abrasive particles in suspension as opposed to particle agglomeration and deposition on the sliding surfaces.

IR examination of copper surfaces that had been immersed in heated air-blown mineral oils, *n*-decane, and *p*-isopropyl toluene showed rapid growth on the metal of thick copper oxalate films when rapid oxidative deterioration of the hydrocarbon occurred; rapid oxidation of decahydronaphthalene, i.e., decalin, produced a copper nitrate reaction product film on the copper surface and no oxalate (ref. 80). Addition of benzotriazole to a mineral oil produced a thick adsorbed film of copper benzotriazole and retarded the oxidation-promoting catalytic action of the metal. This indicates that bulk lubricant oxidation can determine the nature of the solid surface and that an adsorbed additive can react to produce a protective film on the metal that inhibits bulk lubricant oxidation. Presumably, physical adsorption of the additive is a prerequisite to chemical reaction, but the process is controlled by the reaction product characteristics.

Wear of steel sliding on steel in the presence of paraffinic hydrocarbons and dilute solutions of carboxylic acids in the hydrocarbons was shown to catalytically promote bulk lubricant oxidation. The hydrocarbon oxidation was shown to promote wear (ref. 81). The active catalyst appeared to be iron carboxylate. This indicates that the chemical reaction of bulk lubricant, chemisorption, and lubrication effectiveness are interdependent.

IR studies of adsorbed zinc dialkyldithiophosphates on metal showed a number of decomposition products in addition to adsorbed molecules (ref. 82). Further, the gentlest possible rubbing of the adsorbed film produced another distinctive decomposition product. Thus, apparently the adsorbed film is a reservoir of reactant that can be chemically transformed by the shear stress involved in sliding.

These illustrations indicate that adsorption is involved in providing boundary lubricant reservoirs, corrosion-resisting protective films, reactants at the surface, dispersants for abrasives and corrosion products, and catalysts for bulk lubricant degradation. The adsorption (and desorption) process, thus, is one of many physical and chemical processes involved in providing lubrication effectiveness. With the complex interactions that appear to occur among these processes, a general correlation with the adsorption process alone seems improbable.

B. W. Hotten (Chevron Research Co., Richmond, Calif.)

Several consequences of crystallinity seem neglected by investigators of adsorbed films. The interfacial orientation of linear organic compounds is usually considered as one of two extremes: horizontal or perpendicular. But the zigzag alkyl chains fit together better when angles between the principal molecular and crystalline axes have intermediate values, such as 55° in lithium and sodium stearates and 75° in calcium stearate; long-chain carboxylic acids adsorbed on metal oxides are probably tilted also when closely packed. This leads to an explanation for the unexpectedly high heat of adsorption observed by Mr. Groszek and recently by Allen and Patel (ref. 83) for higher acids. The heat of crystallization, as Mr. Groszek mentioned in his discussion of octadecanol adsorption, probably contributes to it. Entropy of crystallization is only a small fraction of the enthalpy change. Crystallinity may also explain the higher heats of adsorption observed for mixed films of carboxylic acids and alkanes with matching than with nonmatching chain lengths. Multimolecular layers more probably result from epitactic crystallization than from the action of long-range forces, which have been repeatedly discredited. Finally, and most practically, greater crystallinity is probably responsible for the better antifriction and antiwear action of higher than of lower carboxylic acids.

E. Rabinowicz (Massachusetts Institute of Technology, Cambridge, Mass.)

In the introductory section of his paper, Mr. Groszek makes the point that a traditional explanation of the beneficial effects of adsorbed films on lubrication is that the presence of the adsorbed films leads to a decrease in the surface energy of the contacting solids. I venture to suggest that although this explanation is probably correct, and, in fact, I have advocated this point of view for a number of years (ref. 84), it must be considered at present as a minority view. The majority view is that an adsorbed film has a beneficial effect on lubrication because it introduces a surface layer of low shear strength at the interface (ref. 71).

I venture to suggest the reason why the surface-energy theory has not found more general support lies in the fact it is quite difficult to come up with quantitative expressions that demonstrate explicitly the benefit of lowering the surface energy of adhesion. None of the three earliest groups of workers in the field, Machlin and Yankee (ref. 85), Coffin (ref. 86), and Zisman (ref. 87), derived a quantitative expression. With regard to my own work. I have produced an expression for the reduction of wear particle size produced by lowering the surface energy through use of a lubricant (ref. 88); however, analogous expressions for the reduction in total wear volume and the reduction in friction produced as result of lowering the surface energy are not yet available and are very much missed.

H. E. Sliney (NASA Lewis Research Center, Cleveland, Ohio)

The role of adsorption in liquid lubrication is very difficult to assess in an exact and unambiguous manner. This is a serious dilemma in the very important area of boundary lubrication, where the surface chemistry and physics of film only a few monolayers thick are of primary importance. These very thin films must reduce the adhesive forces between the sliding surfaces to a degree that will result in acceptably low levels of friction and wear. The efficiency of the adsorbed films in performing their function is dependent upon their load-carrying capacity, shear stability, and temperature stability. All of these, in turn, are functions of the molecular structure of the adsorbed films and probably of the chemical composition and orientation of the liquid layers in the immediate proximity of the solid surfaces.

Determinations of compositions in the vicinity of the solid-liquid interfaces are very difficult and are complicated by the fact that interfacial compositions are often quite different from the bulk compositions in either solid or the adjacent liquid phase. For example, Ferrante has shown that alloys often have surface layers that consist primarily of the minor element in the alloy composition. This has been demonstrated, for example, for the Cu-Al system (ref. 89). Buckley and Brainard have shown similar effects for the Fe-Co-Si systems.[2] Surface layers consisting entirely of aluminum or silicon were characterized in these studies by means of LEED techniques for alloys containing bulk concentrations of only a few percent of the surface-enriched element. Before the recent advent of techniques such as LEED, it was almost impossible to characterize these surface segregation phenomena. In regard to the liquid phase and to quote the author, "Separation of individual components of liquid mixtures at solid-liquid interfaces is clearly of fundamental importance to the development of structure of the liquid in the vicinity of the surface and must be related, therefore, to the lubricating action of the liquid." LEED can be employed to characterize adsorbates from the vapor phase, but no technique exists for direct in situ characterization of the films at a solid-liquid interface.

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[2] Buckley, D. H.; and Brainard, W. A.: The Influence of Silicon on the Friction and Wear of Iron-Cobalt Alloys. To be published as a NASA Technical Note.

Much of the necessary information must still, therefore, be deduced from indirect evidence.

An example of the use of indirect evidence and hopefully reasonable assumptions is given in the author's discussion of the nature of the surface layers on lubricated steel in a normal (air) atmosphere. The likely presence of iron oxide and moisture film is recognized, and heats of adsorption for alcohols and acids on comminuted iron and on the various oxides of iron are measured with the objective of relating these data to adsorption phenomena on lubricated steel. The studies described in this paper incorporate a great deal of ingenuity in attempting to characterize surface phenomena without the benefit of direct observational techniques such as LEED. Considerable success has apparently been achieved in reproducibly preparing films and in measuring their effects even when the films themselves are not fully characterized with a satisfactory degree of confidence. Much of the data appear to be useful, and their validity is reinforced by the satisfactory way they can be treated by means of chemical thermodynamics. For example, heats of adsorption obtained by calorimetric techniques can show how film stability can be related to molecular structure of the adsorbate. The work of Askwith, Cameron, and Crouch (ref. 1) shows the effect of chain length matching of adsorbed additives and the liquid carrier on the scuff load for lubricated steel.

In general, it appears that much of the work done on the relationship of adsorption to lubrication has produced useful results, but only a limited knowledge of the fundamental surface phenomena involved. It is to be hoped that more fundamental information will be generated by the use of the modern tools of surface physics.

A. Beerbower (Esso Research & Engineering Co., Linden, N.J.)

Mr. Groszek presented an excellent survey, and the writer does not wish to detract from it in any way. However, having just completed a similar survey (ref. 90), he feels that presenting a contrasting viewpoint may help to add perspective to this rapidly growing field. In particular, the strategies resulting from these two surveys differ, for Groszek apparently plans continued emphasis on work with metal powders, while the writer sees a greater need for analysis of dynamic test data in terms of chemisorption energy.

The emphasis of the writer's survey was on evaluation of test methods for relevance to boundary and partial elastohydrodynamic (EHD) lubrication, particularly in terms of providing useful information for the design engineer's data bank. For this reason, all methods using oxidized surfaces (as in Groszek's fig. 2(*a*)) were immediately given a low rating. These included contact angle, Wilhelmy plate, and calorimetry on oxides.

The vapor calorimeter used by catalyst workers at least provides a clean metal surface, but a new problem arises. The Langmuir isotherm with constant heat of adsorption E is rarely applicable, and the various curves shown by Bond (ref. 91) provide strong evidence of a continuum of site activities. At low surface coverage ($\alpha \simeq 1.0$), E probably represents the heat of adsorption on fully annealed metal with the least energetic faces exposed; at $\alpha \simeq 0$, it is up to 2.5 times as high and must include contributions from high-energy faces, dislocations, and stored strain energy. Unfortunately, this method is not applicable to ordinary low-vapor-pressure lubricants and additives.

Powdered metals are most unlikely to be as clean as the wires and films used in vapor calorimetry. In fact, Groszek himself cited the destruction of hydrocarbons by iron (ref. 52), yet he treats his own iron powder, which was comminuted under heptane, as if this process produced a true metal surface rather than one coated with carbides, polymers, etc. The first question is, "How can such a surface be relevant to lubrication?"

Groszek's surfaces do show a variation in heat of adsorption, which raises another question, "At what value of α should the heat of adsorption be measured to be useful in boundary lubrication?"

The relevance of the powder methods may also be questioned on the basis of the degree and kind of dislocation and strain energy built into the surface. Surely, different grinding processes must be tried; it seems reasonable to expect that the shape of the heat-of-adsorption curve will vary with the process. The third questions is, "Can a process be selected that is relevant to running in, and will not the choice of process be highly dependent on the metal?"

Dynamic methods for heat of adsorption date back to Frewing (ref. 92), but his results were confined to first-pass friction and so tend to represent oxidized surfaces. Askwith (ref. 1) used the same mathematics on more meaningful data from a four-ball machine operated at 200 rpm, where the wear track is traversed repeatedly. The results were most informative, including the chain-matching effect noted by Groszek. (The writer has already explained this in ref. 93 as a necessary consequence of the minimum entropy of mixing when the molar volumes of additive and solvent are equal. The same article also offers a thermodynamic explanation for the fact, noted by many others besides those Groszek cited, that monolayers contain 40 to 60 percent of additive.) The Frewing equation (ref. 92) requires that both temperature and concentration be varied to obtain the heat of adsorption and so cannot be applied to pure liquids. It assumes that the fractional base area α is a constant independent of temperature for a given additive, from which

$$\ln C = \frac{-E}{RT_t} + K \tag{27}$$

where C is volume fraction of additive, E the heat of displacement of solvent by additive, R the gas constant, T_t the temperature at which transition to high erratic friction takes place, and K an integration constant (dependent on the critical α value of the additive).

Kingsbury (ref. 94) took a further step by deriving an equation for pure liquids, in which the variable concentration was replaced by the deBoer concept that fractional coverage results from decreased residence times of liquid molecules. Rowe (ref. 95) put this into better form for analysis of wear rate data, and the writer (ref. 96) simplified it to

$$\frac{V}{d}=\frac{k_m \gamma \alpha W}{P_m} \tag{28}$$

where V/d is the wear volume rate in cm^3/cm, k_m is 1/3 for hemispherical wear particles, γ is $(1+3F^2)^{0.5}$, F is the coefficient of friction, W is the load in grams, P_m is the penetration hardness of softer metal in kg/mm^2, and

$$\alpha=1-\exp\left[\frac{-\exp(-E/RT_s)}{(3.23\times10^{-5})U(M/T_m)^{0.5}}\right] \tag{29}$$

where U is the velocity in cm/sec, M is the molecular weight, and T_m is the melting point in °F, and

$$T_s=T_b+\frac{1.040\times10^{-5}\,FU(WP_m)^{0.5}}{k_1+k_2} \tag{30}$$

where T_b is the bulk lubricant temperature and k_1 and k_2 are the thermal conductivities of the metals.

Using these equations, Rowe found E for cetane essentially constant. Garabrant[3] analyzed data from Appeldoorn (ref. 97) on 13 pure hydrocarbons (table 5) and five jet fuels without additives (table 6). He found that E was not constant, but that E/T_s was, as shown in the tables. The wet-air data in table 6 should be comparable to table 5.

This result is consistent with equation (27) because when $C=1.00$, $E/RT_t=K$. It is interesting that E/RT_s is also independent of hydrocarbon, which Frewing had no way of determining. A very limited study indicated that E/RT_s was slightly dependent on metal hardness P_m. As implied by the writer (ref. 96), E should be roughly proportional to $(P_m)^{1/3}$.

While there is more to be done before this method is fully validated, it appears that dynamic friction and wear measurements from any test machine can be converted to E values, using these equations. The surfaces, which are formed beneath the test liquid, meet every requirement for cleanliness and relevance. The measurement is automatically made at an appropriate value of α. The final questions is: "Would it not be more appropriate to obtain E values from dynamic measurements, rather than to struggle with the problems of static testing?"

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[3] Garabrant, A. R.: Personal communication, 1970. Quoted in more detail in ref. 90.

TABLE 5.—*Heats of Adsorption of Pure Hydrocarbons on Steel Calculated From Wear Rates*

Code	Lubricant	Heat of adsorption, kcal/mole							Ratio E/T_s, cal/mol-deg-K						
		Load, g							Load, g						
		30	60	120	240	480	1000	2000	30	60	120	240	480	1000	2000
1	*n*-Octane	12.7	12.8	13.5	14.3	15.6	-------	-------	38.5	40.6	39.8	40.6	43.0	-------	-----
2	*n*-Nonane	12.4	12.1	12.0	12.7	-------	-------	-------	38.4	38.5	35.3	35.1	-------	-------	-----
3	*n*-Butylbenzene	12.5	11.9	12.0	13.0	15.7	15.9	-------	38.0	36.4	35.4	36.5	39.2	38.0	-----
4	Diethylcyclohexane	13.3	13.1	13.2	14.0	15.1	-------	-------	39.5	39.5	38.8	39.6	39.8	-------	-----
5	*n*-Dodecane	12.2	12.6	13.3	14.0	15.7	-------	-------	39.0	40.0	40.9	40.9	42.1	-------	-----
6	Tetralin	12.7	12.9	13.4	13.9	14.7	18.1	24.5	40.6	40.3	41.1	41.0	40.2	41.1	41.7
7	Decalin	13.0	13.0	13.8	14.3	14.5	15.8	-------	41.2	40.9	38.5	41.0	40.2	39.9	-----
8	1-Methyl naphthalene	13.1	13.6	14.1	14.8	15.7	-------	-------	41.7	43.2	43.6	44.3	44.5	-------	-----
9	1-Hexadecene	12.7	13.2	13.5	14.1	15.0	16.3	18.2	40.6	42.0	41.7	42.5	43.3	43.8	43.4
10	*n*-Hexadecane	12.6	13.1	13.5	14.1	15.0	16.3	-------	41.0	41.9	42.5	43.3	42.0	42.3	-----
11	Heptamethylnonane	12.4	12.7	13.4	14.0	15.0	16.4	-------	40.0	40.3	41.3	41.7	41.0	41.5	-----
12	*i*-Propyl bihexyl	12.7	13.3	13.8	14.3	15.1	-------	-------	41.6	42.7	42.8	42.8	43.5	-------	-----
13	Dimethano decalin	13.1	13.6	-------	14.7	15.5	-------	-------	42.9	43.2	-------	43.5	43.8	-------	-----

TABLE 6.—*Heats of Adsorption of Commercial Liquids on Steel Calculated From Wear Rates*

Liquid	Atmosphere	Heat of adsorption, kcal/mol			Ratio E/T,		
		Load, g			Load, g		
		240	480	1000	240	480	1000
Synth. Isopar	Dry argon	16.4	17.9	20.0	43.1	44.5	45.7
	Wet argon	16.1	17.5	20.4	43.5	44.8	45.8
	Dry air	16.2	16.9	17.6	42.5	40.5	41.7
	Wet air	15.3	15.2	18.5	40.4	36.8	38.1
JP-5	Dry argon	17.1	17.7	20.0	44.8	44.3	44.5
	Wet argon	17.2	17.8	18.6	44.5	44.2	42.3
	Dry air	19.2	18.1	28.4	44.7	42.0	42.2
	Wet air	15.5	16.5	25.2	38.6	40.0	40.0
RAF-176-64	Dry argon	16.6	17.2	18.5	46.0	44.0	45.0
	Wet argon	16.7	17.6	18.4	44.3	45.0	43.7
	Dry air	17.4	16.9	-------	43.7	41.9	-----
	Wet air	15.6	16.7	17.6	41.3	41.0	40.7
PW-523	Dry argon	17.9	17.2	19.2	45.2	42.9	46.2
	Wet argon	17.4	18.0	19.3	44.1	44.3	45.2
	Dry air	14.8	15.5	22.0	39.4	40.1	39.7
	Wet air	15.7	15.7	19.5	38.7	38.8	38.2
JP-4	Dry argon	17.0	18.1	22.2	45.0	46.3	46.2
	Wet argon	17.3	18.5	19.8	45.1	45.9	44.5
	Dry air	16.7	18.2	-------	44.7	45.6	-----
	Wet air	16.2	15.8	-------	42.8	38.4	-----

Conditions: 52100 steel, 240 rpm, 32 min.

LECTURER'S CLOSURE

Professor Barwell's statements illustrate very well the complexity of wear and friction phenomena. Insofar as my paper is concerned, I have attempted to visualize initially well-defined solid surfaces; i.e., the surfaces of single crystals. These may in practice correspond to a part of a clean asperity surface consisting of individual crystals forming grains, which in turn may be constituent parts of an asperity. I assume here, of course, that a surface of an asperity is heterogeneous on the atomic scale presenting a mosaic of various atomic arrangements. To reduce this complex surface to simplest possible terms, we can consider individual elements of the mosaic in which atoms form well-defined structures. The surface of these elements may be covered by various adsorbed atoms and molecules, but the structure of these adsorbates would depend in the first place on the atomic arrangements within the surface element and, of course, the nature of the atoms. Adsorbate films deposited on the total surface of an asperity should be viewed as composite structures, their macroscopic properties, relevant to antiwear action and lowering of friction, representing combined properties of individual portions of the adsorbed film residing on different elements of the asperity surface. Explanation of the behavior of a single asperity may be complex enough, but explanation for the behavior of a real engineering surface containing a large number of asperities would be even more complex. I agree here that a very large computer program would be needed to analyze such a surface.

I believe, however, that in order to obtain a proper and fundamental understanding of wear and friction phenomena, we should study tribological properties of surfaces with a known and well-defined atomic structure; i.e., individual faces of single crystals. This may be a hard and costly truth to swallow by applied tribologists, but, as in other scientific disciplines, the rewards of a good understanding of fundamental factors affecting wear and friction may be expected to be considerable.

In reply to Dr. Fein, one of the difficulties in the interpretation of various boundary lubrication studies that have been carried out in the past is that the surfaces studied have been poorly characterized. Very often so-called clean metal surfaces are in fact complex polycrystalline surfaces grossly contaminated with carbon, sulfur, and possibly other impurities. Even the surfaces of very pure single crystals can only be cleaned with the greatest difficulty as evidenced by recent LEED studies by, for example, Buckley (ref. 3) and Pitkethly (ref. 64).

The surfaces of all the metals mentioned in the examples have an unknown surface composition, and therefore in any adsorption process studied, it was not possible to state unequivocally what was the chemical nature of surface on which adsorption took place and what was the structure of the adsorbate. For example, the formation of a close-packed monolayer of a long-chain fatty acid on a polished metal surface was assumed by Dacus, Coleman, and Roess (ref. 75), but there was no direct evidence that this was so, the electron diffraction patterns not differing greatly for the surfaces covered with multilayers and those covered only by a supposed monolayer.

Tingle (ref. 77) has shown that preadsorbed water is important in the boundary lubricating action of carboxylic acid; but we do not know what was the nature of the surface onto which water and the acid were adsorbed. The fact that the freshly cut metal surfaces behave differently from the aged surface is, of course, interesting, but I think that in both cases we are dealing with the adsorption onto metal oxides and/or metal carbides, which are different for the freshly cut and aged surfaces. We have recently examined spectroscopically pure metal powders ground in sealed tubes filled with highly purified and dried liquid hydrocarbons. The surfaces of ground powders contained substantial amounts of oxygen and carbon as shown by electron spectroscopic chemical analysis (ESCA), and the porportions of the two elements on the surfaces of the ground and unground powders were similar. We concluded that the freshly formed surface in the ground metal powders was essentially that of an iron oxide and possibly iron carbide. This is clearly one area where much more work is needed.

Turning to the effectiveness of adsorbable compounds in lubrication when the adsorption occurs from various solvents, I agree completely that this effectiveness should be and has been shown to depend on the solubility of the compounds in the solvents used in the process. This incidentally correlates directly with the heats of solvent displacement from various solvents, the heat of adsorption from poor solvents being generally higher than those for the adsorption from good solvents. Competition of solvent and solute for the surface obviously plays a role here.

Speaking more generally, I agree again that physical adsorption is not the only factor involved in the lubrication of highly stressed contacts. There is, however, a lot of evidence, as shown in my paper, that it strongly contributes to the effectiveness of adsorbed films in lubrication. Adsorption on metal oxides and clean metals invariably involves chemical and physical bonding. The loss of the physically bound molecules may make the adsorbed films less effective in preventing wear and may lead to catastrophic wear if the increased solid-solid contacts taking place after desorption of the physisorbed material led to a rapid increase in interfacial temperatures.

I agree with Dr. Hotten that the so-called vertically oriented long-chain molecules adsorbed onto metal oxides are probably tilted with respect to the solid surface, the angle being less than 90°. Essentially the high heat of adsorption observed for the long-chain fatty acids and alcohols is caused by intense intermolecular interaction between individual molecules forming the close-packed film and the energy of this interaction probably would not vary greatly with the inclination of the molecules, providing their packing density remains substantially the same. I consider, however, that the high heat of solvent displacement by the long-chain compounds is predominantly entropic in nature as the heat of crystallization of these compounds is equal to the product of the temperature of crystallization and the entropy change. The heat effects in table 4 of my paper indicate that for the same amounts of adsorption, i.e., similar free energy changes, the short-chain compounds give much less heat than the long-chain compounds. The difference can only be explained by substantial differences between the entropy changes involved in the two types of adsorption.

There are two points I would like to make in reply to comments by Professor Rabinowicz. I have been aware, of course, of his pioneering work leading to realization of the importance of the reduction in surface energy of solids occurring on adsorption of the lubricating liquid. His work led, I believe, to the valuable contribution by Dr. C. N. Rowe, who related wear in liquid lubrication to adsorption of the solvent and surfactants (additives) dissolved in the solvent. However, I believe that quantitative treatment at the present stage of our knowledge is not likely to explain many practical cases of lubrication simply because the assumptions that are made in such treatments are generally inapplicable in practice. One such *important assumption is that there is only one type of adsorption* controlling or affecting wear, whereas in practice the adsorption takes place on many different surface sites with different surface energies. Desorption in such a case is likely to be gradual, precluding the existence of sharp transition phenomena. This is, in fact, the case for most practical steel surfaces.

An effective quantitative treatment could be made, however, if a well-defined solid surface was considered such as the basal plane surface of graphite.

Turning to the question of the majority supporting the view that beneficial lubrication is due to deposition of surface layers having low shear strength, I would like to refer again to the recent work of Tabor, Skinner, and Gane (ref. 59) who have demonstrated the importance of low surface energy in the lubrication of single crystals of graphite and MoS_2. Reference 71 deals with the views of Dr. Tabor, which he has probably modified in view of his recent work.

I agree entirely with Mr. Sliney that the role of adsorption in liquid lubrication can only be completely and usefully elucidated if the adsorption is carried out on well-defined solid surfaces and if the methods used to study the adsorption would enable the experimenters to determine the structure of the adsorbate films at the solid-liquid interface.

In reply to Mr. Beerbower, I would like to stress the necessity to analyze two distinct situations in boundary and mixed EHD lubrication that can arise in practice. I referred to these situations in the introduction of my paper.

Static experiments are relevant to the behavior of aged surfaces; i.e., surfaces covered with products of interaction with air and moisture and then lubricated by a given liquid. The stability of adsorbed lubricant films in this case depends on the properties of the undisturbed surface that has not suffered any material loss and/or deformation. On the other hand, dynamic tests are clearly relevant to running-in phenomena and the lubrication of the run-in surfaces. A better understanding of adsorption processes taking place during or immediately after running in is of course also very important. Thus, I believe that the work in the field of boundary and mixed lubrication should follow two separate lines of investigation dealing with well-characterized static surfaces and deformed surfaces resulting from running-in processes. However, the problem of surface characterization in the latter case must be considered at present to be more intractable than that of characterizing static surfaces.

The iron powders ground in sealed tubes filled with liquid hydrocarbons represent materials having surfaces that might be expected to be similar to the surfaces produced in certain running-in processes. It must be understood, however, that they are not cleaner than the surfaces of the unground powders; they are, however, different. As mentioned above, our recent examination of the ground powders by electron spectroscopy (ESCA) shows that the surfaces still contain oxygen and carbon apart from iron. The next step would have to be to find out in which form the oxygen and carbon are present on these surfaces. The ground iron powders represent, of course, a relatively simple case. Much more complicated surface compositions no doubt result when the grinding or running in occurs in the presence of additives.

With reference to heat of adsorption, I believe that the integral heat of adsorption for a given surface is probably much more relevant to stability of adsorbed films than the differential heats obtained at any given coverage. There is no a priori reason why a specific value of α should be chosen for correlation with boundary lubrication.

As mentioned above, the adsorption in practice occurs on a large number of sites possessing different energies, and desorption with increasing temperatures is probably a very gradual process. This applies especially to surfaces during and after running-in processes, which can hardly be considered as clean surfaces, although they are most probably relevant to lubrication practice.

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Wear—Corrosion and Erosion

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Corrosion processes are understood on a macroscale, but are less well understood at the microscale and submicroscale level associated with metallurgical defects in the surface. This is especially true for surfaces under stress and for surfaces that have been freshly created as in systems undergoing wear.

This paper reviews the various forms of corrosion and considers the role of localized electrochemical reactions in the wear of sliding surfaces, both from a viewpoint of corrosive wear and as a means of controlling metallic wear. Evidence is mounting that such phenomena as fretting corrosion, stress corrosion cracking, corrosion fatigue, and erosion corrosion have as a common basis the localized electrochemical reactions caused by a combination of the induced inhomogeneity in the surfaces and the corrosive environment. It is also evident that very little is known about the detailed chemical mechanisms and the kinetics of the reactions in lubricated systems. Several processes leading to erosive wear are discussed.

WEBSTER DEFINES "CORROSION" as "the action or process of corrosive chemical change not necessarily accompanied by loss or compactness; a gradual wearing away or alteration by a chemical or electrochemical essentially oxidizing process." Any exchange of electrons between an atom in a surface and its environment, as in metal oxidation, falls within this definition and is therefore corrosion. Superimposing upon this definition the steady mechanical removal of surface reaction products that occurs between relative moving load-bearing surfaces leads to a situation that is extremely conducive to corrosion and to what is called corrosive wear. This enhancement in the rate of corrosion is due to a number of factors. These include the continual removal of the surface corrosion products that otherwise would be diffusion limiting, higher surface temperature due to the frictional heating, and the enhanced activity associated with freshly formed surfaces. Not only do these factors increase the rate of corrosion, but they also add enough complexity to the system that it is difficult to elucidate and to evaluate the magnitude of the contributing factors.

Depending on the magnitude, corrosion in sliding systems can be a cure or it can be a disease. It is one of those situations where a little is good, but a lot is bad. For example, chemical reaction of lubricant additives with metal at the tips of surface asperities to give products that are readily mechanically removed may be considered polishing of a rough surface to give a smoother surface that will allow the generation of a thicker elastohydrodynamic (EHD) film. However, if the lubricant is so reactive that it corrodes the entire geometrical area of contact, the amount of metal lost will be large and the life of the sliding component will be limited by the corrosive wear.

The literature on corrosion in aqueous and aggressive environments is large, and this discussion does not attempt to cite all or even the pertinent references in discussing certain points. Rather, it will attempt to highlight the general types of corrosion in nonsliding conditions and, with this information as background, examine corrosion and erosion in lubricant systems. In general, corrosion scientists and engineers have not investigated corrosion processes in both hydrocarbon environments and under sliding, nor have the lubrication chemists and engineers developed any in-depth understanding of corrosive wear processes and the influence thereon of operating variables. In fact, the concepts of lubrication and corrosion are frequently not connected. Hopefully, this discussion will bring into closer focus the similarities of corrosion and lubrication science.

LUBRICANT-METAL CHEMICAL REACTIONS (CORROSION)

Nonrubbing Surfaces

Theory of Corrosion

The majority of metals are thermodynamically unstable in atmospheric and most other environments. The change in free energy leads to oxidation of the surface metal atoms, and this oxidation can be direct or electrochemical. In electrical conducting media, the latter occurs to almost complete exclusion to the former. Because most environments contain oxygen or materials that react with clean surfaces, the question is not whether it will corrode. Instead, the questions are: In what manner will it corrode? How fast? What factors accelerate or retard corrosion?

As illustrated in figure 1, corrosion proceeds by the coupling of two simultaneous and equal rate processes. On the anode part of the surface,[1] the metal atoms lose electrons ($M \rightarrow M^{2+} + 2e^-$), and the ions can go into solution or they can remain on the surface as an insoluble salt (oxide). At the cathode part of the surface, a reduction process occurs; in the presence of oxygen and water the reaction is

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[1] The word "surface" as used refers to the interface between a solid and the environment and not what can be readily seen. Thus, the surfaces of cracks and micropits are included.

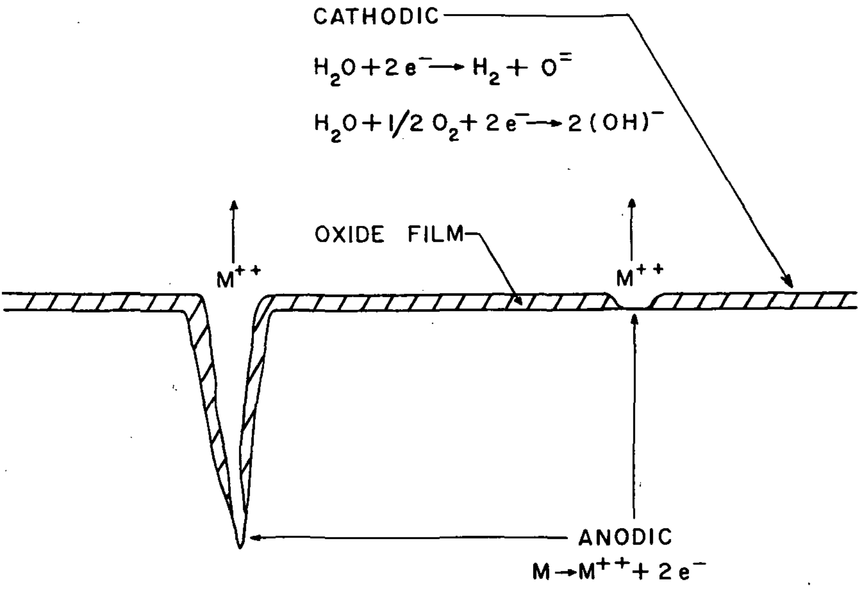

FIGURE 1.—Illustration of anodic and cathodic regions on a surface.

$$H_2O+1/2O_2+2e^- \rightarrow 2(OH)^-$$

while in the absence of oxygen, the reduction reaction (ref. 1) is

$$2H^+ + 2e^- = H_2$$

Each of these two types of surface sites has an associated electrical potential, and the rate of corrosion is a function of the difference in the potentials.

In this context a metal surface undergoing corrosion is composed of many galvanic corrosion couples. Depending on the heterogeneity of the surface the dimensions of these anodic and cathodic sections may be macroscopic, microscopic, and submicroscopic in size. Furthermore, these couples can remain fixed or change positions in time. Tomashov (ref. 2) has characterized the size of the couples as shown in table 1. It is evident that the electrical effects, and thus the electrochemical cell, can be confined to the immediate vicinity of the reactions so that it has the appearance of direct chemical attack. The oxidation of metals at high temperatures was once thought to be direct chemical reaction, but the work of Wagner (ref. 3) demonstrated that the mechanism is one of the metal ions diffusing outward through the corrosion-product film coupled with a flow of electrons. The film acts as both an internal and external circuit of a closed cell.

As table 1 shows, the distribution and uniformity of the corrosion couples is controlled by metallurgical factors. Homogeneity with regard to

TABLE 1.—*Characterization of Galvanic Corrosion Couples*

[N. D. Tomashov, ref. 2]

Type	Dimensions	Uniformity of position	Examples of electrochemical heterogeneity causing couples to function	Character of surface deterioration
Macrocouple	>1 mm	Fixed	Contact between different metals.	Local corrosion of different sections in a structure.
Microcouple	0.1 μm to 1 mm	Possible gradual change in position from anode to cathode.	Differences in composition, or orientation of various crystallites. Presence of inclusions, grain boundaries, etc.	Microscopic, nonuniform deterioration in macroscale (may be considered uniform by some).
Submicrocouple	10 to 1000 Å	Constantly changing positions between anodes and cathodes (fluctuating couples).	Defects (dislocations) in the crystal lattice. Heat fluctuations.	Complete, uniform deterioration as observed by conventional techniques.

composition is all important (ref. 4). Alloys of metals of varying electrochemical potential can be prime targets for corrosion. An example is the corrosion of copper-lead bearings in which the less noble metal (lead) becomes the anode and is selectively removed leaving a porous copper structure (ref. 5). Iron carbides are more noble than iron and can act as cathodes in acid media (ref. 6).

Surface integrity is equally important. Cold-worked layers, crystal orientation, microcracks, and surface inclusions can set up galvanic cells (ref. 4). On a smaller scale, the grain boundaries are usually less noble than the crystalline grains and lead to intergranular corrosion. Dislocations and slipbands within the grains have a higher potential and thus become anodic, leading to transgranular corrosion. Residual stresses in the metal can also influence corrosion. Clearly, the makeup of the metal surface can be such that on a macroscale a number of electrochemical processes are occurring simultaneously. The relative rates of the various processes depend on the metal-environment conditions and can vary over a broad range.

Forms of Corrosion

Corrosion can be classified into a variety of forms. The number of types and description varies somewhat in the literature (refs. 1 and 7 to 9). The most prominent forms, which are frequently identified by the appearance of the metal, are—

(1) Uniform attack or general corrosion, in which corrosion occurs evenly over the exposed surface

(2) Galvanic corrosion, the corrosion that occurs when two dissimilar metals are in direct contact or electrically connected and are immersed in a conductive liquid

(3) Concentration cell corrosion, the chemical attack of metal due to a difference in concentration of the electrolyte. The metal-ion cell results when a single piece of metal is in contact with a common or electrically connected electrolyte at two different metal ion concentrations. Metal corrodes at the lower concentration until the ion concentrations are equal, and the flow of current ceases. A second type of a concentration cell corrosion is a differential-aeration cell in which the metal reacts at the point of lowest oxygen concentration. An example is the corrosion in a crevice at a weld or joint that has a limited supply of oxygen.

(4) Pitting, in which corrosion occurs at selected areas such as a surface dent, inclusion, or a surface dislocation

(5) Intergranular corrosion, the selective attack of the grain boundaries due to a difference in potential between the grain boundary and the grains

(6) Erosion corrosion, corrosion induced by the impingement of solid

particles on the surface or by the flow of liquids at very high velocities that continually remove what otherwise would be protective films

(7) Stress corrosion cracking, microcracks formed by internal or external stresses act as sites for enhanced chemical attack

(8) Dezincification or demetalification, selective removal of zinc from copper-zinc alloys. Other alloys may undergo a similar attack in specific environments; the elements include aluminum, cobalt, and nickel (ref. 9).

Although eight forms of corrosion are described, the actual mechanism is chiefly electrochemical in nature. Generally, however, types (2) and (3) are thought of as being primarily electrochemical corrosion, because a current flows through the metal where no attack is occurring (ref. 10).

Corrosives

Given the right conditions, many inorganic materials can be considered as corrosive (ref. 11). Inorganic acids, alkalis, and many neutral salts in water are corrosive under ambient conditions. The presence of oxygen generally increases the rate of corrosion.

Most organic compounds are not considered active corrosives under most conditions (ref. 11). But carboxylic acids, anhydrides, aldehydes, and halogenated and sulfur-containing compounds can be corrosive. Of the carboxylic acids, formic acid followed by acetic acid are the most corrosive. Increasing the chain length decreases the ability to corrode; in fact, long-chain acids are corrosion inhibitors at low temperatures. At high temperatures all organic acids become corrosive. At 600° F stearic acid corrodes 302 stainless steel at a rate of 0.14 in./year (ref. 12).

Organic halides hydrolyze to form the halide acid, which then corrodes. Hydrolysis normally occurs at elevated temperatures but also has been reported at ambient temperatures (ref. 13). Organosulfur compounds become corrosive at high temperature due to the formation of hydrogen sulfide. In an oxidizing environment, sulfur dioxide and sulfur trioxide are formed. Sulfur dioxide is far more corrosive than the other two forms of sulfur in the atmosphere (ref. 11). At elevated temperatures, hydrogen sulfide can produce severe sulfidation of steel, which is the formation of a brittle, nonprotective film of FeS.

Rate Factors

Six factors basically control the rate of corrosion in aqueous systems (ref. 14). These are the acidity, oxidizing agents, films, temperature, velocity, and heterogeneity of the metal and solution. Many of these factors are also important in lubricant systems. Lubricant oxidation leads to corrosion by the acids formed. Atmospheric oxygen is the most common oxidizing agent and becomes the corrosive at high temperatures. At low temperatures the combination of oxygen, water, and acids can lead to corrosion in engines.

The nature of the film formed in the initial stages of corrosion is all important in controlling the extent of corrosion. The film may be very thin or invisible as the oxide film present on chromium and stainless steels. A thin film is generally more protective or passive than a thick film (ref. 14) because thick films tend to be permeable. The effect of temperature is rarely exponential because of the various factors controlling the corrosion. Generally, corrosion increases with temperature, but it can also decrease due to a decrease in availability of dissolved oxygen. Sometimes maxima are observed (ref. 15). Increasing the rate of movement of the environment with respect to the corroding metal generally accelerates corrosion due to the greater availability of the corrosives and the carrying away of soluble corrosion products.

Most of the corrosion research dealing with mechanisms has been done in aqueous systems, salts, or liquid metals. Very little work has been done in hydrocarbon systems because the problems are less numerous and less severe. Even so, the principles that are operative in aqueous systems also apply in hydrocarbon systems.

Rubbing Surfaces

Role of Surface-Chemical Reactions in Controlling Adhesive Wear

Adhesive or metallic wear occurs when two asperities on opposing sliding surfaces overlap and come together to form a metal junction, which subsequently shears at a point other than the original interface. Figure 2 illustrates the collision and the formation of a metallic wear particle. Adhesive wear can occur despite the presence of an intervening lubricant film between the two macroscopic surfaces. During the collision process, high hydrodynamic pressures are generated that elastically deform the metal and squeeze out the lubricant until only a very thin surface film separates the surfaces (ref. 16). Concurrently, the intimate contact area grows due to the high normal and tangential stresses on the metal (plastic deformation as well as elastic deformation can occur) so that the trapped surface film is stretched to the point that it ruptures, thereby permitting the formation of a metal-metal junction. In addition, the high shear stresses lead to local heating, and the adsorption forces of the surface film become weakened. Hydrocarbon and simple polar compounds, such as long-chain alcohols, amines, and esters, essentially desorb under these extreme conditions, and their effectiveness under the local high shear stresses is greatly reduced.

Work hardening occurs at the metal-metal interface, so the junction becomes stronger than the bulk metal. Consequently, as shown in figure 2, the junction will shear at some point away from the interface. If this occurs simultaneously on both surfaces, a wear particle is formed. More

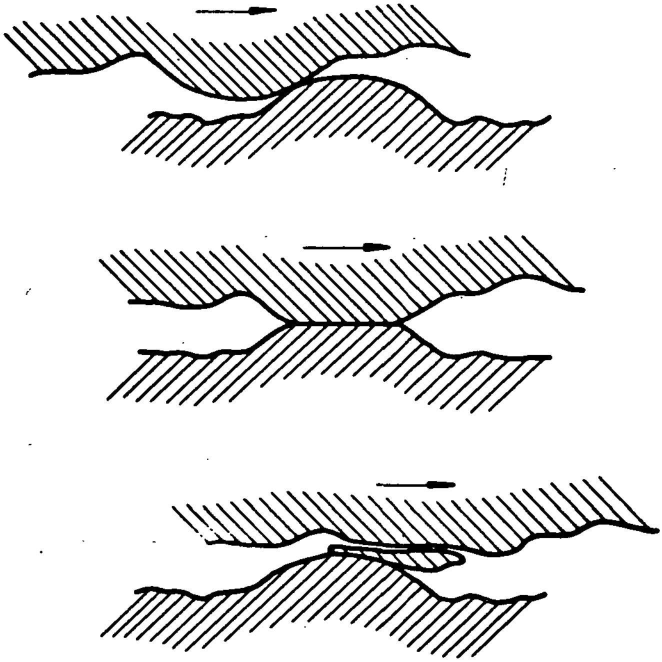

FIGURE 2.—Schematic representation of a unit event in adhesive wear.

likely, shearing occurs preferentially on one surface so that metal is momentarily transferred to the other. The resultant high spot will subsequently come in contact with an opposing asperity, and on some succeeding collision it will become mechanically separated from the surface. At low wear rates, the adhesive wear particle will be able to escape the contact area without causing serious trouble. At high wear rates, however, the individual particles will aggregate and work harden so that the large aggregates further disrupt the lubricant film and carry the load. In so doing, the wear process becomes catastrophic, either by rapid plowing wear of the surfaces or by scuffing wear. At the extreme the sliding components will weld together, and the system becomes completely inoperable.

Under severe conditions of sliding, adhesive wear is controlled by lubricants or lubricant additives that chemically react with the surface to form reaction products with a high affinity for the surface. The reaction is essentially irreversible. Because the new species formed is primarily inorganic in nature, it will have a very low solubility in the oil. Thus the adsorption equilibrium strongly favors the species to remain on the surface. For example, an oil-soluble organosulfur compound reacts with iron to form iron sulfide, which will remain on the surface until it is mechanically removed.

With hydrocarbons and many polar materials that are physically adsorbed (heats of adsorption of 3 to 10 kcal) or chemisorbed ($>$10 kcal), the surface species can desorb or be mechanically removed from the surface without carrying along any metal. However, in the case where a chemical reaction occurs to form a new species (FeS, for example), the loss of product during sliding leads to some loss of metal. The extent of this loss of metal will depend on a variety of factors, some of which will be discussed later, but the important thing is that the degree of chemical reaction can exceed the minimum rate necessary to control adhesive wear. Under these circumstances the adhesive wear problem has been replaced by a corrosive wear problem, although it may be of a lower magnitude with regard to the life of the sliding components. Generally, the term "corrosive wear" is used only when it exceeds by a wide margin (>10 to 1) the amount required to control adhesive or scuffing wear. Strictly speaking, however, any corrosion product removed by sliding is corrosive wear.

Adhesive-Corrosive Wear Balance

Intuitively, it is reasonable to expect an optimum balance between adhesive and corrosive wear. Under operating conditions in which the chemical reactivity of the lubricant is too low, the adhesive wear process will dominate, while at a chemical reactivity greater than necessary, the corrosive wear process will dominate. Under all conditions probably neither process occurs to the complete exclusion to the other. Figure 3 shows a schematic plot of wear rate versus lubricant reactivity with the rubbing surface.

The definition and measurement of a parameter describing the chemical reactivity at a wearing surface is most difficult because the rate of corrosion is exceedingly low with normal surfaces under ambient conditions. However, attempts have been made to correlate the amount of corrosion of fine, electrically heated iron wires by an oil additive with its antiwear properties (refs. 17 and 18). Figure 4 shows a plot by Sakurai and Sato (ref. 19) of wear versus corrosion rate of an iron wire for a variety of organic phosphites and phosphates in a refined bright stock oil. Rowe and Dickert (ref. 20) measured the rate of decomposition of zinc *O*,*O*-dialkylphosphorodithioates and found the correlation shown in figure 5 for the wear rate of a copper pin against steel versus the rate of hydrogen sulfide formation. At the employed conditions of sliding, the adhesive wear portion of the curve was not observed; however, the data demonstrate the existence of corrosive wear.

An optimum balance between adhesive wear and corrosive wear is also found as the concentration of the additive is varied. Figure 6 shows wear as function of concentration for two organic phosphates in SAE 20 grade mineral oil (ref. 21). Figure 7 shows the wear rate of a copper pin as a function of zinc *O*,*O*-dialkylphosphorodithioate concentration in *n*-hexadecane (ref. 22). Both figures show that at extremely low additive concentrations, where the surface film is a mixture of additive and base oil, the surface is

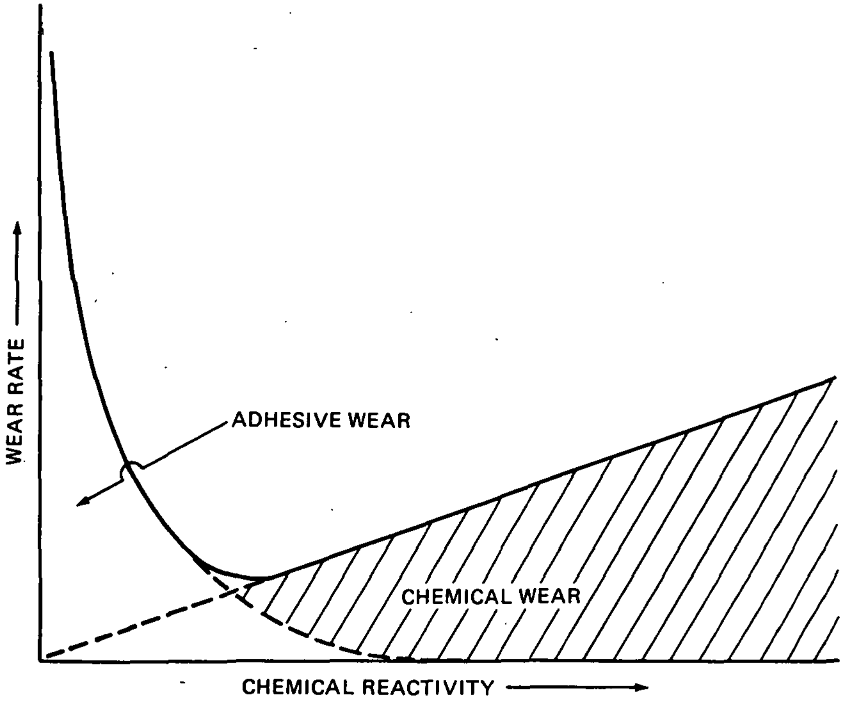

FIGURE 3.—Schematic plot of wear rate as a function of lubricant reactivity.

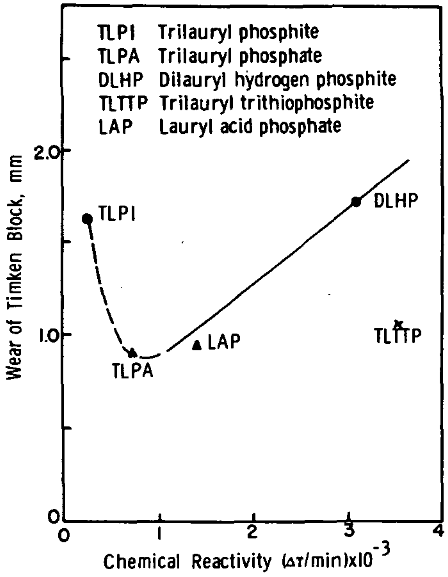

FIGURE 4.—Relation between wear and rate of reaction for phosphorus compounds (ref. 19).

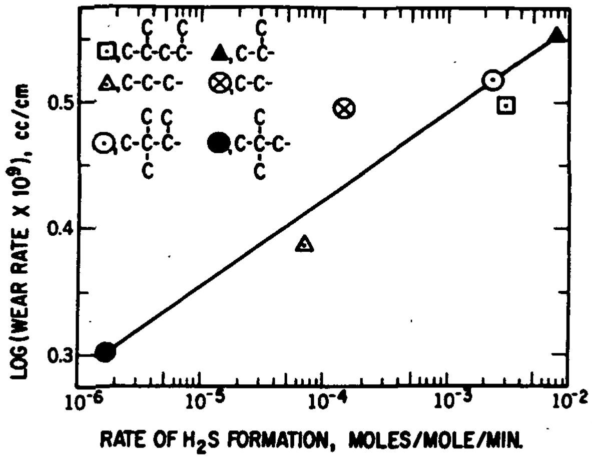

FIGURE 5.—Relation of wear rate of copper pin to thermal stability of zinc *O,O*-dialkylphosphorodithioates (ref. 20).

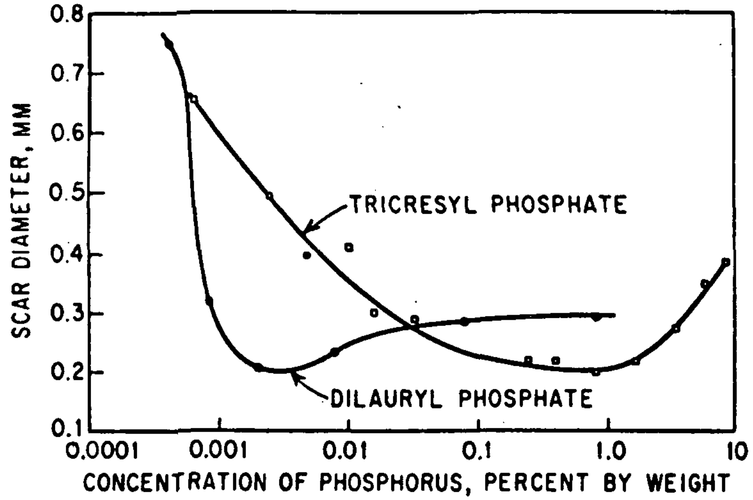

FIGURE 6.—Effect of concentration of phosphorus compounds in SAE grade mineral oil on wear as measured by the four-ball machine (ref. 21).

only partially protected and adhesive wear predominates. At high additive concentrations, an excessively thick corrosion film is formed and is removed during rubbing. Just what the reaction products are in both systems is not precisely known but most probably include iron phosphate and iron organophosphates in case of figure 6 (refs. 23 and 24).

Oxidation of sliding surfaces is a form of corrosive wear (ref. 25). As shown in figure 8, Klaus and Bieber (ref. 26) observed an optimum con-

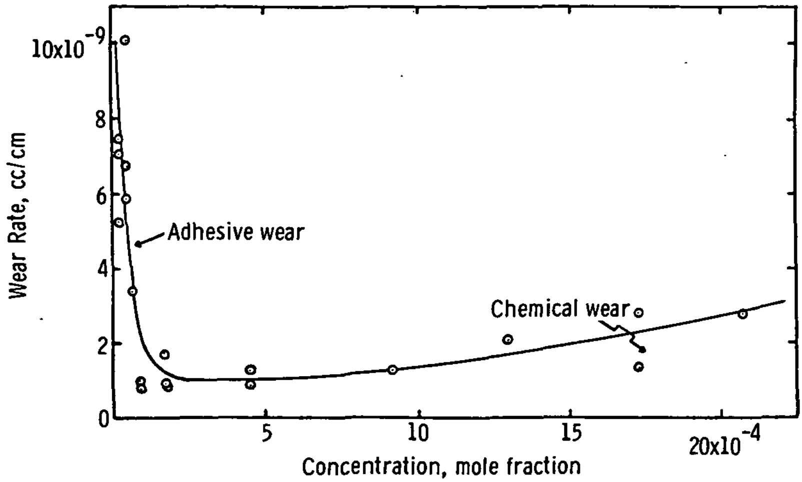

FIGURE 7.—Effect of concentration on wear rate of a copper pin with a zinc O,O-diisopropylphosphorodithioate additive in cetane (ref. 22).

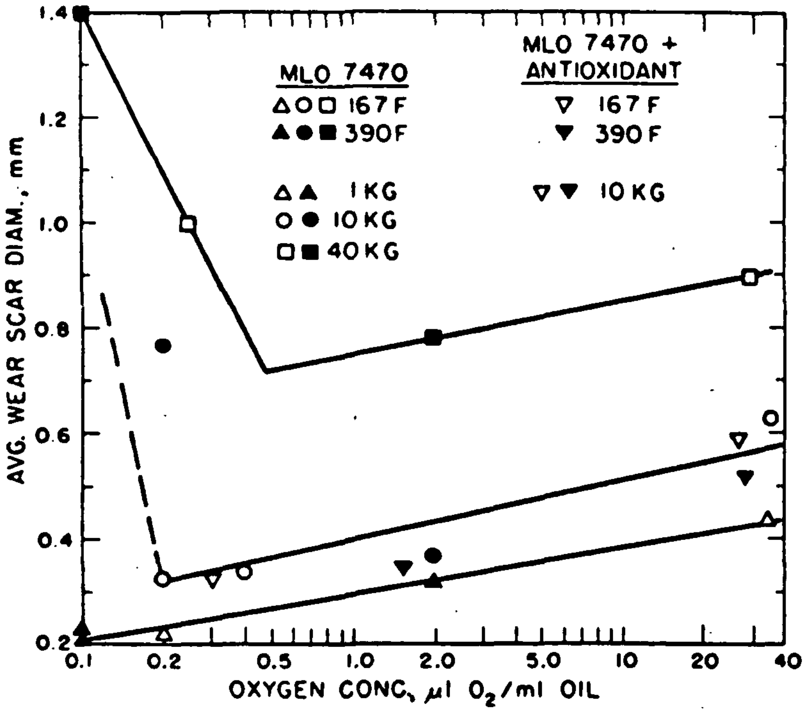

FIGURE 8.—Effect of dissolved oxygen on the wear behavior of a mineral oil (ref. 26).

centration of dissolved oxygen in mineral oil for the best balance of adhesive and corrosive wear. The optimum oxygen concentration increases with load, showing that more corrosion is necessary to control the increasing tendency for adhesive wear.

The optimum additive concentration or additive reactivity for achieving the lowest wear is dictated by the severity of sliding conditions and, of course, the metallurgy. More severe sliding conditions dictate greater chemical reactivity or higher additive concentrations for achieving the optimum balance between adhesive and corrosive wear. Consequently, the curve in figure 3 will shift to the right, as shown in figure 9. The observed wear with reactivity *A* will be controlled by corrosive wear for severity I, optimum balance of adhesive and corrosive wear in II, and adhesive wear in III. This figure illustrates the difficulty frequently encountered in rating antiwear additives among various wear tests and field applications arising from the variation in severity at the rubbing interfaces. Figure 10 shows the dependence of load-carrying capacity on chemical reactivity as measured by corrosion of a fine electrically heated wire (ref. 19). The separate curves for the sulfur- and chlorine-containing compounds demonstrate that the effectiveness of the surface reaction product is also an important parameter. What properties of the surface film control the performance are not precisely known; several possible factors will be discussed later.

From a practical standpoint, the best situation for long-wear life is an optimum balance of both adhesive and corrosive wear. The question, then, is how to achieve this situation scientifically in practical systems. Unfortunately, answers based on sound scientific information are not avail-

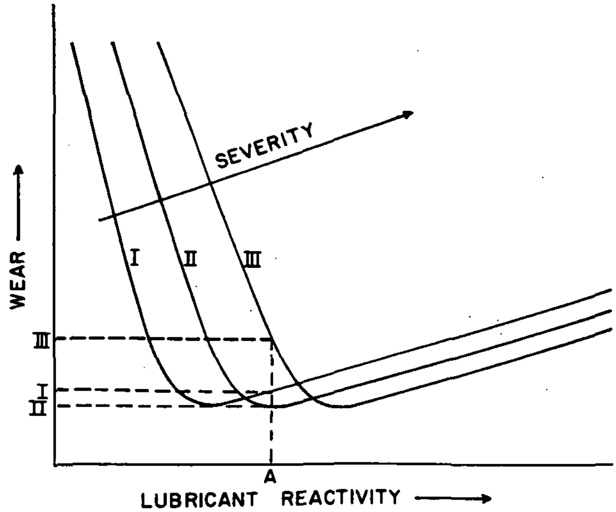

FIGURE 9.—Schematic plot illustrating effect of severity of sliding on adhesive-corrosive wear balance.

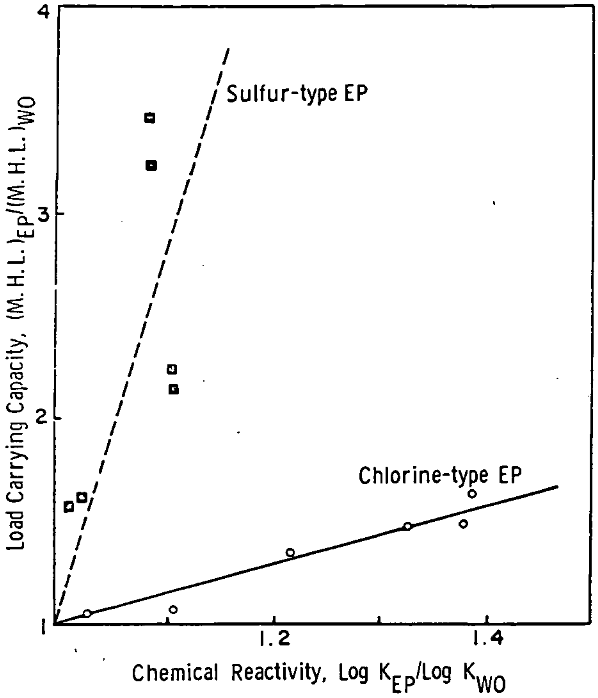

FIGURE 10.—Dependence of load-carrying capacity on chemical reactivity (ref. 19).

able, due to a lack of detailed knowledge of actual conditions of temperature, pressure, etc., at the sliding surface; lubricant-metal chemistry on rubbing surfaces; surface reaction kinetics, diffusion kinetics, and bulk lubricant residence time in the contact zone; optimum surface film thickness for maximum antiwear response; and the underlying properties of the surface film that control its rheology and thus its effectiveness as a lubricant. In addition, a given lubricant may be required to simultaneously lubricate different types of contacts that can have varying levels of severity, as well as different metallurgies that can give entirely different surface reaction products with diverse lubrication properties. A consideration of all these factors illustrates the complexity of the problem in selecting or formulating the best lubricant for a practical system.

Kinetics of Surface Reactions

The kinetics of chemical reactions of antiwear additives with sliding surfaces is all important for maximum effectiveness. Despite this fact, very few attempts have been made to evaluate rate constants and their dependence on operational conditions such as temperature, speed, and oil film thickness. Sakurai and coworkers (refs. 27 to 30) have investigated the kinetics of the reaction of radioactive S^{35} extreme-pressure (EP) additives with rubbing surfaces on a pin-on-disk apparatus and have derived expressions containing several rate constants that can be calculated, provided a number of important assumptions are employed. This series of papers represents a formidable beginning to sort out the kinetics of adsorption, chemical reaction, and wear of reaction products in the true and apparent contact regions, but the validity of several of the assumptions must be suspect, which makes the results tentative. Nevertheless, these workers found appreciable dependence of the kinetics on the molecular structure of the sulfur compounds. Clearly, this is an area of lubrication science that is in need of research using the latest analytical tools.

That adsorption and the configuration of the adsorbed molecule is important before chemical reaction is illustrated in the recent work of Forbes et al. (ref. 31). Diester disulfides having the structure

$$[\text{—S—}(CH_2)_nCOOC_2H_5]_2$$

where $n = 1$, 2, or 3 are effective antiwear compounds at low concentration but are completely ineffective at high concentrations. At high concentrations, they possess poor EP properties, so the high wear is not corrosive wear. Electron microprobe analysis showed appreciable sulfur present on the wear scar at low concentrations but very little at high. Heats of adsorption data in table 2 show that the ester groups contribute more to the adsorption than the sulfurs. Thus, it is concluded that at low concentrations, both sulfur and ester groups lie on the surface and the sulfur is available for forming iron sulfide (ref. 32). At high concentrations, the more strongly adsorbed ester groups push the sulfurs off the surface, thereby making them inaccessible for chemical reaction.

The fact that oxygen is a prominent corrosive permits the sliding of many metals under dry sliding conditions. Numerous investigations have been made on the role of oxygen in the self-lubrication of metals and have identified the oxides formed (refs. 25 and 33 to 36). Quinn (ref. 37) has applied the oxidation kinetics of steel to wear and has derived an equation for mild wear between 150° and 450° C based on the parabolic rate of oxidation. His model assumes that oxidation occurs during the flash temperature rise period and proceeds for $1/K$ traversals until the film reaches a

TABLE 2.—*Heat of Adsorption on Iron Oxide*

Additive	cal $\times 10^{-3}$/g Fe_2O_3
$[CH_3(CH_2)_{11}\text{—S—}]_2$	4.9
$[\text{—}(CH_2)_4COOC_2H_5]_2$	7.0
$[\text{—S—}(CH_2)_2COOC_2H_5]_2$	11.4

critical thickness ξ, at which time the entire film flakes off. Coupling these assumptions with Archard's (ref. 38) wear equation and the parabolic oxidation rate equation (ref. 39), Quinn derives the expression for wear rate V/L

$$\frac{V}{L}=\left[\frac{d}{\xi^2}\right]\left[\frac{W}{\rho^2 U P_m}\right] A \exp\left(\frac{-Q}{RT}\right) \tag{1}$$

where d is the length of a contact, W is the load, ρ is the density, U is the sliding velocity, P_m is the yield pressure, A is the oxidation rate at infinite temperature, T is the hot-spot temperature, and Q is the activation energy for oxide formation. From wear rate measurements and calculated average hot-spot temperatures of 1000° C, Quinn finds that the quantity d/ξ^2 is constant at 1×10^6 at high temperature. Because no value for d is known, he is unable to calculate the critical oxide film thickness. Rowe and Fowles (ref. 40) have pointed out that K is related to the probability of forming a wear particle through the term ξ/d, so the first term in the brackets in equation (1) is ξ^{-1}. Thus, Quinn would find that the critical oxide film thickness is 10^{-6} cm, in good agreement with the value suggested by Rabinowicz (ref. 41).

Subsequently, Quinn (ref. 42) arrived at a surface temperature of 600° C. Again, if we let ξ (and not ξ^2/d)$\sim A \exp(-Q/RT)$, with ξ being 10^{-6} cm, we calculate a value of 32 kcal/mol for Q, relatively close to the 46 kcal/mole found in oxidation studies (ref. 39). Since the very troublesome parameter d can be disposed of, Quinn's work shows that the oxidation rate is a fair indication of the wear rate. Critical testing of Quinn's model must await improved measurements or estimations of the surface temperature. More recently, Quinn (refs. 43 and 44) has proposed a modified linear oxidation model, but again critical testing of the model is hindered by lack of accurate data on the surface temperature. Activation energies of 4 to 18 kcal/mol are calculated, which are exceedingly low compared to 46 from oxidation studies in reference 39, but close to 9.6 kcal/mol observed elsewhere (refs. 45 and 46). Tenwick and Earles (ref. 47) have developed similar equations to Quinn's and calculate activation energies of 2.5 to 5 kcal/mol, which they are unable to explain satisfactorily. These low values would suggest that the activation energy for oxidation is considerably less on nascent surfaces. However, it may be that what is being calculated is the heat of adsorption of air on the metal oxide. Certainly, values of 3 to 10 kcal are more in line with physical adsorption than a chemical reaction; the kinetics of corrosion may be very rapid, and the wear rate of the oxides is being controlled by adsorbed gases rather than the rate of oxidation.

Tao (ref. 48) studied corrosive wear of steel with a mineral oil present and developed a model based on the diffusion of the oxygen to the surface. Oxygen solubility proved to be a key factor, and the model correlated some of the data, but the oil film thickness proved to be a difficult parameter to correlate. Subsequently, Tao (ref. 45) considered two additional models for corrosive wear. In the first, the parabolic rate of corrosion is considered the rate-controlling step, with wear being rapid. In the second, the corrosion is rapid, and the wear was rate controlling. It is concluded that the rate of oxidation is the more important model, but as with Quinn's studies, the inaccuracy in estimating the surface temperatures prevents a critical test of the model. Tao does conclude that the activation energy for corrosion is lower with a sliding surface than on a static surface.

As an overall assessment on the kinetics of corrosive wear, the described works of Sakurai et al., Quinn, Tenwick and Earles, and Tao, which comprise the chief efforts to date, point up the complexity of corrosive wear systems and the dangers in ascribing all of the observed wear to corrosive wear. It is likely that either some metallic, fatigue, or abrasive wear occur concurrently with corrosive wear. For example, fine metallic wear particles can corrode after formation so that a post mortem analysis of wear debris does not necessarily indicate it to be corrosive wear. Also, it would be expected that adsorbed lubricants on the metal oxides can influence the wear of the oxides in a manner similar to that proposed for adhesive wear (ref. 49). Nevertheless, these efforts offer some hope that the critical parameters can be elucidated and that they can be related to lubricant structure factors.

No attempt will be made to evaluate these models in terms of other published corrosive wear data, a critical test of the versatility of the concepts. This is currently being done by Beerbower and Tao (ref. 50). Suffice it to say here that they are finding it difficult to categorize observed wear as a single-wear mode. They further suggest that models of corrosive wear must interact with models of adhesive and abrasive wear to obtain an all-encompassing model that can apply to most wear systems.

Mechanical Properties of Corrosion Films

The extent to which corrosive wear occurs depends on the mechanical properties of the surface film. If the film has a lower shear strength than the metal substrate, it is expected that only a fraction of the film depth will be worn away at any given time (ref. 51). Examples of corrosive wear involving ductile films include lubricant systems containing chlorine, sulfur, and phosphorus compounds, as well as carboxylic acids.

For films that are harder and more brittle than the substrate, the probability is high that the film will completely break away from those regions under high tangential stress. Examples of this type of corrosive wear are found with most oxide-forming metals sliding in air at high temperatures. Hard oxides can lead to abrasive wear as well. At low temperatures the oxide film thickness is low, and the film is less vulnerable to wear.

The importance of good adhesion of surface films to the substrate has been demonstrated with boundary lubricants (ref. 52). Of course, it is important that the film have a high melting point, because a solid film is much more effective in keeping surfaces apart than a liquid-like film (refs. 52 and 53). For this reason inorganic salts are superior to metal organic compounds.

Cohesion or compactness of the film is important on two counts. First, a loose film is permeable and will permit excessive corrosion and will have a low resistance to wear. A cohesive film will lead to a lower corrosion rate and will have a high resistance to wear.

Composition of the surface film can be heterogeneous so the significance of the physical properties may be obscure. Godfrey (ref. 54) finds that sulfur and oxygen in a mineral oil corrode simultaneously to give Fe_3O_4 and FeS, which is superior to FeS alone in reducing friction and wear. Evidently, the simultaneous formation of oxide and sulfide led to a thinner and a more tenacious film than the thicker, less adherent pure sulfide film. A more complete description of the physical properties of surface films can be found in reference 55.

Film Thickness

Research with solid lubricants has shown that there is an optimum film thickness for maximum wear life and that the value depends on the particular lubricant (refs. 56 and 57). Rabinowicz (ref. 41) has calculated a critical oxide film thickness of 1×10^{-6} cm on a variety of metals from the dependence of the coefficient of friction on temperature. These results illustrate the significance in the corrosion rate in obtaining the proper film thickness for optimum balance between adhesive and chemical wear (fig. 3).

At the moment no knowledge exists on the optimum film thickness values for various types of EP lubricant additives. Such information coupled with the kinetics of formation could be invaluable in matching lubricant performance with the severity of operating conditions.

MechanicoActivated Surfaces (Tribocorrosion)

Although chemical reactions with clean surfaces have been studied extensively in the field of catalysis, the lubrication chemist has made little use of this information in unscrambling the pertinent chemical factors at sliding surfaces (ref. 58). A logical explanation is that the reactivity of rubbing surfaces can be very much different from that of nonrubbing surfaces, so the chemical reactions can be unlike those in catalytic systems. A vast amount of energy is stored in the asperity tips on a wearing surface, and a freshly created surface will contain many of the surface defects described earlier. Hence, a mechanically prepared surface should contain an abundance of sites for corrosion.

As shown by Kramer (ref. 59), Grundberg (ref. 60), and Tamai and

Momrose (ref. 61), surfaces formed by cleavage or mechanical deformation emit exoelectrons (Kramer effect). Unexpected surface chemistry has been attributed to exoelectron emission. Chaikin (ref. 62) concludes that the polymerization of hydrocarbons on rubbing surfaces of noble metals is due to the combined process of catalysis and charged particle bombardment, the latter due to the interaction of an exoelectron and a neutral species. Whatever the exact mechanism, the significant point is that polymerization would not occur on noble metals under the same conditions in the absence of rubbing. Smith and McGill (ref. 63) attribute the direct formation of metal soaps when carboxylic acids adsorb on freshly formed surfaces in the absence of air and water to the Kramer effect. These tribochemical reactions are being extensively investigated by Heinicke (refs. 64 and 65) using a vibrating mill to create an activated surface. He is able to calculate thermodynamic quantities as well as activation energies. Heinicke also considers stress corrosion as a tribocorrosion process (ref. 66). It is visualized that the root of the crack is the anode due to the high negative potential (20 mV) on the fresh surface generated by the bending stress.

Although very little is known about the detailed chemistry on mechanicoactivated surfaces, it is clear that a new surface possesses enhanced activity and therefore is highly corrosive. This so-called phenomenon of tribochemistry must be considered the key to a better understanding of such applications as polishing, grinding, metalworking, and lubrication in general.

Fretting Corrosion

Fretting corrosion may be defined as the corrosion associated with fretting, which is a form of wear that occurs with contacting surfaces having oscillatory relative motion of small amplitude. Fretting may occur in any assembly of mechanical components where small amplitude slip occurs. Operating conditions are unpredictable in that increased load can give less or more wear depending on whether the load influences the amplitude. Variation of the amplitude can lead to more or less wear depending on whether the lubricant can get in and the wear debris can get out. A classic example of fretting is the wear in wheel bearings of automobiles while being shipped on railroad cars or truck vans if not properly tied down. Fretting wear differs from other forms of wear because most of the wear debris is retained in the geometric contact area. With steel surfaces the debris is characterized by red rust, $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Fretting has been considered a combination of adhesive, corrosive, and abrasive wear (refs. 67 and 68). The exact sequence of events is still a matter for discussion. Uhlig (refs. 69 and 70) believes that the oxide film is removed by an opposing asperity to give clean metal that immediately oxidizes before making a second contact. On occasion a set of asperities may penetrate the oxide film to give some metallic wear, but the debris as it is formed is predominantly oxide. Waterhouse (ref. 71) also feels that in the presence of oxygen, the wear debris leaves the surface as oxides.

Others (refs. 72 to 75) theorize that metallic debris occurs from adhesion between asperities and that the wear particles then oxidize. The fact that noble metals undergo fretting supports metallic adhesion as a first step. The abrasive action of the metal oxides has also been proposed (ref. 76).

Hurricks (ref. 77) in a recent in-depth review of fretting concludes no single mechanism is operating at the exclusion of the others. He proposes a three-stage process. The initial stage leads to a dispersion of the oxide film with the formation of metallic junctions and metal transfer. In the second stage, metallic debris is generated that oxidizes and reduces further metallic contact. Finally, in the steady state, the valleys fill with oxide and metallic debris, and further wear occurs by a surface fatigue mechanism. It is concluded that abrasion is not a contributing factor. The fatigue mechanism is also proposed by others (refs. 78 and 79). Furthermore, in a corrosive environment, such as air, corrosion fatigue will be a factor since the adhesive junctions undergo cyclic strain. The significance of fatigue and the interaction of corrosion and fatigue is also found in reference 80. It is evident from this recent literature that fatigue may be an important parameter in fretting. Possibly with a better understanding of fatigue will come a better understanding of fretting and fretting corrosion.

Stress Corrosion Cracking

The conjoint action of a tensile stress and a corrosive environment to cause cracking of the metal is known as stress corrosion cracking (SCC) (ref. 81). The stress may be either an externally applied stress, or it can be a residual stress resulting from the fabrication or heat treatment. The stress will be a maximum at the tip of a localized surface crack, and, as already described, the crack tip will probably be anodic (fig. 1). Corrosion at the crack tip can raise the stress level and thus accelerate propagation of the crack to eventual failure. Cracking may be either intergranular or transgranular. The season cracking of brass and the SCC of stainless steel in aqueous chloride solutions are classical examples.

SCC can lead to solid products that occupy a larger volume than the original metal. These will exert a wedging action to develop additional stresses, which coupled with the existent stresses can lead to early failure (ref. 82). There is mounting evidence that the hydrogen liberated at cathodic sites of stainless steels diffuses into the metal and causes hydrogen embrittlement (refs. 83 and 84) and may also result in the formation of martensite platelets along slipbands that subsequently become the anodic path (ref. 85). Nielsen (ref. 81) concludes that the role of hydrogen as an embrittling agent may be the key to developing a unifying mechanism of stress corrosion in steels.

Corrosion Fatigue

The primary distinction between corrosion fatigue and SCC is that the applied stress is alternating or cyclic. Cyclic stresses tend to rupture any protective surface film that normally would retard corrosion. This results in a large reduction in the fatigue life and the elimination of the endurance limit (ref. 86). Failure generally occurs by intergranular cracking (ref. 4).

Both gaseous and liquid environments influence the fatigue life. Oxygen in gaseous environments decreases the fatigue life (ref. 87), and in one case this was shown to occur by increasing the rate of crack propagation (ref. 88). The presence of water vapor in air reduces the life further. This is evidence that fatigue proceeds by an electrochemical process.

In aqueous media, corrosion in the cracks proceeds by conventional electrochemical processes. Rebinder et al. (ref. 89) and Galvin and Naylor (ref. 90) have shown that certain organic liquids and additives can reduce the fatigue life in bearing steels, although the mechanism is not known. Rounds (ref. 91) observed that additives can either enhance or reduce bearing fatigue life. Schatzberg (ref. 92) observed that 1 percent sea water in a hydraulic fluid reduced the fatigue life of 52100 steel and that small concentrations of isopropylaminoethanol counteract the deleterious influence of the sea water. He suggested that the compound captures the hydrogen ions produced within the crack and prevents the hydrogen from diffusing into the metal and causing hydrogen embrittlement.

It is evident that a better understanding of corrosion processes on stressed metal and freshly created surfaces in hydrocarbon media is needed to have a better understanding of the role of lubricant factors in rolling-contact fatigue. Such an understanding could lead to important advances in bearing lubrication.

Electrochemical Corrosion Induced by High Wall Shear Stress

Beck, Mahaffey, and Olsen (ref. 93) have ascribed the wear of aircraft slide and sleeve hydraulic servovalves in the presence of a phosphate ester fluid to the generation of an electrokinetic current. As shown in figure 11, the wear occurs on the upstream side of the valve, and it occurs most rapidly when the valve is in the closed position with a large pressure drop (3000 psi) across the small orifice. Cavitation erosion was eliminated as a cause because increasing the back pressure had no effect and because wear occurs only on the upstream side, not on the downstream side. Particle erosion was also discounted because a 1-μm filter had no effect on the wear rate.

The authors employed the well-known streaming-current theory that states that the flow of a fluid will sweep free charges in the diffuse outer regions of the electrical double layer downstream (fig. 12), thereby setting up an electrokinetic potential between the solid and the fluid outside the

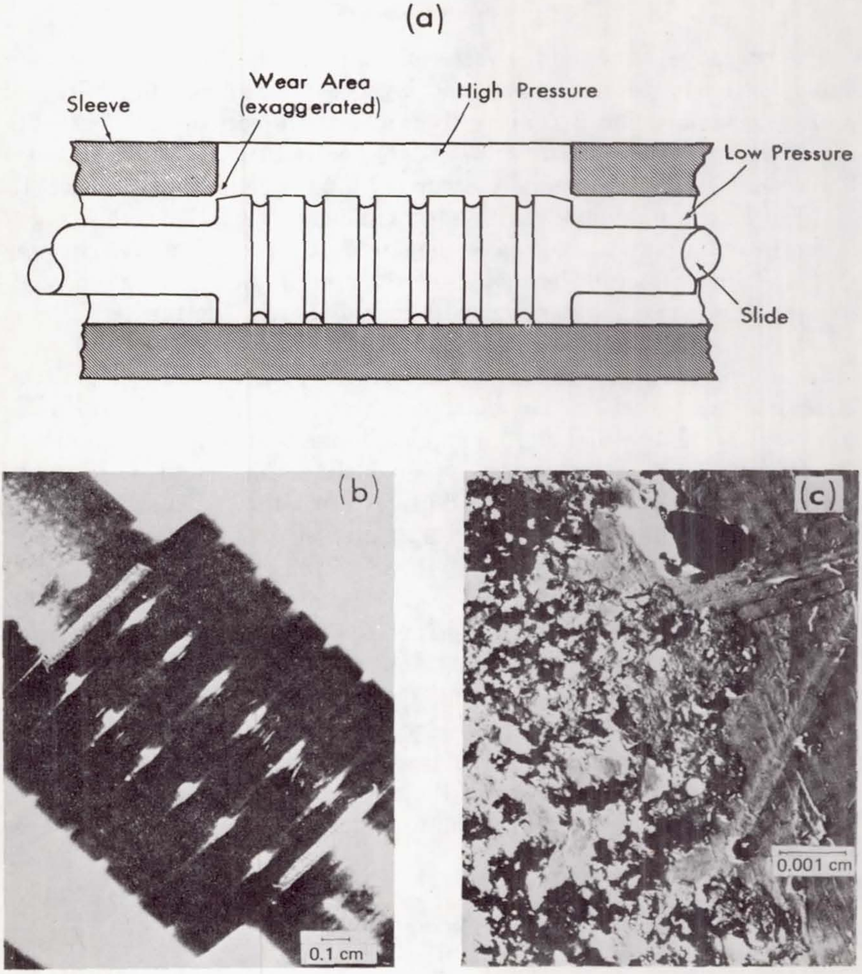

FIGURE 11.—(*a*) Schematic of valve. (*b*) Damaged areas on slider. (*c*) Enlargement of damaged area (ref. 93).

diffuse layer. Because of the geometry of the valve, the flow is not a parallel shear flow but a convergent-divergent flow, and the conservation of charge imposes a current flow between the metal and fluid, known as the wall current. This wall current causes electrochemical reactions in the regions where the streaming currents are generated on the upstream side of the valve. The application of this wall effect to the corrosion process is considered to be new by the authors. Measurements of the amount of current developed in a ring-disk electrode apparatus could account for all of the corrosion. For this new kind of corrosion to occur, it is assumed that the fluid must meet two conditions: the electrical double layer is thin com-

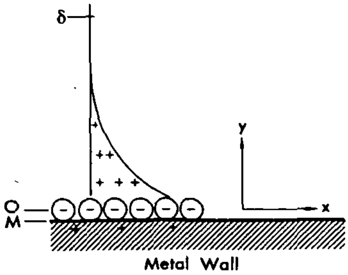

FIGURE 12.—Distribution of charges in the electrical double layer.

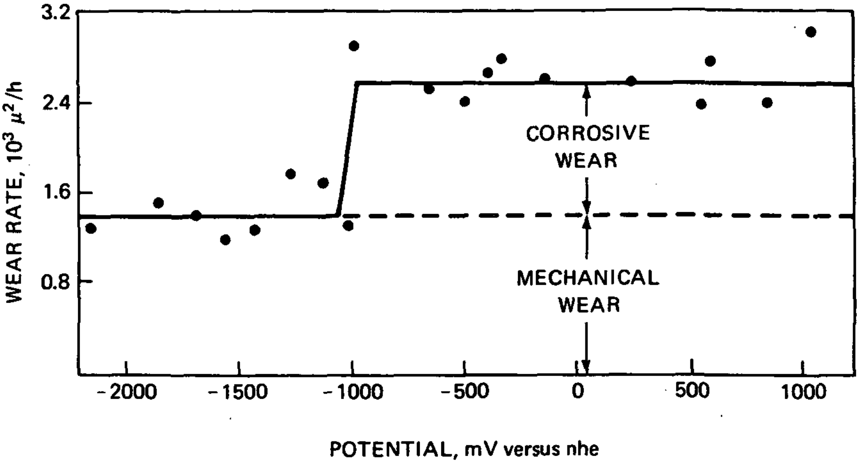

FIGURE 13.—Effect of potential on wear rate of a chromium-plated surface in a cationic emulsion (ref. 95).

pared to the hydrodynamic boundary layer and the conductivity of the fluid is relatively low compared to that of the metal. Low-conductivity fluids violate the first condition, while high-conductivity fluids fail the second. Evidently, a phosphate ester has been the only fluid found to meet these conditions and to cause this type of wear.

This concept of corrosive wear will undoubtedly stimulate others and further research to determine the validity and the generality of the concept. For example, are wall currents generated in sliding and sliding-rolling systems? If so, are they of sufficient magnitude to initiate and enhance the rate of corrosion at the various existing cells on the surface?

Miscellaneous

Waterhouse (ref. 94) has recently drawn attention to the possibilities of investigating friction and wear in water-based (emulsions) lubricants by electrochemical methods. As an example, figure 13 shows the wear rate of a chrome-plated yarn guide as a function of the potential in the presence of a cationic emulsion (ref. 95). It is concluded that the technique distinguishes between adhesive and corrosive wear. For some unexplained reason, anionic detergents did not show the same step function in the wear rate.

EROSION

Erosion may be defined as the deterioration or the loss of material from a solid surface due to abrasive action or impingement of fluids or solid particles suspended in the fluids. If the fluid is corrosive, then the phenomenon may be called erosion corrosion. The collapsing action of gas bubbles at a surface can lead to cavitation erosion. The intent of this section is to discuss each of these briefly and show how they can lead to wear and how they can set up electrochemical cells on surfaces.

Solid Particles

Erosion by solid particles can shorten the life of gas turbine blades and the regenerators and cyclones in catalytic cracking installations. On the credit side the impingement of particles in shot peening, sandblasting, and erosive drilling are useful applications.

Finnie (ref. 96) views the particle as a cutting tool that penetrates the surface, causing plastic deformation of the surface and wear. Experimental results are in agreement with the theory for low angle of attack and ductile surfaces. Bitter (ref. 97) considered the case of particle impingement at high-impact angles and developed a model that allows for deformation wear associated with repeated blows that cause cracking and spalling. This model when coupled with his intricate cutting model correlated results for hard and brittle, and soft and ductile materials. Neilson and Gilchrist (ref. 98) use a much simpler model to investigate the effect of particle shape, velocity, and angle of attack. In experiments assimilating nozzles of rocket motors, they found that the attacked surface heated up 300° F above ambient as detected by a thermocouple one sixty-fourth of an inch below the surface, and it was concluded that the actual surface temperature was much higher (ref. 99).

Under conditions where the solid attacked by particles is in a corrosive environment, the particles will disrupt the passive film or oxide film, thereby adding a corrosive wear component to the cutting and spalling wear described above.

High-Velocity Liquid Impingement

Erosion by liquids has been a concern with steam turbine blades and with rockets and high-velocity aircraft moving through rain (ref. 100). Bowden and Brunton (ref. 101) investigated the impact of liquid drops on solids at velocities up to 1200 m/sec (2700 mph). Figure 14 shows a photograph of the surface damage of aluminum and stainless steel at a 750-m/sec impact velocity. Part of the deformation is due to the compressive

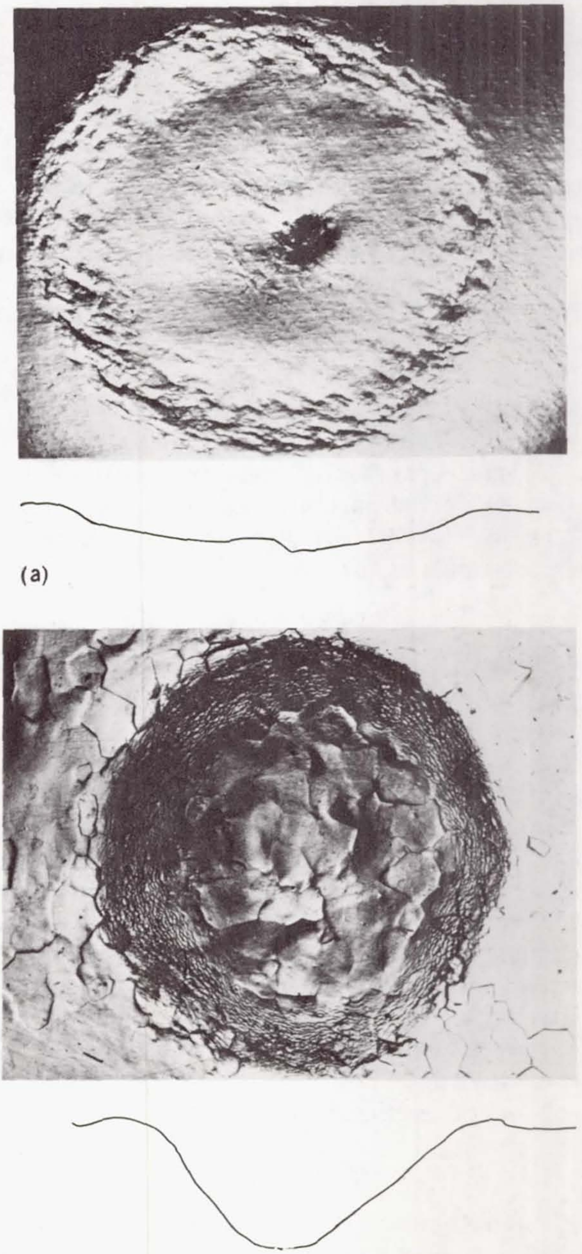

FIGURE 14.—(*a*) Deformation of stainless steel by a water jet at 750 m/sec (magnification × 17). (*b*) Deformation of aluminum at 750 m/sec (magnification × 12). Cross sections through the depressions are shown (ref. 101).

forces on impact, and part is due to the shearing action of the liquid as it flows across the surface. It is believed that the surface velocity may actually exceed the impact velocity. The pressure P developed can be expressed as

$$P=\rho CV$$

where ρ is the density of the fluid, C the compressional wave velocity for the liquid, and V the impact velocity. Because C is about 1500 m/sec for water, it is estimated that a 3-mm-diameter drop with an impact velocity of 1000 m/sec develops a peak pressure of 1.5×10^{10} dyne/cm^2 (220 000 psi) which lasts for 1 to 2 μsec. Experimental measurements are in fair agreement with theory (ref. 102).

Erosion corrosion occurs with nonresistant metals at water impingement velocities as low as 3 ft/sec. The impingement causes local disruption of the protective oxide film, rendering the region anodic, and thereby maintaining conditions for rapid electrochemical corrosion (ref. 103). The effect of tangential velocity of aqueous systems generally increases the corrosion rate due to increased availability of oxygen but can decrease at higher velocities due to turbulence (ref. 104).

Cavitation Erosion

Cavitation is a problem of major proportions confronting the designers of high-speed hydrodynamic systems (ref. 105). Cavitation is generated either hydrodynamically or acoustically, and the collapsing of the gas or vapor bubble at or near the surface causes erosion. The erosion of ship propellers constituted one of the first field problems (ref. 106). Plesset and Ellis (ref. 107) established that the surface damage was indeed mechanical and not corrosive.

The detailed mechanism of cavitation erosion is not known. Figure 15 shows the collapse of a bubble with the formation of a microjet in the center (ref. 108). Similarity of these jets to liquid impingement suggests that cavitation erosion and impact erosion phenomena are similar. All liquids do not form microjets (ref. 109). Surface tension increases the rate of collapse, while compressibility, viscosity, and noncondensable gas tend to decrease the rate (ref. 110).

The rate of depth of erosion dy/dt can be expressed as

$$\frac{dy}{dt}\sim\frac{\rho_i Rn}{S}$$

where ρ_i is the impact pressure, R the size of the bubble, n the number of impacts per unit time, and S the strength of the material (ref. 109). If the impact pressure is below a critical value, no erosion occurs (ref. 111). The fact that dents have been observed shows that the implosion pressure can exceed the yield strength of the solid. Cavitation erosion damage can be divided into three basic types. The most severe conditions lead to metal

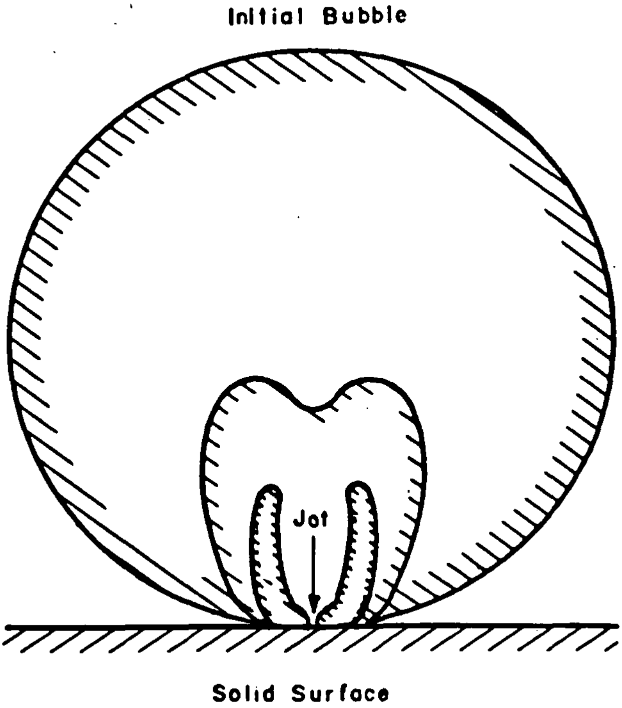

FIGURE 15.—Collapse of a bubble (ref. 108).

deformation and work hardening. Less severe conditions lead to fatigue cracking and loss of metal, while the least severe conditions lead to corrosion (ref. 9). Little is known about the inception of cavitation, the distribution of nuclei, growth to critical size, etc. An improved understanding at higher intensity ranges is motivated by recent attempts to utilize the destructive forces of cavitation erosion in the drilling of rocks and the cleaning of surfaces (ref. 112).

Surface damage due to cavitation erosion can be reduced by elastomer coatings (ref. 113) and cathodic protection (ref. 114). The latter protects because the liberated hydrogen acts as a cushion for the impact.

Whether cavitation corrosion is important in the wear of rolling-contact bearings is not clear. Tichler and Scott (ref. 115) recently observed that the resistance to fatigue in a four-ball rolling-contact fatigue test correlates with the resistance to pitting in a cavitation erosion test. This led them to pose the questions, "Is cavitation erosion a contributory factor in the initiation of surface fatigue?" and "Is there a fatigue process interpretation of cavitation erosion?"

AREAS OF NEEDED RESEARCH

The preceding sections summarize in broad terms the present state of the knowledge of the various corrosion and erosion processes. In general, the variously named corrosion types are manifestations of the appearance of the metal surface after being subjected to different environments. On a more fundamental level, however, the underlying basic mechanisms involve chemical oxidation and reduction reactions on a heterogeneous surface, and the initiation and the kinetics of these reactions are related in some manner to the properties of the physical and chemical environment.

Although the corrosion scientist has enjoyed a certain amount of success in understanding the basic chemical mechanisms for well-defined aqueous systems, the lubrication scientist has made very little progress in translating these concepts to nonaqueous systems. Thus, an urgent need exists for the identification of the oxidation-reduction reactions that occur on well-defined metal surfaces with known lubricant base stocks and lubricant additives over a wide temperature range. Since oxygen and water are of paramount importance in the lubricant-metal chemistry, these must be carefully controlled at various concentration levels to determine their precise role. It is possible that the ability of water to diffuse into and concentrate in surface microcracks will lead to conditions for conventional aqueous corrosion mechanisms to function locally, even though the water is only a contaminant in the oil. There is evidence that small concentrations of water in lubricants reduce the fatigue life of bearings. Thus, there is a need to employ known corrosion concepts to lubricant systems.

The shearing action between sliding, load-bearing surfaces leads to increased heterogeneity of the surface in terms of dislocations, slipbands, microcracks, and residual stresses. These surface characteristics can have a large influence on the kinetics of the chemical reactions and may lead to different reaction products. Although they severely increase the complexity of the system, research is needed to identify and quantify these catalytic factors in corrosion processes and lubricated systems. In so doing, clues should be obtained with regard to modifying the metallurgy or lubricant environment so that these catalytic factors can be altered in either direction as dictated by the severity of operating conditions.

For minimum wear and surface damage, the physical properties of the in situ surface reaction products are also of paramount importance. Such data are practically nonexistent because of the present inability to make measurements. Hence, research is needed to develop techniques for measuring the rheological (flow) properties of in situ formed surface films and their ability to adhere to the surface and resist removal. Because there will be some continual removal of the film due to the sliding action, information on the kinetics of removal as well as on the kinetics of formation and their dependence on operating variables is needed.

It is evident that many areas exist that require research using the latest sophisticated tools and techniques. The challenge to the researcher is to select a series of defined systems so that the results obtained will provide a broad, sound understanding of the basic critical metal surface-environment reactions as well as their dependence on a range of realistic, physically imposed set of conditions. Such information will be useful in understanding the various corrosion-erosion processes described, which now often appear to be unrelated, but which probably in fact have a broader common base than sometimes appreciated.

CONCLUSIONS

The surfaces of most metals contain surface defects, so in atmospheric and most other environments, electrochemical cells exist on the microscopic and submicroscopic scale. In nonrubbing systems the extent of the corrosion is governed by the porosity of the film and the nature of the environment.

In sliding systems the film is being continuously disrupted, and corrosion can proceed as long as corrosion products are mechanically removed. Furthermore, new surface created during a wear process is considerably more reactive than a normal surface, so unexpected electrochemical reactions can occur and the rates of corrosion are considerably greater. A wearing surface must be viewed metallurgically as having a high density of imperfections, thus the number and distribution of electrochemical cells will be considerably different from that of a nonrubbing surface.

Lubrication scientists, in general, have made little use of the concepts of corrosion in understanding wear phenomena, including fatigue. It appears that the basic principles of electrochemical corrosion could be a key to understanding such wear processes as fretting corrosion, electrochemical wear due to high shear rates at the wall, corrosion fatigue, erosive wear under low-velocity impact, and corrosive wear in general. Equally important, a better appreciation of the concepts could lead to a better understanding of how lubricants function in controlling adhesive and scuffing wear; that is, of how to attain the optimum balance between metallic and corrosive wear. Advances, however, will be slow because the rubbing action adds several dimensions of complexity to the conventional corrosion processes. Nevertheless, the lubrication scientist must accept the challenge if he is to improve his knowledge of the surface chemistry and the kinetics of chemical reactions, as well as their dependence on operating and metallurgical parameters, in lubricated systems.

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The author thanks Dr. C. J. Polk for his constructive criticisms during the writing of this paper.

DISCUSSIONS

F. F. Ling (Rensselaer Polytechnic Institute, Troy, N.Y.)

It was a pleasure to read the clear and detailed account by Dr. Rowe of the present status of corrosion and erosion. In addition to a splendid set of references, the paper is accompanied, in Dr. Rowe's view, by the areas of research that are needed in the future.

This paper stresses once again that lubrication, in the boundary and the mixed regimes, is a controlled corrosion process. Erosion is used to lump all the noncorrosive processes by which loss of material from a solid surface takes place.

As the control of wear is generally the ultimate goal in lubrication, it is good to read in this presentation the emphasis that the surface layer has distinct physical and mechanical properties that need to be better known. In this regard, this writer would heartily join in urging future work on the surface layer(s). It is known *that the* layer is *anisotropic.* Because anisotropic materials under pressure are piezoelectric, what effect do the phenomena have on wear? What effect does the plastification by adsorption (ref. 116) have on the wear process? What of the anisotropy of the thermal properties of the layer? What effect do the aforementioned phenomena have on the intermediate factor associated with wear: fracture and microcrack initiation?

E. Rabinowicz (Massachusetts Institute of Technology, Cambridge, Mass.)

In his interesting review, Dr. Rowe discusses the factors that cause the wear in a sliding system involving metals to be either adhesive or corrosive in nature. In the adhesive case, wear occurs by the formation of large metal particles, while in the corrosive case, wear is by means of much finer particles produced by corrosive interaction between the metal and the environment.

In a few systems the two processes can occur side by side, so for a while metal particles are formed, while at a later time corrosive-product wear debris is produced. But this seems to be an exceptional situation. More commonly, a sliding system operates in one regime to the exclusion of the other. Apparently, there must exist a criterion that determines whether a sliding system wears by adhesion or by corrosion, but this criterion has not yet been discovered. At any rate, Dr. Rowe does not mention it.

There is a rather analogous problem with regard to the process of polishing, in which the wear of a sliding system can take place either through the formation of large particles or through the removal of very small particles on a molecular scale. This polishing problem is simpler to analyze than the corrosive-wear problem because in this case no chemical reaction need be involved; however, for the polishing case also, no criterion has yet been discovered that allows us to determine whether or not polishing will occur.

That is to say, as far as I know, no successful attempt to compute the transition point between the large-scale wear regime and the polishing regime has yet been published.

Very recently, however, we have carried out an analysis that leads to a simple expression for the factors which govern the transition from adhesive wear to polishing wear. This analysis is presented here both for its intrinsic interest and for its possible application to the corrosive wear case.

Assume that a sliding system consists of a soft material I of hardness p, sliding on a harder material II, that the apparent area of contact is A_a, and that the wear consists of material removal in the form either of large wear particles or of molecular-sized wear particles.

At any instant, there will be a number of particles adhering to the harder surface that have been transferred from the softer surface. Each such particle is assumed to be a hemisphere of diameter d. With time, each particle tends to be worn away by polishing and to be augmented by the arrival of an additional particle deposited next to it. It is postulated that if the second particle arrives before the first one has been worn away, large-scale wear occurs. If the particle is worn away before a second one can arrive next to it, the condition for the occurrence of large-scale wear is not fulfilled (refs. 68 and 117), and polishing constitutes the only measurable weight loss (fig. 16).

The total load at the interface is L, and the Archard wear coefficient for the formation of adhesive wear particles derived from the softer material is k_a. Thus the volume of material V transferred in the form of large-scale adhesive wear particles in sliding a distance x is given by Archard's equation in the form

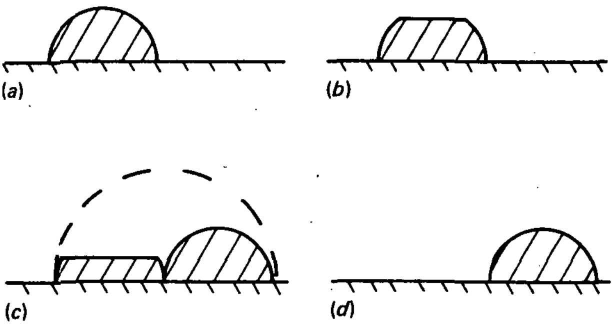

FIGURE 16.—Schematic illustration of possible wear processes. (*a*) Initially a hemispherical adhesive particle forms. (*b*) The particle starts to wear away by a polishing process. (c) If a new particle arrives next to the original particle before the latter is worn away, large-scale adhesive wear occurs. The final loose wear particle is shown by a dashed line. (*d*) If the original particle is worn away by polishing before the new particle arrives, then only polishing wear occurs.

$$V=\frac{k_aLx}{3p} \tag{2}$$

Because each wear particle is a hemisphere of volume $\pi d^3/12$, the number n formed is given by

$$n=\frac{4k_aLx}{\pi d^3p} \tag{3}$$

The number of possible sites n_s on the surface is given by

$$n_s=\frac{4A_a}{\pi d^2} \tag{4}$$

if it is assumed that each site is of area $\pi d^2/4$. Because there are about six sites next to the original wear particle, if deposition is at random after $n_s/6$ particles have been transferred, it is likely that the next particle will be one adjacent to one formed at the beginning of sliding, and we postulate that in that case adhesive wear on a large scale occurs.

The distance of sliding x_a required for depositing a new particle next to an original particle is obtained by equating n from equation (3) with $n_s/6$ as derived from equation (4) to give

$$x_a=\frac{p\,A_ad}{6k_aL}=\frac{pd}{6k_a\sigma} \tag{5}$$

where σ is the apparent pressure L/A_a.

Now while the adhesive wear particle is waiting for the arrival of an adjacent wear particle, it is being worn down by the removal of individual molecules by a polishing mechanism. For this we may write an expression using Archard's equation, but with a polishing wear constant k_p. We may assume that the normal load carried by each particle is determined by plastic flow and is thus $\pi d^2p/4$. This gives for the rate of removal of volume from each particle

$$V=\frac{k_p\,(\pi d^2p/4)x}{3p}=\frac{k_p\pi d^2x}{12} \tag{6}$$

The distance x_p required to remove the whole adhesive wear particle is given by equating V in equation (6) with $\pi d^3/12$ to give merely

$$x_p=\frac{d}{k_p} \tag{7}$$

It is postulated that adhesive wear is prevented if wear particles are polished down faster than they can build up by accretion. This occurs if

$$x_p<x_a$$

namely,

$$\frac{\sigma}{p}<\frac{k_p}{6k_a} \tag{8}$$

Thus polishing occurs if the ratio of the apparent pressure to the hardness pressure is less than the ratio of the polishing wear constant to six times the adhesive wear constant.

The relationship given by equation (8) certainly appears to agree reasonably well with practical experience. For example, it suggests that unlubricated metallic sliding surfaces, which typically have values of k_a and k_p of about 10^{-2} and 10^{-6}, respectively, will only operate in the polishing regime at very low apparent pressures, of the order of 10^{-5} of the hardness. Thus, a typical medium-strength metal like copper or nickel, with a hardness of the order of 150 000 psi, can only be operated in the polishing regime at applied stresses of below 2.5 psi, and even then special care must be taken that the contact points are well spread out over the apparent region of contact. Equation (8) suggests that it will be much easier to observe polishing with unlike metal combinations because these have much lower values of k_a. Possibly, applied stresses as high as 10 or even 100 psi might then be used.

The hexagonal metals cobalt and rhenium, which produce very low wear coefficients k_a of about 10^{-5} and 10^{-6}, are of special interest. It is found experimentally that in their case polishing can take place even under very high apparent stresses (ref. 118). This is in excellent agreement with equation (8), which suggests that this comes about because the k_a/k_p ratio is close to 1 in this case.

The case of lubricated sliding is of great practical interest. In the presence of lubricants, k_a drops by a factor of about 10 000 to about 10^{-6}, while k_p seems to drop only by a factor of 10 to about 10^{-7}. It will be seen by the use of equation (8) that because of this effect, lubricated surfaces of medium-strength metals can operate in the polishing region at apparent stresses as high as 2500 psi. Interestingly enough, there seem to be a number of experimental observations which suggest that with lubricated surfaces an apparent pressure level of this order of magnitude does represent the transition from a polishing to an adhesive wear regime.

Applying the concept underlying equation (8) quantitatively to the transition between adhesive wear and corrosive wear may be more difficult because of the more complex nature of corrosive wear. But the assumption underlying the model shown appears to be correct insofar as it suggests that a high rate of corrosion inhibits adhesive wear, while a high rate of adhesion inhibits corrosive wear. Furthermore, the form of equation (8), suggesting that a high σ/p ratio favors corrosive wear, is probably also correct.

R. W. Wilson (Shell Research Ltd., Thornton Research Centre, Chester, England)

The author is to be congratulated on presenting a mass of information in an easily digestible form. As a metallurgist I am gratified to see the way in which corrosion mechanisms are described and then applied to tribological situations. I do not question the author's hypothesis that corrosion reactions, or more specifically reactions between metals and their environment, play a major role in many wear processes. However, great caution is required when one attempts to apply corrosion concepts, developed specifically with regard to aqueous environments and conducting electrolytes, to nonaqueous systems such as lubricants. This vital distinction is not really brought out until the very end of this review. In fact, in the section on lubricant-metal chemical reactions, the example of the corrosion of lead in copper-lead bearings is unfortunate. This corrosion reaction occurs in completely dry oxidized oils, and the lead is dissolved by the weak organic acids present in degraded lubricants. The fact that the lead is embedded in copper is irrelevant; lead in aluminum-lead bearings is equally subject to corrosion by oxidized lubricants. This is not an electrochemical reaction, it is a chemical reaction taking place in a nonconducting liquid, and the lead is not attacked because it is anodic to copper. It is for the above reasons that the lead in most aluminum-lead bearings is alloyed with tin, the tin being necessary to render the lead phase resistant to corrosion by oxidized oils, and the resulting bearing alloy is generally known as an aluminum-babbitt.

The inclusion of cavitation erosion in this review is to be commended. One point that should be made clear is that two kinds of cavities occur in liquids: gas-filled cavities and vapor-filled cavities. Gas cavities can only form and collapse slowly, because it takes a finite time for gases to come out of solution and go back into solution in liquids. Therefore, the collapse of gas cavities can never cause direct mechanical damage of the type observed with vapor cavities. Indeed, air injection has been used as a means of combating vapor cavitation damage.

Another aspect of cavitation deserves mention. It has been shown experimentally that the final stage of cavity collapse gives rise to very high local temperatures and pressures. These extreme conditions may damage certain compounds present in lubricants and may induce reactions between lubricant components and metal surfaces that might not otherwise take place. This could be a rewarding area for research.

The author rightly says that oxygen and water are of paramount importance in lubricant-metal chemistry. Most test rigs investigating fundamental aspects for lubrication and wear operate at temperatures at which water can condense. Many practical situations exist in which the lubricant operates at temperatures in excess of 100° C, when water will not be present in the liquid phase, or in a sealed environment where any water or oxygen present will soon be used up. In these instances there is little or no possibility of any of the corrosion reactions listed under "forms of corrosion" being operative. While I agree that corrosion and wear are often inseparable, we must beware of transferring electrochemical concepts of corrosion, developed round aqueous electrolytes, to nonaqueous systems.

Finally, with regard to the low values for activation energy for the oxidation of iron reported by Quinn and other workers, has due consideration been given to the fact that the metal surface in these cases is in a very highly deformed state (as the Kramer effect shows) and that the energy associated with this disordered state facilitates the oxidation reaction?

LECTURER'S CLOSURE

The author expresses his thanks to the discussers for their appropriate comments and suggestions; they represent an effective contribution by clarifying certain aspects of the paper and through suggestions for future research.

Professor Ling's questions on the role played by the various anisotropic properties of the surface film in wear and fracture are most interesting and should stimulate future research efforts. I am not aware of any definitive data on the significance of anisotropy of surface films on their effectiveness to prevent wear. Considerable data do exist demonstrating that surface-active materials affect the deformation properties of solids. However, decoupling the influence of the film on the substrate deformation, and the resultant effect on wear of sliding surfaces, from the normal boundary lubrication concepts appears inherently difficult. It is very doubtful that definitive experimental results exist at this time. Nevertheless, Professor Ling's questions should stimulate interdisciplinary thinking on these phenomena.

Professor Rabinowicz comments that a criterion must exist that determines whether a sliding system wears by corrosion or by adhesion and, then by analogy to polishing concepts, suggests a similar relation for the transition between adhesive and corrosive wear. The ability to predict whether the wear for a given sliding metal couple will be predominantly corrosive or adhesive would be most welcome. However, unlike the polishing system he describes, the mechanical properties of the chemical reaction products and the kinetics of formation must have a large influence on the k-parameter for corrosive wear and the position of the adhesive-corrosive wear balance. Furthermore, these factors, in particular the kinetics, must depend on operating conditions, so it is not likely that a simple criterion exists predicting the controlling wear process. I cannot agree with Professor Rabinowicz that a high σ/p ratio favors corrosive wear; in fact, it should favor adhesive wear.

Dr. Wilson is correct in stating that the surface damage caused by cavitation of gas-filled cavities is less than that caused by vapor-filled cavities. Lubricant-metal reactions caused by cavitation phenomena may be attributed to both the enhanced reactivity of the deformed surface and the local high pressure and temperature. I have no knowledge of investigations where these factors have been decoupled. In addition to these factors, which can induce chemical reactions between lubricant components and between lubricants and gases, is the compressional heating of gas bubbles before their collapse.

As stated in the paper, many chemical reactions occurring on freshly formed surfaces have been attributed to the Kramer exoelectron effect, and certainly the enhanced oxidation of iron at sliding surfaces falls in this category. I am not aware, however, that definitive experiments have been made on the oxidation kinetics of highly stressed and nascent iron surfaces to evaluate their effect on the activation energy for oxidation. Without a doubt, the exoelectron phenomenon is a contributing factor in lubrication phenomena. For this reason many researchers are inclined to attribute disagreement of experimental results with a model to the Kramer effect. What is urgently needed is good quantitative data to judge the true significance of the phenomenon in sliding systems. This necessitates the decoupling of the catalytic activity of clean surfaces and the influence of high local temperatures and pressures from the effect of exoelectron emission, a difficult task experimentally.

I agree in principle with Dr. Wilson that caution must be exercised in the transfer of corrosion concepts in aqueous media to nonaqueous systems; namely, lubricants. However, in keeping with the theme of the symposium of fostering interdisciplinary thinking and dialog, I intentionally exercised some liberty in an attempt to fuse the concepts of the two fields since I believe the basic underlying phenomena are frequently similar. For example, a dry system to one researcher may be wet to another; the question of when a system is dry is analogous to the question of when a surface is clean. It is reasonable to expect that in most dry systems, even at temperatures above 210° F, there exists at least a partial monolayer of tightly bound water on the surface. In all probability, the adsorbed material on a heterogeneous bearing metal surface in an oxidized oil is polar in nature, will contain trace amounts of water, and will have sufficient conductivity that highly localized electrochemical cells can occur.

Dennison (ref. 119) has shown that peroxides formed from hydrocarbon oxidation react with lead to form lead oxide and that the lead oxide then reacts with organic acids to form lead soap and water. This represents a situation where water is being produced at the bearing surface, and thus it may not be at all unreasonable to apply the conventional corrosion mechanisms for aqueous media to the corrosion of copper-lead bearings in oxidized oils. Furthermore, little is known about the relative oxidation potentials of metals in oxidized hydrocarbons and their comparison to the values in aqueous systems. Although the potentials probably differ in magnitude and may even show some reversals, is it still not possible that the underlying basic oxidation-reduction concepts of corrosion still apply? Hopefully, future research will answer some of these questions.

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