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LITERATURE REVIEW OF SOLID LUBRICATION MECHANISMS

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By

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) For this report, five phenomenological models are proposed for solid lubrication. These models are: 1) Viscous flow of the solid lubricant due to strong attachment to both surfaces and with uniform shear across the gap; 2) Plastic flow of solid lubricant; 3) Substrate/film slip model in which the sliding takes place between one substrate and the surface of the film; 4) Interfilm slip model when lubricant film is strongly attached to the two substrate surfaces. The sliding takes place at the interface. 5) Intercrystalline slip model which is basically a modification of the plastic flow process. The lubricant film is composed of small crystalline blocks of lubricants which slip past each other. (Cont'd)			
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The expected tribological behavior is suggested for each model. A review of the literature was conducted to determine which model could be supported by the evidence available. The report includes a discussion of the following topics:

- Observation of Film Behavior
- Substrate Adhesion
- Film Formation, Wear, and Failure
- Crystal Structure Effects
- Surface Chemical Effects
- Frictional Behavior.

It is concluded that the primary factors in determining the appropriate shear models would be the adhesion of the film to itself and to its substrate, the effect of vapors on friction and wear, the effect of velocity on friction, and the effect of pressure on friction.

Based on existing evidence extracted from the literature review, it is proposed that a dual model exists for each lubricant. At low pressures, either interfilm (Model 4) slip or substrate/film (Model 3) slip occurs, depending on the type of solid lubricant. At high pressure, the shear (Model 2) or viscous flow (Model 1) occurs, again depending on the material. At low pressure, frictional behavior is essentially the same as the bulk solid lubricant sliding against itself.

The dual model suggests that a low-energy interface exists and slip will occur at that interface until the imposed shear stress reaches the shear strength of the film; film flow then occurs. An interesting aspect of the model is that it suggests that film hardness may be as important as interfacial bonding energies in determining low friction. This, in turn, suggests a new approach to improved solid lubricant development.

Equations have been developed which predict friction as a function of pressure and a criteria suggested for the transition from slip to shear. This criteria is that shear (or viscous flow) will take place when $f \cdot p > \tau_0$; where f is the friction coefficient, p is pressure, and τ_0 is the shear strength of the lubricant. The limited data which are available support both of the hypotheses and the criteria; however, considerably more data are needed for confirmation.

FOREWORD

This work was conducted at the Belvoir Fuels and Lubricants Research Facility (SwRI) located at Southwest Research Institute (SwRI), San Antonio, TX under Contract No. DAAK70-85-C-0007 during the period July 1985 through November 1986. The work was funded by the U.S. Army Belvoir Research, Development and Engineering Center, Ft. Belvoir, VA, with Mr. F.W. Schaekel (STRBE-VF), as the Contracting Officer's Representative and Mr. M.E. LePera, Chief of Fuels and Lubricants Division (STRBE-VF), as the project technical monitor.



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I. INTRODUCTION

A. Objective

During the past few years, the U.S. Army has been engaged in the development of an advanced propulsion system for use in future combat vehicles. A low heat-rejection, high-power density diesel engine is one option considered for the development. Such engine design minimizes or eliminates the conventional structural cooling system, and the combustion chamber is insulated so that the predominant heat flow is via the exhaust gas to drive a turbo-compound. This configuration results in the engine components reaching an operating temperature that exceed the useful operating range of currently available liquid lubricants. As a result, it is generally recognized that another approach to friction and wear control will be required at least during the peak operating periods.

The long-range purpose of the overall project was to define and model critical parameters in a high-temperature lubrication system for low heat-rejection adiabatic-type engines with peak ring/liner temperatures above 400°C. The limited effort of this report involved an investigation of the physical/chemical mechanisms occurring in solid-film lubrication and to attempt to mathematically describe those mechanisms for predictive modeling and research on improved solid-lubricant selection.

B. Background

In conventional engines, the rings and liner are lubricated by a film of oil that provides physical separation and carries a series of chemicals designed to provide boundary (surface film) lubrication. In the adiabatic engine, it appears that liquid lubricants will be unusable during some parts of the engine's duty cycle. The peak temperatures will, of course, be design dependent; but, as indicated in Reference 1, studies for future engines have predicted temperatures in excess of 500°C at the upper piston ring reversal point.

The 500°C temperature is a 250°C increase over current designs, and is above the thermal decomposition temperatures of hydrocarbon-type and other liquid organic

lubricants. As a result of the temperature increase, it is generally recognized that some other approach to friction and wear control will be required to supplement liquid lubricants. This need is particularly evident during the peak temperature operating periods in some zones of the engine. Solid lubricants have been widely used at temperatures above 400°C and are a logical choice for advanced engine systems. Unfortunately, several problems exist that must be resolved before they can be applied to the engine environment. The performance requirements for lubricants in the high-temperature engine applications are much more severe than normally encountered. For example (1)* in ring-liner applications, it was found that solid lubricants with friction coefficients less than 0.05 and dimensionless wear rates $K < 10^{-8}$ would be needed for the temperature range 25° to 600°C. Currently available solid lubricants have been determined to be inadequate in several areas.

- (1) Friction coefficients are usually higher than 0.05.
- (2) Even the best materials rarely achieve dimensionless film wear rates of $K = 10^{-8}$ at room temperature. Thus, effective resupply techniques must be developed.
- (3) The current lubricants are not effective over broad temperature ranges.

If solid lubricants are to be used, improved material and adequate resupply techniques must be found.

Solid lubricant work to date has been mostly empirical. Initially, a large variety of inorganic compounds were selected and evaluated under a variety of conditions as solid lubricants. A large number of materials have been isolated and used including organics (soaps, fats, and waxes); polymers (polytetrafluoroethylene (PTFE), polyethylene, methacrylates); metals (indium, tin, lead, silver, gold); inorganic compounds (sulfides, chlorides, iodides, oxides, hydroxides) and glasses (boric oxide, silicates, phosphates). By comparing properties of the most effective lubricants, a qualitative knowledge of solid lubricant behavior has been assembled. Important properties include:

- (1) Lubricant substrate adhesion
- (2) Film cohesion

* Underscored number in parentheses refer to the list of references at the end of this report.

- (3) Crystal structure
- (4) Shear strength
- (5) The presence or absence of adsorbed species
- (6) The presence of film impurities
- (7) The composition and finish of the substrate material

More recent studies have attempted to create materials that have these desired properties. Consideration has been given to double oxides (2), dichalcogenides (3), intercalated layer lattice compounds (4), and mixed fluorides (5). This approach has more or less run its course, and it is now clear that the development of improved solid lubricants requires a more detailed understanding of their rheological processes. More specifically, a working model of solid lubricant behavior is needed which relates material properties with tribological performance.

In order to identify models, a review of the literature was conducted. Data were also selected that which tended to support one model or the other. A working hypothesis was formulated, and experiments defined to evaluate it.

II. MODELS

Several review articles that discussed mechanisms of solid lubrication have been published. A recent workshop sponsored by the Army Research Office entitled "Fundamentals of High-Temperature Friction and Wear With Emphasis on Solid Lubrication for Heat Engines" contained numerous references to rheological behavior.(6) In a 1967 study, Winer reviewed the fundamental knowledge of MoS₂ lubrication.(7) He concluded that three mechanisms could be used to explain the frictional behavior of MoS₂: (a) easy cleavage or shear of the MoS₂ structure, (b) vapor lubrication by absorbed molecules between crystallites, and (c) cleavage along grain boundaries as opposed to cleavage between layers in an individual crystal. Based on his review, Winer favored the first mechanism. This mechanism is also favored by Johnson and Sliney.(8,9) These workers identified other properties important to the performance of solid lubricants including shear characteristics, coherence between particles, resistance to cold flow, adherence to the substrate, and favorable environmental behavior. Ives and Peterson (10) proposed three rheological models: (a) interfilm flow, (b) interface slip, and (c)

interfilm slip. In model (a), the solid lubricant adheres to the two sliding surfaces and allows their relative displacement by flowing like a viscous fluid. In model (b), one body slides over the film without carrying it along since the film is sufficiently plastic or elastic to allow the asperities to move through it. For model (c), the lubricant adheres to both surfaces and slip occurs at some interface established by sliding. It is suggested that different solid lubricants conform to each of these models. Wildorf reviewed slip mechanisms in solids and concluded that they deform through either plastic slip for crystalline materials or through viscous flow for noncrystalline materials. These are the primary mechanisms through which large shears can be tolerated.⁽¹¹⁾ Temperatures must be above the recrystallization temperature to avoid defect accumulation that would ultimately cause cracking of the film. Both viscous flow and plastic flow have strain rate effects of different magnitudes, depending upon the resulting heat dissipation. However, the velocity effect would be much smaller with plastic flow. Fleischauer distinguishes two slip modes; intracrystalline slip of the planes and intercrystallite slip across the crystal surfaces.⁽¹²⁾ He suggests, however, that the actual situation is probably a combination of the two. It is pointed out that intercrystallite slip is controlled by surface properties while intracrystalline slip is controlled by bulk properties. Thus a means to distinguish between the two is available. Holinski, through microscopic observation of MoS₂ film formation, wear, and failure, concluded that intercrystalline slip took place during film formation but that no displacement occurred after run-in.⁽¹³⁾ Sliney made the same observations and concluded that solid lubrication is basically a plastic flow process.⁽¹⁴⁾ Thus, there are a number of proposed rheological models for solid lubrication. These models are listed in TABLE I. Also, TABLE I describes the behavior which might be expected from each model. Although these behavior predictions are speculations at present, they provide a working hypothesis by which the existing literature can be reviewed.

Several interesting points emerge from TABLE I. First, there appear to be two basic models--flow (1, 2, and 5) and slip (3 and 4). It is interesting to note that the same two models can be applied to bulk friction effects. Certain materials (e.g., Fe/Ag) slide with low friction, low wear, and little surface damage while others (Fe/Fe, Ag/Ag) slide with high friction, high wear, and considerable damage. In the former case, interface slip has been proposed. In the latter, high adhesion, junction growth, and surface shear have been proposed. The main differences between the

TABLE 1. Rheological Models for Solid Film Lubrication

<u>Rheological Model</u>	<u>Behavior</u>
1. Viscous Flow	Strong attachment to both surfaces with uniform shear across gap. On separation, both surfaces would be coated and strong adhesion observed with destruction of the film. Strong temperature and velocity effects on friction; friction independent of substrate material and roughness, directly proportional to area and inversely proportional to load.
2. Plastic Flow	Behavior would be similar to flow. Friction proportional to strength properties of lubricant film. Film orientation on surface with the possibility of adiabatic shear.
3. Substrate/Film Slip	Sliding takes place between one substrate and the surface of the film. There would be strong material and roughness effects. Friction would be similar to bulk effects. Very low adhesion or film damage on separation. Friction independent of contact area and viscosity. Strong surface effects.
4. Interfilm Slip	Lubricant film is strongly attached to both surfaces. Sliding takes place at the interface with little or no film movement after run in. Strong vapor and surface adsorption effects. Material and roughness effect would be small. Friction would be similar to bulk film material sliding on itself. Friction independent of area and roughness. Low adhesion and film damage on separation.
5. Intercrystalline Slip	Lubricant film is composed of small crystalline blocks of lubricant which slip past each other. This is basically a modification of the plastic flow process.

two models are in the coefficient of adhesion and the mechanism of deformation in the vicinity of the contacting asperities. One might propose that solid-film lubrication is basically the same as bulk frictional behavior.

Second, slip and flow effects can be distinguished by different behavioral effects. The most pronounced would be the normal adhesion on separating the sliding

surfaces, the effect of velocity, and the effect of atmosphere. Based upon these differences, the literature was reviewed to determine which model applied to each material.

III. OBSERVATIONS OF FILM BEHAVIOR

Very few direct observations have been made of the sliding behavior of solid-lubricant films. The most notable are those reported by the National Aeronautics and Space Administration (NASA). Sliney observed the process using a steel ball and a glass disk.⁽¹⁵⁾ MoS₂ was sprinkled in front of the slider. In operation, the solid-lubricant particles collect in the converging entrance zone, are compressed, and sheared into thin films (streaks) across the face of the slider. Adjacent lubricant particles coalesce and flow together. The flow is described as paste-like, with the contact region continuously being fed by the excess material in the entrance zone. At separation, a complete film was seen on the ball with a patchy film remaining on the glass. Fusaro studied the process with both graphite fluoride and MoS₂, using two steel surfaces.⁽¹⁶⁾ The test was stopped, and the film was examined at regular intervals. With both lubricants, the process was basically the same as that described by Sliney whether the test was conducted in moist air, dry air, or dry argon. A thick film initially was built up on both the wear scar on the rider and on the flat (Fig. 1). This film then gradually wore away more rapidly on the rider than on the flat. The mechanism of film wear differed with different material and atmospheres. Furthermore, this mechanism was found to apply to either the rider or asperity.⁽¹⁷⁾ This same behavior was reported by Lancaster for MoS₂ films and by Fusaro for a polyimide-bonded graphite fluoride film and for graphite films on surfaces with different pretreatments.⁽¹⁸⁻²⁰⁾ Some of the pretreatments appeared to aid in this plastic flow process. In detailed studies of MoS₂ lubrication, Fusaro concludes "that the lubrication process was found to be very dynamic and appears to be due to the plastic flow of individual MoS₂ particles which coalesce together to form continuous films.⁽²¹⁾ When observing the same spot on the substrate or on the rider, the appearance was constantly changing." He concludes that "the propensity of individual particles to coalesce together into a plastically flowing film is a prime prerequisite for a good solid lubricant material."

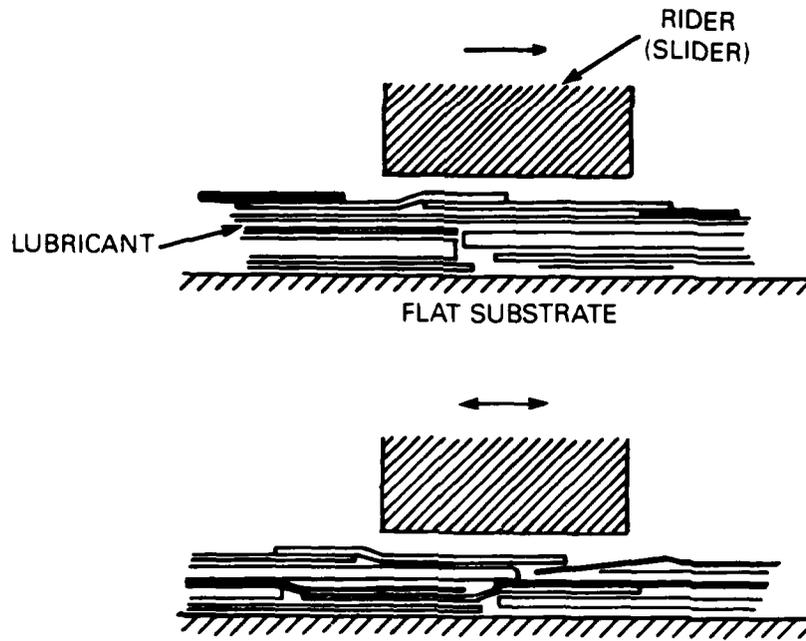


Figure 1. MoS₂ film formation

Holinski and Gansheimer also observed the behavior of MoS₂ films but came to different conclusions.(22,23) Initially, during "run-in", small crystallites of MoS₂ (150 Å = 24 atomic layers) moved about on the surface until a complete film was formed on both surfaces; thereafter, the sulfur layers of the mating surfaces glide over each other without displacement of MoS₂ layers. The nature of the "run-in" film under the two sliding conditions is illustrated in Fig. 1. This is clearly intercrystalline slip (model 5, TABLE 1) followed by interfilm slip (model 4) and is directly opposed to that suggested by the NASA observations (plastic flow-model 2). There is no obvious reason for the difference in behavior except that the NASA work may have been carried out at higher pressure since the ball in flat geometry was used. However, the NASA studies were much more detailed and used a variety of lubricants and surface conditions. Other work also suggests limited movement. Connelly and Rabinowicz used exoelectrons to study migration of MoS₂, graphite, and PTFE on partially coated aluminum disks. They saw little or no migration.(24)

Although these results appear to be contradictory, they may not be. Even with surface slip, there could be appreciable subsurface deformation. For example, lubricated metal surfaces form oriented subsurface structures. Thus, frictional behavior of bulk material is a combination of interface slip and deformation. A means to tag the solid lubricant surface would be required and motions observed

under a variety of conditions for demarcation of the regimes of the predominant mechanisms.

Very little of this type of work has been carried out with other solid lubricants. An early study of high-temperature solid lubricants reported on the sliding behavior of silver.⁽²⁵⁾ When silver was used as a solid lubricant for nickel alloy surfaces, a coefficient of friction of 0.42 was found. When an aluminum slider was substituted, the friction coefficient rose to approximately 1.0. It was found that when an aluminum slider was used, the silver welded to the slider, and the deformation process stripped the film from the surface. In other experiments, attempts were made to use soft aluminum films as lubricants. In all cases, the aluminum bonded firmly to both surfaces. Shearing destroyed the film by what appeared to be a rolling of the material between the surfaces very similar to that which occurs in the galling process. A similar behavior was reported with lead films. (26) In air, the lead films were stripped from the surface, and a large amount of transfer to the slider was observed. In a vacuum, the films gave long life and no transfer. The lead oxide film formed during experiments in air facilitated the transfer.

These results with metals indicate that interface slip (model 3) is the correct model. Poor results and high friction were obtained when conditions (strong adhesion) favored plastic flow (model 2). Under these conditions, the whole film deformed rather than confining slip to the surface layers. For other materials, the mechanism is unclear from direct observations.

IV. SUBSTRATE ADHESION

Although low adhesion between the slider and a metal film is seen to be desirable, the evidence indicates that the film itself should be strongly bonded to its substrate.

In 1954, Peterson investigated the tribological performance of a variety of organic and inorganic compounds and concluded that those which were effective had the best film-forming tendencies.⁽²⁷⁾ Low shear strength compounds such as silver cyanide that did not form films were ineffective, as were layered compounds such as boron nitride, mica, and talc. In later work, it was shown that MoS_2 did not

lubricate titanium, while the more reactive iodides would.(28) Devine showed longer life for MoS₂ films on molybdenum than on titanium, nickel alloys, and steel and attributed this longer life to reactivity.(29) Tsuya also investigated the life of MoS₂ film (unbonded) and concluded that the substrate has a marked influence on life.(30) The longest life was found with "fcc specimens of noble metal" (gold and silver); while the shortest lives were observed with titanium, glass, and iron. Reid and Schey studied the role of the substrate in lubrication with MoS₂.(31) Using materials with different reactivities and hardness, they found that initial film formation was due to mechanical entrapment of lubricant particles; however, "if the substrate material has a high tendency to react and form a sulfide (e.g., Cu, Fe) and the kinetics for such a reaction are favorable, then the film and in particular, its durability are favorably affected by the chemical reaction." They also concluded that shearing takes place between two continuous MoS₂ films that form on both surfaces.

As additional evidence, Holinski demonstrated that chemical effects are important even when solid lubricants are used in oils.(32) Spalvins attributes the long-endurance life of sputtered MoS₂ films to their strong bonding.(33) Wear life tests with bonded films showed superior endurance where binder to substrate wetting was good.(34)

Reactions between MoS₂ and substrate metals have been confirmed.(35-37) A review by Gansheimer concludes that such reactions occur and these reactions are beneficial to the endurance of films.(37) The reactions between MoS₂ and Fe form ferrous sulfide at 700°C and MoFeS₃ at higher temperature.(38) The precise role of the reaction was considered by Stupian and co-workers.(39,40) The adhesion of MoS₂ powder burnished onto titanium, copper, chromium, aluminum, stainless steel, and gold were studied. The degree of coverage correlated well with the relative strengths of the substrate metal sulfur bonds. The bond strengths were estimated from the atomization energies of the relevant bulk compounds, and the atomization energies were calculated from thermodynamic data.

Although improved films are formed on the sulfide surface, reactions can also promote an extreme pressure effect that would extend the life of films. The

extended life is due to the prevention of metallic contact during film formation and when the film becomes very thin on a sulfide surface.

Perhaps the best evidence to support the importance of adhesion in solid lubrication is that provided by SbSbS_4 .⁽⁴¹⁾ When applied as a powder between metal surfaces, the compound formed a thick and extremely tenacious film (even in the presence of a lubricant) which protected the surface. This benefit was achieved despite the compound's high friction coefficient (0.65) and its lack of crystal structure (it is amorphous).

Factors other than chemical reactions are involved. Spengler and Peltzer developed an adhesion theory based on the interaction of polarization forces.⁽⁴²⁾ Lancaster showed that mechanical factors, i.e., physical entrapment in surface depressions and embedding of crystallites in the substrate, were of equal importance.⁽⁴³⁾ With soft surfaces, the solid lubricant becomes embedded in the surface and extends the wear life in much the same way that increased surface roughness does.⁽⁴⁴⁾ Soft metal coatings are proposed to enhance adhesion ⁽⁴⁵⁾, and soft metal oxides and additives to graphite have much the same effect.⁽⁴⁶⁾

Very few investigations have been conducted with metal or other solid-lubricant films. Gerkima attempted to extend the life of lead films with additives that would improve alloying at the lead/steel interface and by imposing interlayers of the same material (Ag, Cu, Mo, Ta, W).⁽⁴⁷⁾ Of these, only copper extended the life by a factor of four and variables other than the adhesion may be involved.

From these results, it is obvious that adhesion in one form or another plays an important role in solid lubrication. To have effective lubrication, a film must first be formed. Lancaster, however, points out that good adhesion will not ensure that a film will form on the surface. Instead, he emphasizes the role of cohesion.⁽⁴⁸⁾ In other words, the solid must bond to itself or sinter to build up the necessary thickness. A number of examples are cited to support this role, e.g., moisture effects in MoS_2 and graphite that aid in film formation; additives that act as binding agents and the role of fluids in destroying already formed films. Other examples could also be cited. Powders like mica that do not sinter are poor lubricants. However, nonbonding organic waxes provide protection. Silver does not

bond strongly to steel, yet it is an effective lubricant, since it sinters rather readily. The separate effects of cohesion and adhesion have not been isolated and should be the subject of further investigations.

The results of these studies do not contribute additional understanding to rheological models. The models presume well bonded films which then behave in some prescribed manner. The studies do indicate that good adhesion and film cohesion allow better films to be formed and extend the life of a performed film.

V. FILM FORMATION, WEAR, AND FAILURE

Films can be formed by supplying powder to loaded contacts or by burnishing a surface with the powder or with a compress of the solid lubricant. Bonded films are prepared by spraying a surface with the solid lubricant contained in an organic or metallic binder. The nature of these films and their behavior under sliding conditions have been studied.

Savage found that a graphite film rubbed on copper with a graphite brush had the basal planes oriented almost parallel to the surface.⁽⁴⁹⁾ That orientation was found to be 5 to 10 degrees to the substrate surface in the direction of sliding.⁽⁵⁰⁾ Basically, the same results have been reported for MoS_2 .^(51,52) More detailed X-ray diffraction studies of MoS_2 lubricant films formed on copper showed the film consisted of a single-crystal layer 2 to 5 micrometers thick with all basal planes oriented parallel to the sliding surface.⁽⁵³⁾ The interesting fact was that this oriented layer was superimposed on a nonoriented layer (Fig. 2). The authors

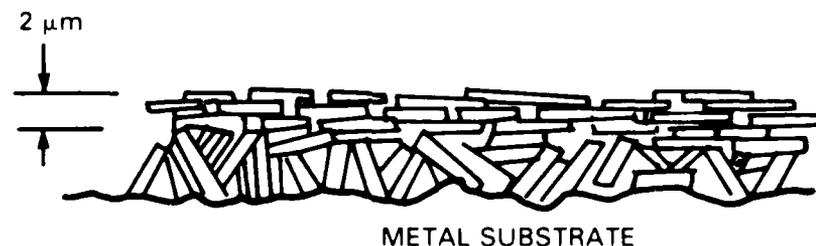


Figure 2. Structure of a surface MoS_2 film

suggest that the strong energy of the crystal edges bonds the oriented layer to the surface and also improves the cohesion of the oriented film. The 2.4-micrometer lubricating film represents about 300 individual S-Mo-S layers. As the film wears, the oriented layer approaches the metal substrate. This relatively thick (2-micrometer) layer indicates that extensive plastic deformation accompanies the sliding process.

Burnished films were first studied by Johnston and Moore.⁽⁵⁴⁾ A cloth-covered cylinder, loaded with MoS₂, was rubbed against copper surfaces of different roughness in different atmosphere. It was found that the first 100 traverses filled the spaces around the asperities to produce a smooth surface. Additional traverses built up the MoS₂ film on itself, and the thickness continued to increase even after 7000 traverses. Others, however, have shown that there is a limiting film thickness that depends upon the load. Rougher surfaces, of course, required more material to fill the asperities. Quite different films were formed in moist and dry air. In humid air, there is a much denser packing of the particles. This packing is attributed to the adsorbed moisture allowing better MoS₂/MoS₂ basal plane bonding. Lancaster showed that on smooth surfaces, 10-micrometer lumps are superimposed on a .05-micrometer thick film.⁽⁵⁵⁾ When a burnished film was simultaneously subjected to sliding conditions, failure eventually occurred due to film wear. Although the lubricant stick wore at a sufficient rate, very little of the worn amount transferred to the existing film. Difficulties in resupplying a film with loose powder have been encountered; the degree of resupplying apparently is dependent upon the shape of the sliding pressure.⁽⁵⁶⁾ This inability to maintain a film would indicate that surface slip is occurring, since shear would require strong adhesion at the MoS₂/MoS₂ interface.

Thus, the first step in the solid lubricant process is the formation of a thin oriented film on both surfaces. Sliding then takes place either between the films or between the substrate and the film. Subsequent sliding produces gradual film wear until the lubricant film is depleted, or else film failure, which is a function of the atmosphere and the sliding condition. Fusaro has studied in detail the wear and failure process of MoS₂ and graphite fluoride films.^(16,21) Wear occurred by the gradual depletion of the thickness by radial or transverse flow of the film out of the contact area. This results from the normal and frictional stresses on the film.

A second wear mode was cracking and spalling of the film (like a fatigue action). It is interesting to note that these are the same modes that are found for soft materials under mild wear condition (e.g., Ag/Fe). In other words, the wear of the film is essentially the same as that for the bulk material and in fact the wear rates have been shown to be similar.⁽⁵⁶⁾ Under these conditions, the more isotropic materials (metals, organics, glasses) fail by flow while MoS₂ or layer-type materials would tend to fail by fatigue of the oriented overlayer.⁽⁵⁷⁾

With both bonded and unbonded films, the wear process has two stages.⁽¹⁸⁾ The process described above applies until the substrate asperities are exposed. The film life then depends upon the ability of the lubricant film around the asperities to cover the exposed tips.

With a complete film, failure can occur for a variety of reasons. Two primary processes account for most failures. The heat generated by the sliding process softens the film or promotes oxidation, both of which can lead to failure. Secondly reactions with the environment can change the film composition. This is particularly true with MoS₂ where it has been shown that oxidation in either H₂O vapor, air, or oxygen causes the films to blister.^(58,59)

VI. CRYSTAL STRUCTURE

Layer lattice structures were cited in the earliest references to lubrication with inorganic solids, and this concept was used as an approach to the earliest selection of compounds for evaluation.⁽²⁷⁾ It was soon recognized, however, that it was not the structure "per se" but the nature of the bonding that was important. Materials with a hexagonal "layered" structure were effective lubricants if the bonding between the sheet-like layers was weak, while strong bonding existed within the layers and perpendicular to the two-dimensional, sheet-like planes. Materials like boron nitride that had strong interlayer bonding were not effective as solid lubricants. Thus, Holinski and Gansheimer and others attributed the effective lubrication of MoS₂ to the strong polarization of the sulfur atom, which allowed the layered structure to form.⁽⁶⁰⁾ Graphite did not have the weak boundary unless the layers were covered with lubricating vapors.⁽⁴⁹⁾ Early investigations of PTFE lubrication attributed its low friction to minimum interchain bonding forces

between large fluorine ions that shield the charge on the carbon atoms.(61) Thus, PTFE lubrication is essentially the same as MoS_2 except that the PTFE molecules consisted of chains instead of layers, with very weak bonding between chains. The initial formation of a transferred layer of PTFE on the opposing surface was seen to be essential for effective lubrication.(62) Sliding then becomes essentially PTFE on PTFE. When PTFE (bulk) slides against itself, two friction regimes exist--a high friction regime characterized by lump transfer and a low friction regime characterized by oriented sheared films at the interface. As discussed later, MoS_2 and other solid materials (e.g., silver/iron) have the same characteristics.

This weak interlayer approach has been thoroughly investigated by Jamison.(63-65) He concludes that the weak interlayer bonding is responsible for effective solid lubrication. However, MoS_2 has a unique structure among the layer lattice compounds that makes it particularly effective. Basically, lubrication performance is controlled by the distance between the basal planes. This distance is a function of the electronic structure of the metal atoms. In the MoS_2 structure, the molybdenum atoms are situated above and below holes in the adjacent layer rather than above or below other molybdenum atoms. This unique structure is attributed to the spin pairing of the electrons so there is no residual interlayer bonding. It was further shown that this type of arrangement could be promoted by intercalation of copper and silver atoms into layer structures with stronger interlayer bonding such as NbS_2 or NbSe_2 . Friction coefficients in such instances were reduced from 0.30 to 0.10. Intercalation of graphite with chlorides and metals also improved wear life and load capacity.(66)

Along somewhat different lines, it has been found that sputtered MoS_2 films would not lubricate if they were applied under conditions that made them amorphous (145°C). (67-69) In addition, an effective lubricating film was found at a thickness of 2000 \AA , which is only 300 MoS_2 layers. However, when sputtering was done at higher temperatures (150°C), the wear life was shortened even though friction remained constant. This result was attributed to a more porous irregular film with lower sulfur content.(70)

Fleischauer has carried out detailed studies of sputtered films.(12,71,72) He finds that the films can be deposited in two ways: crystallites with basal planes parallel

to the surface and crystallites with basal planes perpendicular to the surface. Lubrication performance is different, and this difference is attributed to the different chemical effects of the crystal planes and edges. The basal planes have weak bonding and poor reactivity, while the edges have strong bonding and rapid oxidation. Thus, lubrication performance is strongly related to crystal orientation.

VII. EFFECT OF ATMOSPHERE

The work of Savage showed that water vapor was required for the effective lubrication of graphite.⁽⁴⁹⁾ Water and other vapors adsorbed on the basal planes of graphite reduced friction coefficient from 0.80 to 0.18. High wear, called dusting, occurred in vacuum. Subsequently, it was shown that graphite has rather strong bonding between the basal planes. The vapors act as a lubricant. These experiments were conducted with graphite rods sliding against copper, but films of graphite behave the same way at room temperature. A moist film gave a friction coefficient of 0.12, which failed as the film was dried by heating. This behavior suggests that interfilm slip (model 4, TABLE 1) is taking place. Graphite surfaces are being lubricated by vapors in much the same way that diamond surfaces are lubricated by moisture and metal surfaces are boundary lubricated by organic films.

These results prompted early investigations of MoS₂ humidity effects.⁽⁷³⁾ It was found that friction was low in dry air; however, the friction increased as the humidity increased up to approximately 85 percent, decreasing thereafter. The increase in friction was attributed to metal contact through the film, while the subsequent decrease was due to chemical reactions between MoS₂ and the surface that reduced the metal contact. This was confirmed in later studies; however, friction rose at lower humidities even with no metallic contact.⁽⁷⁴⁾

Matsunaga ⁽⁷⁵⁾ ran pellets of MoS₂ against steel and found:

	<u>Friction Coefficient</u>	<u>Wear Rate</u>	<u>Transfer</u>
Dry	0.15	2×10^{-6}	Thin film
Wet	0.30	90×10^{-6}	Isolated lumps

These results, like those for graphite, suggest that MoS₂ is sliding against MoS₂; however, the adsorbed vapors increase friction. This increased friction causes the transfer of MoS₂ to itself in the form of lumps--characteristic of a galling process common in metals.

It was soon learned that sliding at higher loads, velocities, and temperatures would have the same effect as dry air. An increase in the film temperature would dry the film and reduce friction and wear.⁽⁷⁵⁻⁷⁷⁾ For example, Fig. 3 (taken from Reference 75) illustrates the effect of MoS₂ drying on the friction and wear rate. Haltner studied the effect of various vapors on MoS₂ lubrication in vacuum. He concluded that vapors were not required and that at 10⁻⁹ torr, the coefficient of friction was 0.08.⁽⁷⁸⁾ Higher friction recorded in lower vacuum (10⁻⁶ torr), was consistent with adsorption of contaminants on the MoS₂ surfaces. Thus, adsorbed vapors have the effect of increasing adhesion. Similarly, talc interlayers that are bonded together with van der Waals forces are more tightly bonded in the presence of water vapor; the weaker bonds are replaced by hydrogen bonds.⁽⁷⁹⁾

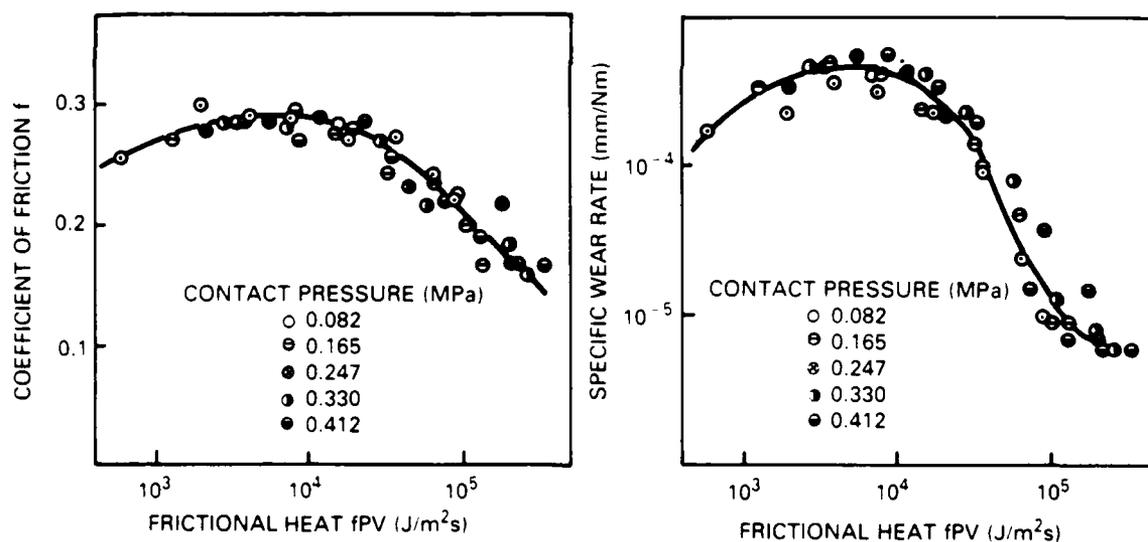


Figure 3. Effect of film drying on friction and wear rate of MoS₂

Haltner also studied the behavior of WS₂. In high vacuum, friction was more or less independent of the atmosphere; however, in lower vacuums (10⁻⁵ torr), hydrocarbon vapors gave low friction, as shown below:⁽⁸⁰⁾

Atmosphere	Friction Coefficient of WS ₂ Pellets
Vacuum (5×10^{-10} Torr)	0.17
Iso-Amyl Alcohol (5×10^{-5} Torr)	0.09

It was concluded that certain organic vapors would lubricate layer lattice compounds; however, the pressure had to be low enough for a substantial film to form. The same kind of results have been reported for MoS₂ in which friction was determined for sputtered films and single crystals.⁽⁸¹⁾ This behavior does indicate surface slip may be taking place, but other chemical and physical effects should also be considered. For example, none of these investigators has considered how vapors might affect the hardness of the film. For softer films, friction would also increase. Fleischauer showed that film orientation also affected the chemical behavior.⁽⁷¹⁾ As shown by Johnston and Moore ⁽⁵⁴⁾, it is quite possible that humidity could affect the way the film is orientated.

Cleavage studies have been reported by several investigators. Braynt measured the interlayer cohesive energy of graphite in high vacuum and found it to be 1,750 ergs/cm².⁽⁸²⁻⁸⁴⁾ This is an order of magnitude higher than that found in air. The results of cleavage of various layer's lattice materials are shown in TABLE 2

TABLE 2. Relationships Between the Binding Energy and Ambient Atmosphere for Seven Lamellar Solids ⁽⁸²⁾

Relatively low binding energy is shown as "easy cleavage in ultra-high vacuum" (UHV) while high binding causes "no" easy cleavage in UHV; a reduction of binding occurs in the presence of those "interacting gases" listed.

Lamellar Cleavage Samples	Easy Cleavage in UHV	Interacting Gases
Graphite	No	Air, O ₂ , H ₂ O
Molybdenite	Yes	-
Talc	Yes	-
Phlogopite	No	Air, H ₂ O
Pyrophyllite	Yes	-
Muscovite	No	Air, H ₂ O
Margarite	No	Air, H ₂ O

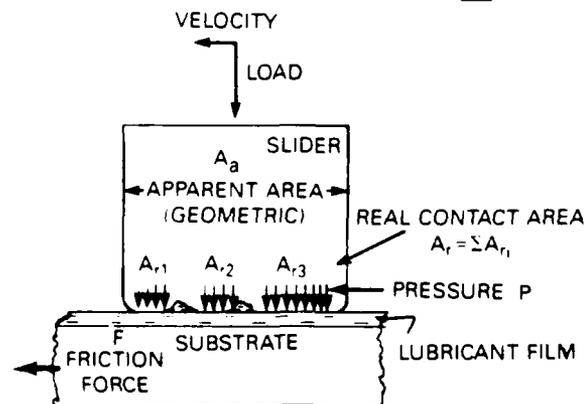
(reproduced from Reference 82). The authors conclude that the intrinsic lubricants are MoS₂, talc, and pyrophyllite. These materials cleave easily without requiring interacting gases. The other materials require the presence of vapors to promote lubricating capacity. An important question is why is talc a much poorer lubricant than MoS₂. The obvious answer is that it does not bind to the surface reactively. Mechanically, it should bind as well as MoS₂ but there are no obvious chemical reactions. Secondly, the film cohesion may be poor. An interesting experiment would be to find conditions or materials under which talc would be an effective lubricant. This would provide appreciable insight into the lubrication criteria.

Matsumaga cleaved MoS₂ single crystals and found excess sulfur on the cleaved faces.⁽⁸⁴⁾ Sliding experiments produced the same result.⁽⁸⁵⁾ In stick slip sliding of diamond on a single crystal of MoS₂, it was found that sulfur content increased in the stick region and that slip occurred when the sulfur surface density increased to an appreciable value. A sulfur-adsorbed layer on MoS₂ hypothesis has been proposed by Johnson and Vaughn but refuted by Haltner, who could not observe the effect at higher vacuums.⁽⁸⁶⁾ He concluded that stick-slip effect was due to some form of contamination from the vacuum system.⁽⁸⁰⁾ However, it should be noted that Bridgeman very often found free metal in high-pressure shear tests on inorganic solids ⁽⁸⁷⁾; i.e., CuCl₂, CuBr₂, PbO, PbI₂, PbS, Bi₂S₃, and Ag₂SO₄. All of these materials are effective lubricants. If pressure decomposes the compound, some friction effect should result. This idea needs further investigation.

VIII. FRICTIONAL BEHAVIOR

Bowden and Tabor first developed a theory of thin film lubrication using films of indium, lead, and copper on substrates of steel, nickel, copper, and silver.⁽⁸⁸⁾ Films of various thicknesses were applied, and the friction was measured with steel sliders of various radii. They found that the friction force under all circumstances was determined by track width (contact area). This is, of course, a statement of the fact that:

$$F = AS_f \quad (1)$$



where:

F = Friction force

A = Contact area

S_f = Shear strength of film material

Changing such factors as film thickness, specimen geometry, load, and substrate hardness changed the contact area and thus changed friction. Their concept of thin film lubrication was that:

$$f = \frac{S}{P} = \frac{S_f}{P} = \frac{S_f}{H_s} \quad (2)$$

where:

f = Friction coefficient

P = Pressure

H_s = Hardness of substrate

In other words, the hardness of the substrate determined the contact area while the shear strength of the film determined S. Friction of a metal film was much lower than the same metal in bulk form because in bulk form:

$$f = \frac{S_f}{H_f} \quad (3)$$

where:

H_f = Hardness of film material

This explains the lower friction but applies to a very limited condition that rarely occurs in actual practice. For example, in Reference 89, it is shown that for lead films (1 to 12 micrometers) on steel substrates loaded with spheres (r = 8 mm and 3 mm) that the contact area is primarily determined by the elastic deformation of the steel. Thus,

$$f = \frac{S_f}{P} = \frac{a S_f}{L} = \pi \left[\frac{3LR}{4E} \right]^{2/3} \frac{S_f}{L} \quad (4)$$

where:

a = Area

L = Load

R = Ball radius

E = Elastic modulus of substrate

Plastic deformation of the film begins to influence the contact area when the contact radius is less than 5 times the thickness of the lubricant film. Thus, both elastic and plastic deformation of the film can influence the contact area.

Bridgeman's results, as well as those of numerous other investigators, have shown that the shear strength increases with pressure; thus, Equation 4 must be modified by substitution of S_f by S_p .(37)

$$S_p = S_f + \alpha P \quad (5)$$

where:

S_p = Shear strength of film material at pressure

α = Constant

Thus Equation 4 becomes:

$$f = \pi \left[\frac{3LR}{4E} \right]^{2/3} \left[\frac{S_p}{L} \right] \quad (6)$$

$$f = \pi \left[\frac{3LR}{4E} \right]^{2/3} \left[\frac{S_f + \alpha P}{L} \right]$$

For plastic deformation of the film:

$$f = \left[\frac{L}{H_f} \right] \left[\frac{S_p}{L} \right] = \frac{S_f}{H_f} + \alpha, \quad (7)$$

Since P = Hardness of film

However, one is usually working with flat surfaces either intentionally or because wear has produced a flat on the curved slider. Under these circumstances, the contact area may be determined by the film (Equation 7) or the geometric area of contact. Friction coefficient then becomes a function of load or pressure as shown in Fig. 4. Under these circumstances, many investigators have shown that the frictional behavior is best described by the equation:(90-94)

$$f = \frac{S}{P} + \alpha \quad (8)$$

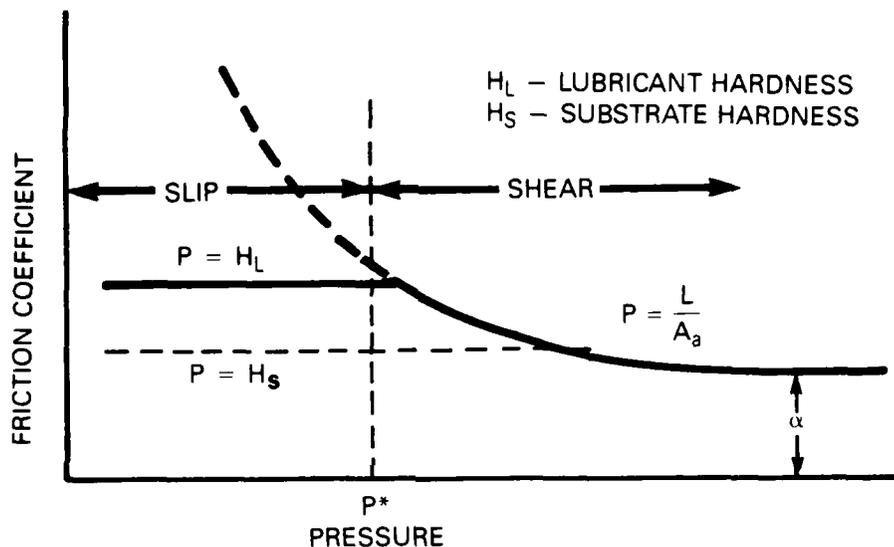


Figure 4. Frictional behavior of solid lubricants as a function of pressure

This equation shows that the friction coefficient decreases, as the pressure increases since both S and α are constants. When a material is applied as a film, its shear strength and α values apply. S may be the shear strength of the film S_f or the shear strength at the interface S_i if that is where slip occurs. P may have different values. At low pressures, P may be the hardness of the film (Equation 7). Under these circumstances, the contact area is incomplete (A_f) and is limited to the tips of the asperities. Thus, friction would be the same as if a solid block of lubricant were sliding against itself. With very thin films, it is possible that plastic or elastic reformation of the substrate material may influence the contact area so in the limit $P = H_S$. Under these circumstances, friction would be very much lower as shown in Fig. 4.

As the load is increased, the area grows and the friction remains constant, up to some critical pressure $P = P^*$. Above this pressure, $A_r = A_a$ (geometric area) and $P = L/A_a$. Friction will then decrease until, at a sufficiently high pressure, $f = \alpha$. Thus, three equations might apply for flat surfaces.

$$f = \frac{S_f}{H_L} + \alpha_L; \text{ for } P < P^* \text{ and } A_r \propto L \quad (9a)$$

Where H_L = Hardness of lubricant.

$$f = \frac{S_f}{H_s} + \alpha_L; \text{ for } P < P^* \text{ and } A_r \propto L \text{ (For thin films)} \quad (9b)$$

$$f = \frac{S_f}{P} + \alpha_L; \text{ for } P > P^* \text{ and } A = A_a = \text{Constant (determined by system geometry)} \quad (9c)$$

Thus, it can be proposed that there are two friction regimes in solid lubrication, a surface slip regime at low pressures, and a shear regime at high pressures. In the surface slip regime, either viscous or plastic flow mechanisms apply. The friction coefficient is directly proportional to the area of contact. This area is determined by the geometric area of contact for flat specimens or by the elastic deformation of the substrate for curved contacts. In the slip region, the contact area is determined by either the hardness of the lubricant film, or for very thin films, by the hardness of the substrate. Slip mechanisms that apply are described by models 3, 4, or 5 in TABLE 1. Under these circumstances, S_f may be the shear strength of the film or S_i , the shear strength at the interface.

If Equations 9a, 9b, 9c apply, then several critical questions must be answered:

1. For what material should S_i replace S_f ?
2. At what film thickness will the behavior of a film be described by 9b rather than 9a?
3. At what pressure, P^* , will 9c apply and how does the pressure relate to the film properties?

The answer to Question 1 is straight forward and has been extensively studied in connection with solid friction. Primarily it will be material with little adhesive interaction that may be indicated by limited solubility and their electronic characters, or minimum surface energy.⁽⁹⁵⁻⁹⁸⁾ Examples of those materials are listed in TABLE 3 for steel. This concept has been successfully evaluated for thin films on cutting tools.⁽⁹⁹⁾ The list does not include low shear strength, high-adhesion materials (such as aluminum, zinc, or copper) that are rarely used as solid lubricants. Some caution must be exercised since it is known that in air a material like lead can transfer via the metallic oxides.⁽¹⁰⁰⁾ If oxides are formed, it is the adhesion to the oxide that is important.

**Table 3. Low Adhesion
Lubricating Materials
for Steel**

Indium
Lead
Tin
Cadmium
Magnesium
Silver

The answers to questions 2 and 3 are much more complex. Although some information is available in the literature, additional research will be required. If then the previous concepts are applied to real materials, the curves shown in Fig. 5 can be generated for silver, MoS₂, lead and a viscous material (2000 poise). Data on hardness and shear strength were obtained from several sources.^(101,102) Values of α were derived from the work of Bridgeman.⁽⁸⁷⁾

These curves are based upon simple concepts and are not intended to be rigorous. They do, however, demonstrate trends in the behavior under conditions of solid-film lubrication. Note that at low pressure, friction would be extremely high if pure shear or flow took place. Obviously, either seizure would occur or a transition would take place to another mode of sliding. What this usually means is a transition to slip or a large reduction in the contact area due to a reduction in the normal load by the material deformation.

The important point is that one of the best methods to determine the lubricating mechanisms is to determine the f versus pressure behavior and compare the results with those shown in Fig. 5.

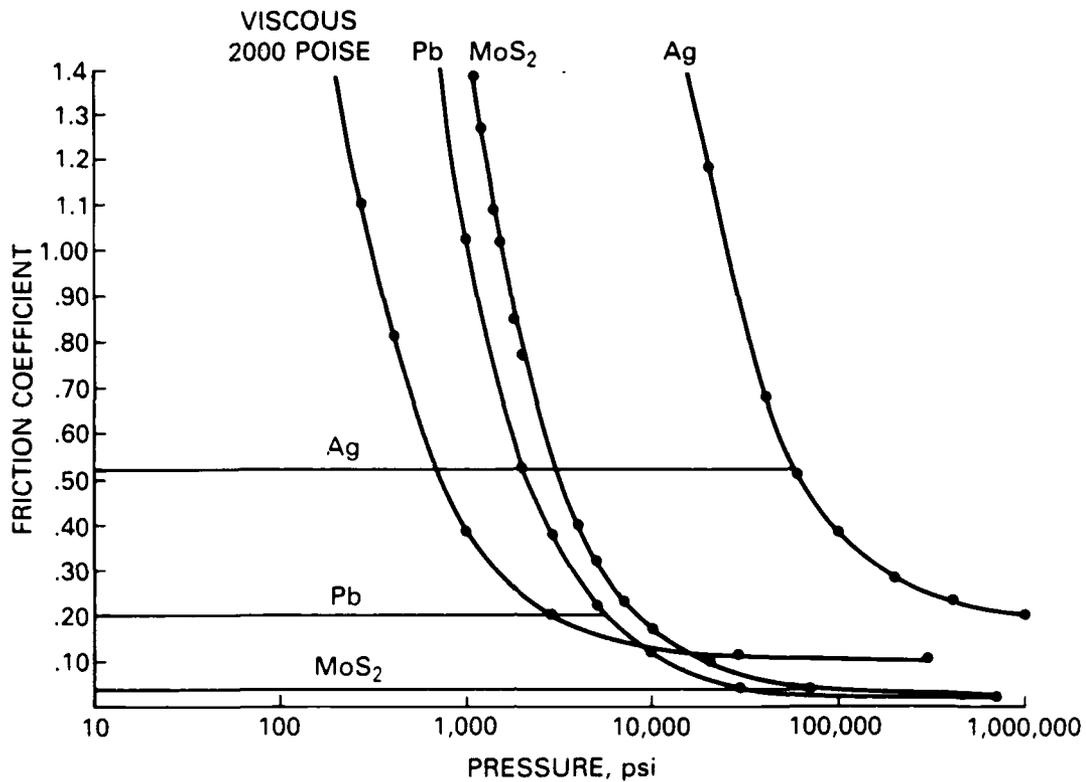


Figure 5. Friction coefficient as a function of pressure

After pressure, the velocity effects should be the most significant variable in describing solid lubricant behavior. Interface slip, S , and consequently f should be independent or decrease with velocity. The decrease would be due to shorter time in contact, which results in decreased friction. For shear, S and f should increase with velocity unless adiabatic shear influences the results. Such information can also be obtained from the literature.

Temperature is also important, since changing temperatures would produce an effect similar to pressure changes. At low temperatures, Equation 9a applies. As the temperature is increased, both S_f and H_L decrease proportionally so that friction remains constant. At some critical temperature $fP > S_f$ and shear will begin; then friction will decrease. At higher temperatures, friction is proportional to the strength/temperature properties of the lubricant film.

IX. LUBRICATION MECHANISMS FOR SPECIFIC MATERIALS

As indicated in the previous discussions, a better understanding of lubricating mechanisms can be obtained by observing the following effects for a specific material:

1. Frictional behavior as a function of pressure.
2. Frictional behavior as a function of temperature.
3. Velocity effects on friction.
4. A comparison of film friction with solid friction.
5. Atmospheric vapor effects.
6. Adhesion and adhesion damage upon separation of specimens after sliding.

From the literature, these concepts can now be applied to specific materials. Particular attention is paid to frictional behavior a function of pressure.

Before isolating specific lubricants, some overall trends should be examined. To this end, the experimental data of Bridgeman are replotted as friction coefficient against pressure in Figs. 6 and 7.⁽⁸⁷⁾ The trends are similar to that of Figs. 4 or 5. The softer material such as lead and tin give almost constant friction with increasing pressure. This represents the value of α since even at a pressure of 100 kg/mm², they are at a value of 25 times their hardness. Some of the harder material like Zn, Cd, and Al show decreasing trends, while the hardest materials (Mo and W) show only an increasing trend. These same trends are apparent for the inorganic materials. The MoS₂ values are from Reference 90 using similar equipment. Note that the friction behavior of MoS₂ is similar to other soft materials with a variety of structures. Thus, at high pressures, MoS₂ is no better than any other material from a friction stand point.

In some materials such as PbO, Au, and Ag, some linear trends are seen at low pressures. With the other materials, an increasing trend was reported. The increasing trend is explained by Bridgeman as surface slips; however, such behavior would not be expected. In any case, these results should not be stretched too far since the pressures are very high. Also, there is some questions concerning contamination in the powders or errors in the experimental procedure.

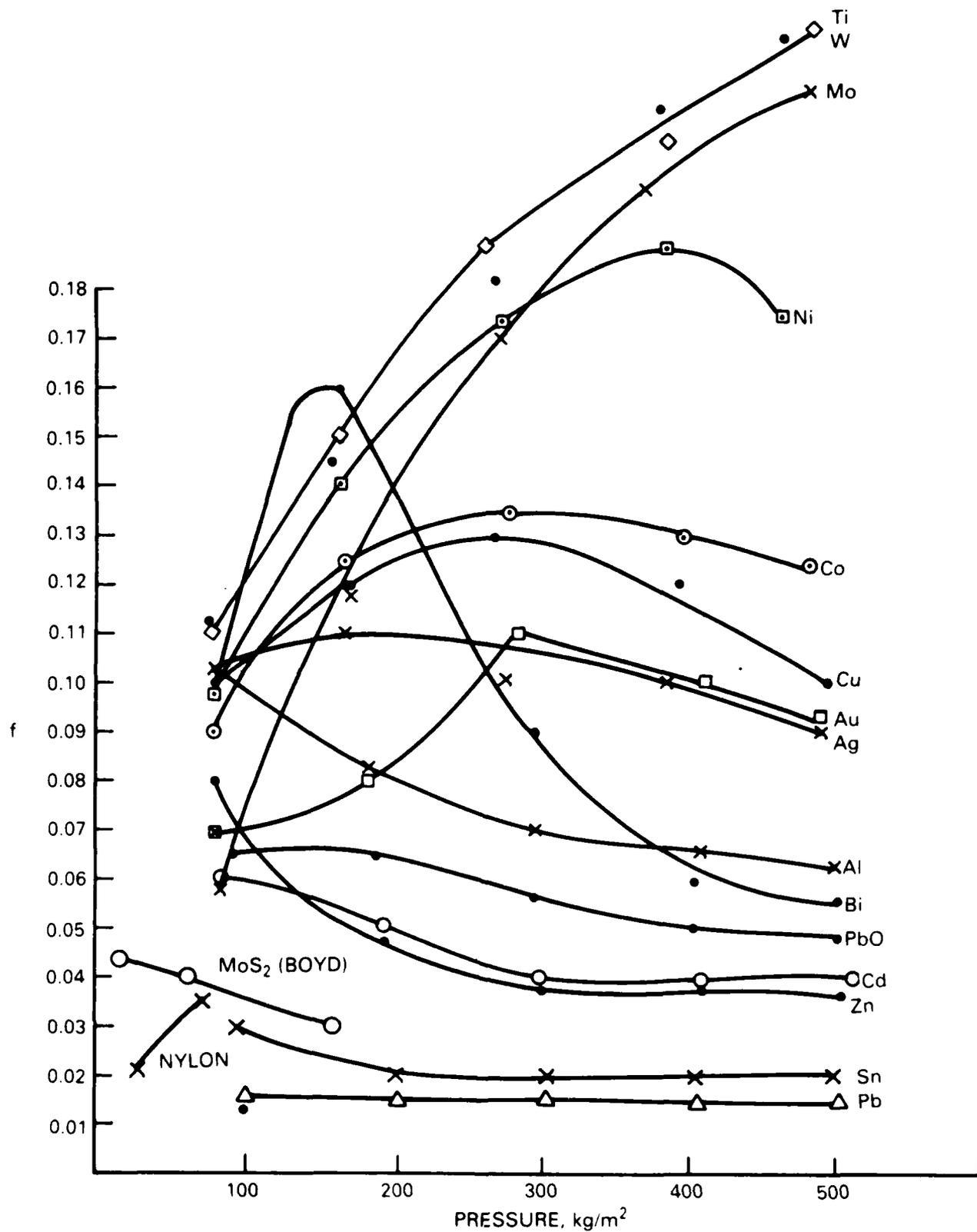


Figure 6. Frictional behavior of metals as a function of pressure

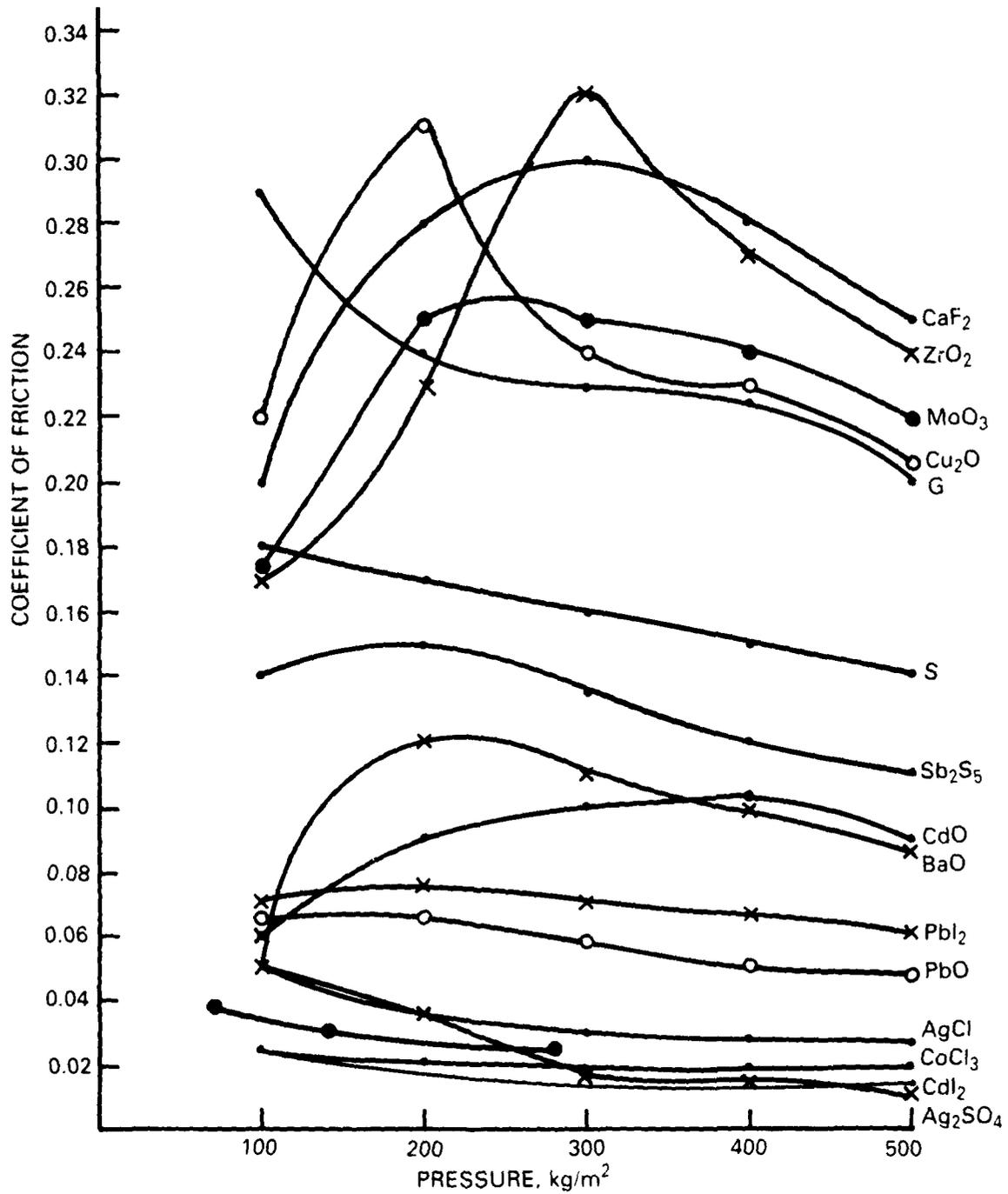


Figure 7. Frictional behavior of selected solid lubricants as a function of pressure

Other investigators have considered the shear properties of materials at high pressure.(91-94,103) Most of these efforts are concerned with very high pressure in which the shear behavior has been established. In order to establish trends over a broad pressure range (10 to 10^6 psi), a data search was conducted from a wide variety of sources for MoS₂, lead, and tin. The results are shown in Figs. 8 to 10. These data can be compared with the curves of Fig. 5, which are shown as dashed lines in Fig. 8.

For MoS₂ films, the data* assembled from the literature fit curves of Equations 9a and 9c almost exactly. The friction coefficient is 0.04, up to a pressure of about 30,000 psi. Then it begins to decrease. It is interesting to note that the hardness

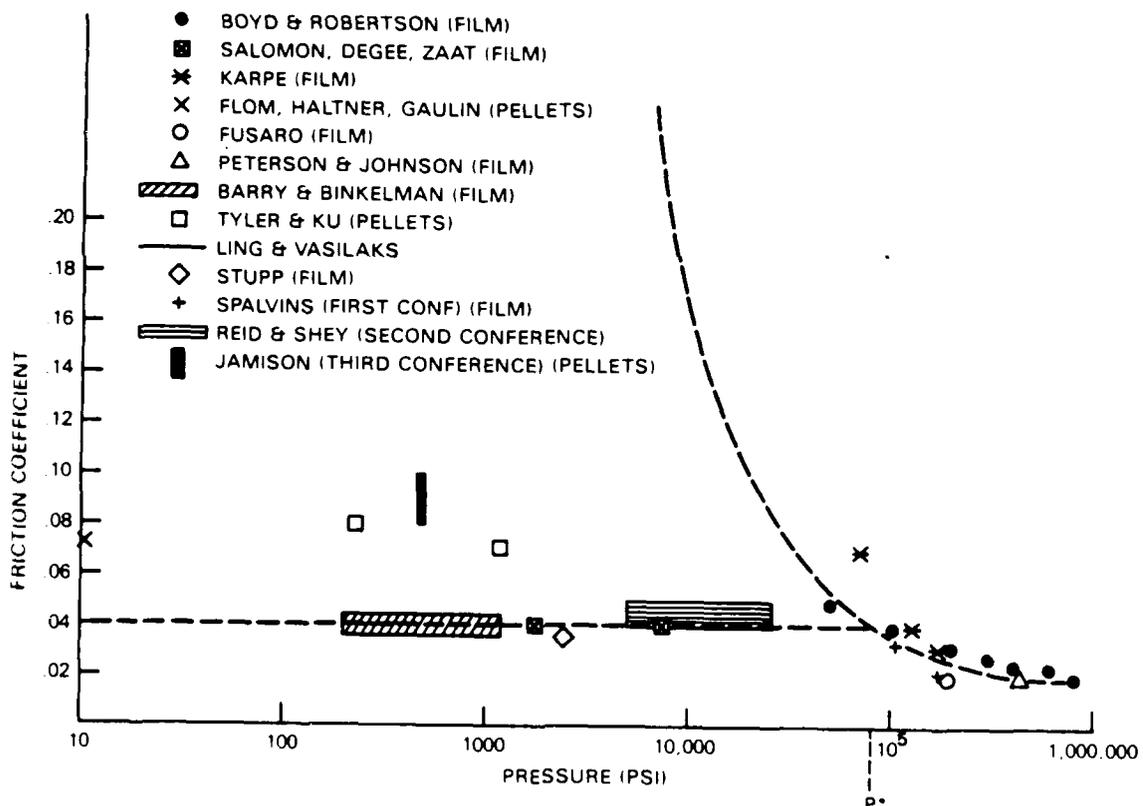


Figure 8. MoS₂ friction behavior over a broad pressure range

* All of the data were taken from experiments conducted under dry conditions.

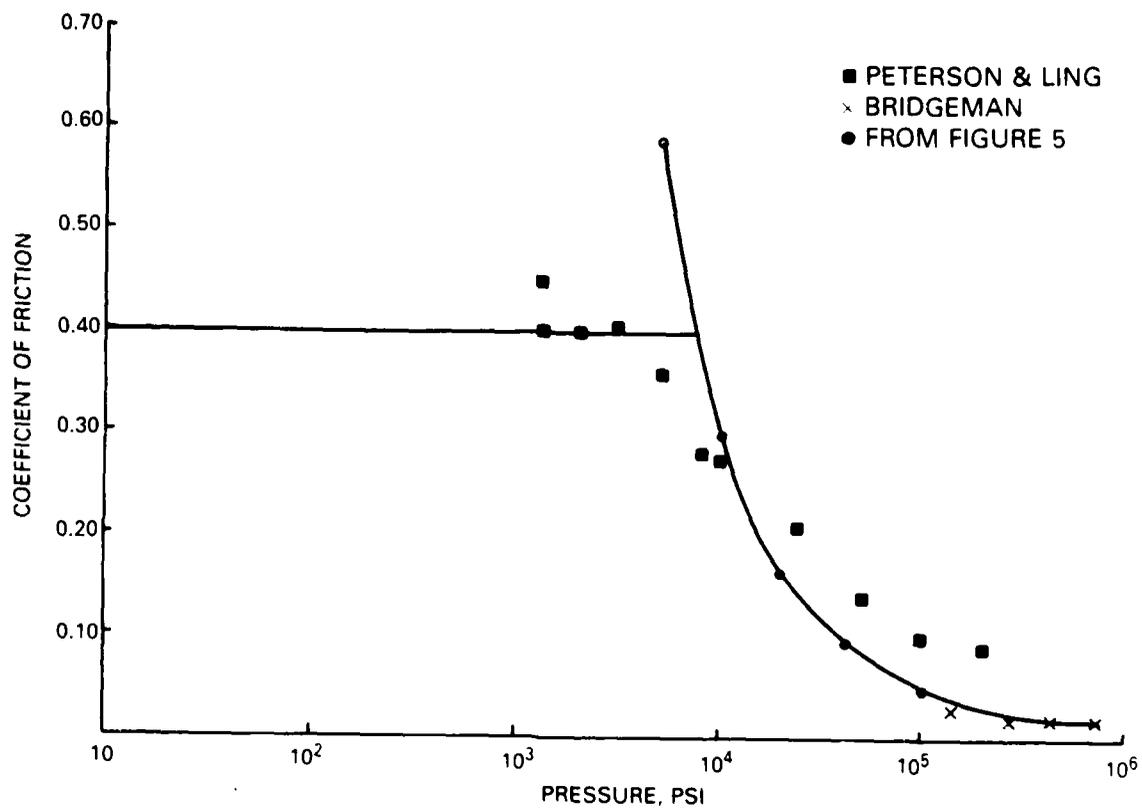


Figure 9. Tin friction behavior over a broad pressure range

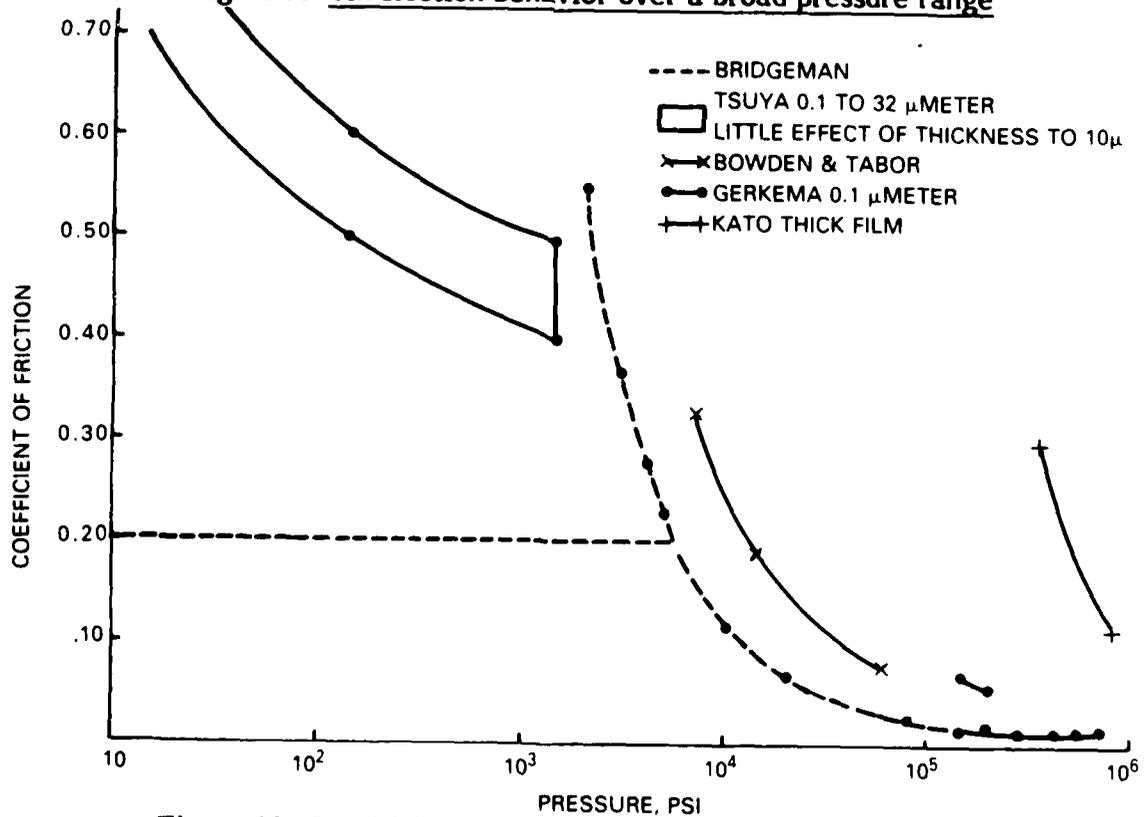


Figure 10. Lead friction behavior over a broad pressure range

of the oriented MoS₂ layer is 60 kg/mm² (85,200 psi) so that for MoS₂, P* = H_f (hardness of the film). At low pressures, it was found by both Barry and Binkelman, and Reid and Shey that friction is independent of the hardness of the substrate. Thus Equation 9b does not apply. All the low-pressure experiments were conducted with different geometric areas so friction is independent of apparent contact area.

This is a confirmation of the fact that the film hardness establishes the real contact area. Thus, the following tribological behavior is hypothesized.

The MoS₂ film is not perfectly smooth. When a light load is applied, the film "asperities" support the load by deforming to establish the real area of contact. Shearing these junctions produces the measured friction force. In other words, the adhesion theory of friction applies to MoS₂ films. As the load is increased, the real area of contact increases proportionally to load. Thus, the friction coefficient remains constant. Eventually, when the pressure equals the hardness of the MoS₂ film, all of the available area is in contact. Then friction begins to decrease, since A_r and S_f are now both constant.

$$f = \frac{A_r S_f}{L} + \alpha ; \quad \text{where} \quad \frac{A_r}{L} = \frac{1}{H}, \quad \text{and} \quad A_r = A_a \quad \text{when} \quad P^* = H \quad (10)$$

At pressures higher than P*, friction decreases to a value equal to α since the term $A_r S_f (L)^{-1} \rightarrow 0$. If the shear strength did not increase with pressure, α would be zero and the friction coefficient would approach zero. Thus, the low friction coefficient of MoS₂ is attributed to the high hardness of the oriented film.

With very soft substrates, friction can increase as shown in Fig. 11 (from the results of Barry and Binkelman). If the substrate hardness is less than the hardness of MoS₂, then friction increases, possibly because the deformation of the substrate then controls the contact area. With thicker films, the effect may disappear.

Fig. 8 shows friction coefficient of 0.08 for pellets of MoS₂ sliding against metals. From the information shown in Fig. 11, this behavior is also understandable based

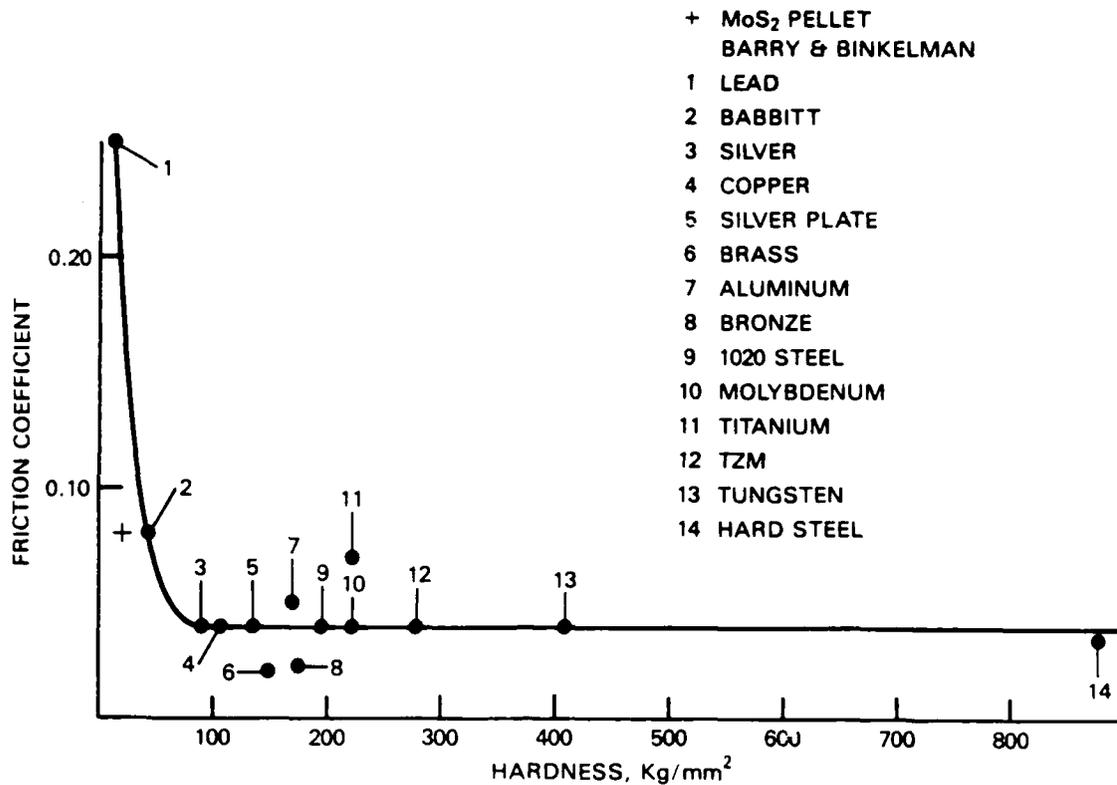


Figure 11. Effect of substrate hardness on the friction coefficient of MoS₂

on Fig. 11. The bulk hardness of the MoS₂ pellets was measured to be 18 kg/mm². Using this value as the substrate hardness, a friction coefficient of 0.08 is reasonable.

No substantial decrease in friction is seen with very hard substrates (greater than 800 kg/mm²), although brass and bronze gave lower friction and titanium higher friction. At pressures higher than 80,000 psi, a complete film of MoS₂ is sheared. The friction coefficient is directly proportional to the area of contact at a given load. The contact is determined by the specimen area or by the elastic deformation of concentrated contact. With softer substrates, plastic deformation can also occur which would increase the coefficient of friction slightly. However, as f approaches $\alpha = 0.02$, the effect of these pressure differences becomes insignificant.

The value of friction coefficient (0.02) at 400,000 psi (Peterson and Johnson) is for a very thin film applied to the tips of the asperities of a metal substrate. Under these circumstances, the pressure is equal to the hardness of the substrate, and the contact area is very small. The other values are for complete films. Thus, in the shear region, friction is primarily determined by the pressure; friction is constant at a given pressure.

The data for tin films are shown in Fig. 9. Although the data are limited at very low pressures, the same trend shown in Fig. 4 is noted in Fig. 9. There is reasonable agreement between Equations 9a and 9c and the experimental results. At low stresses, a friction coefficient of 0.40 is obtained. This value is very similar to that for solid tin sliding against steel (0.29 to 0.51) as reported by Rabinowicz.⁽¹⁰⁴⁾

The data for lead are shown in Fig. 10. Although the same trends are seen, there are some discrepancies, particularly at low pressures. Friction coefficients are in the range of 0.40 to 0.70, rather than the predicted 0.20. They are lower, however, than that for lead sliding against steel which Tsuya reported to be 1.30.⁽¹⁰⁵⁾ This effect is understandable, based upon the adhesion theory of friction. The strong bonding of lead to steel causes an increase in the contact areas as tangential forces are applied.⁽¹⁰⁶⁾ This effect was observed by Kato, who was working with thick films.⁽¹⁰⁷⁾ Tsuya also observed that thicker films gave higher friction coefficients, approaching solid lead.

Since Tin and MoS₂ do not experience junctions growth, they give more predictable frictional behavior. This may be due to low adhesion (Sn/Fe and MoS₂/MoS₂) or may be due to the fact that the deformation process with these materials does not lead to friction growth. Several investigators have noted high friction (0.30) for MoS₂ sliding against MoS₂ films in moist atmospheres. The high frictions were accompanied by lump transfer. This effect was attributed to increased MoS₂/MoS₂ adhesion. There are other examples of this adhesion effect. Silver behaves like tin and MoS₂ when used as a film to lubricate steel or nickel, but behaved like lead against aluminum surfaces.⁽¹⁰⁸⁾ Aluminum films were ineffective lubricants for the same reason.

Thus, from observing the friction/pressure behavior of solid film lubricants, a better understanding of their tribological behaviors can be obtained. From the data assembled, a simple theory consistent with the information reported in the literature has been proposed. This theory states that the friction and wear behavior of solid lubricant films is merely an adaptation of their behavior in bulk form. This adaptation is the limited junction growth that can take place with a thin film.

This concept is, of course, speculative and based on limited data derived under a variety of conditions. These data should be repeated with a single apparatus over a broad pressure range where the contact area is measured and controlled. Micro-hardness measurements of the surface should be made after sliding to determine the hardness of thin films. The critical experiments would be to separate adhesion effects and deformation effects in the junction growth process. Current junction growth concepts do not provide for different deformation processes, for example between a hexagonal and cubic structure.

X. CONCLUSIONS AND RECOMMENDATIONS

Five different models of solid-film lubrications have been proposed. An extensive review of the literature was conducted in order to determine which of the models were consistent with the body of knowledge available on solid lubricant tribological behavior. Consideration was given to observations of film behavior; substrate adhesion; film formation, wear and failure; crystal structure; effects of atmosphere and frictional behavior. Based on limited data, it is concluded that the currently accepted adhesion theory of friction applied equally well to thin films. The primary difference is the limited junction growth in effective films. Two friction regimes are proposed: a slip regime at low pressures and a shear regime at high pressures. The transition occurs when the pressure is approximately equal to the hardness of the film. In the slip regime, the contact area is controlled by the hardness of the film rather than the substrate. In the shear regime, the contact area is determined by the geometric area, which is influenced by the elastic deformation of the substrate material. Vapors lubricate solid-lubricant films, and surface oxidation modifies their frictional behavior. Data assembled on the

frictional behavior of MoS₂, lead, tin, silver, and PTFE tend to support the proposed model. However, additional data are needed. These data include:

1. Friction versus pressure (10 to 16⁶ psi) data should be assembled for these materials and other (PbO, Co, Al, B₂O₃, CuReO₄) solid lubricants over a wide temperature range. The results should be compared with those obtained with solid lubricant pellets sliding against themselves and metal substrates.
2. Techniques should be developed to measure the surface hardness of very thin films, since it is proposed that the hardness of the oriented solid lubricant film controls the frictional behavior.
3. Studies should be conducted to determine factors that influence the contact area with thin films. Specifically, it would be valuable to know (1) the pressure at which the area of contact is complete; (2) how the interface adhesion affects junction growth with solid lubricants; (3) how is junction growth affected by crystal structure and film thickness; and (4) mechanical properties of typical solid lubricant material.

In order to understand lubrication with solids, it will be necessary to answer several critical questions:

1. Do vapors affect the adhesion of solids in contact or do they affect the mechanical properties of the films? There is evidence in the literature to support both points of view.
2. Does the crystal structure of the solid lubricant influence primarily the contact area and hardness or its shear properties?
3. To what extent is the junction growth process limited when applied to thin films (1 to 30 micrometers).
4. What wear mechanisms apply to solid lubricant films?

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GLOSSARY

Adhesion	The intimate sticking together of surfaces under compressive stresses by metallic bonds that form as a function of stress, time, and temperature.
Crystal Structure of Metals	The structure of most metals are face-centered cubic (fcc), close-packed hexagonal (cph), or body-centered cubic (bcc).
Dislocation	A lattice imperfection in a crystal structure, classified according to type, e.g., edge dislocation, screw dislocation.
Elasticity	The proportionality between stress and strain.
Elastic Limit	The maximum stress to which a metal may be subjected without suffering some permanent or plastic deformation.
Grains	Metal crystals, of irregular shape, in contact at all points with other similar crystals (continuous).
Grain Boundaries	The surface separating two regions of a solid in which the crystal axes are differently oriented. It has been shown that such a boundary may be thought of as built up of an array, or network of dislocations, whose spacing depends on the tilt θ of the axes across the surface. Grain boundary relaxation is a source of internal friction in solids due to the motion of grain boundaries under stress.
Interface	A common boundary between two phases of a system.

Ion-Implantation	Impurities are introduced by firing high-energy ions at the substrate material.
Junction Growth	Transfer of material from asperities due to adhesion.
Plastic Flow	Material flow characterized by permanent deformation caused by stresses beyond its elastic limit.
Slip	The translation along parallel planes within a crystal lattice.
Sputter	A material in the finely divided state produced by passing a high-potential discharge between two electrodes of the material in a dielectric liquid or gaseous medium.
Young's Modulus	The ratio of the tensile stress in a material to the corresponding tensile strain in the elastic domain.

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DIRECTOR
APPLIED TECHNOLOGY DIRECTORATE
U.S. ARMY R&T ACTIVITIES (AVSCOM)
ATTN: SAVDL-ATL-ATP (MR MORROW) 1
SAVDL-ATL-ASV 1
FORT EUSTIS VA 23604-5577

CDR
US READINESS COMMAND
ATTN: J4-E 1
MACDILL AIR FORCE BASE FL 33608

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DIRECTORATE OF INDUSTRIAL
OPERATIONS
FORT RICHARDSON AK 99505

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STRGP-FE, BLDG 85-3
(MR GARY SMITH) 1
STRGP-FT (MR FOSTER) 1
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CHEMICALS COMMAND
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ROCK ISLAND ARSENAL IL 61299-6000

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US ARMY COLD REGION TEST CENTER
ATTN: STECR-TA 1
APO SEATTLE 98733

HQ, DEPT. OF ARMY
ATTN: DAEN-DRM 1
WASHINGTON DC 20310

CDR
US ARMY LABORATORY COMMAND
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AMSLC-TP-PB (DR GONANO) 1
AMSLC-TP-AL (LTC SCHRADER) 1
ADELPHI MD 20783-1145

CDR
US ARMY FORCES COMMAND
ATTN: AFLG-REG 1
AFLG-POP 1
FORT MCPHERSON GA 30330

CDR
US ARMY RES & STDZN GROUP
(EUROPE)
ATTN: AMXSN-UK-RA (DR OERTEL) 1
AMXSN-UK-SE 1

BOX 65
FPO NEW YORK 09510

PROJECT MGR, M113 FAMILY OF
VEHICLES
ATTN: AMCPM-M113-T 1
WARREN MI 48397

CDR, US ARMY AVIATION SYSTEMS
CMD
ATTN: AMSAV-EP (MR EDWARDS) 1
AMSAV-NS 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
US ARMY BALLISTIC RESEARCH LAB
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SLCBR-TB-E 1
SLCBR-SE-D (MR THOMAS) 1
ABERDEEN PROVING GROUND MD
21005-5006

CDR
US CENTRAL COMMAND
ATTN: CINCCEN/CC J4-L 1
MACDILL AIR FORCE BASE FL 33608

CDR
US ARMY ABERDEEN PROVING
GROUND
ATTN: STEAP-MT-U 1
ABERDEEN PROVING GROUND MD
21005

CDR
US ARMY YUMA PROVING GROUND
ATTN: STEYP-MT-TL-M 1
(MR DOEBBLER)
YUMA AZ 85364-9103

CDR
CHEMICAL R&D CENTER
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ABERDEEN PROVING GRD MD
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PROJ MGR, BRADLEY FIGHTING VEHICLE SYS ATTN: AMCPM-FVS-M WARREN MI 48397	1	PROG MGR, TACTICAL VEHICLE ATTN: AMCPM-TV WARREN MI 48397	1
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CDR 105TH S & T BATTALION 5TH INFANTRY DIV (MECH) FORT POLK LA 71459	1	CDR US ARMY DEPOT SYSTEMS CMD ATTN: AMSDS-RM-EFO CHAMBERSBURG PA 17201	1
PROJ MGR, MOBILE ELECTRIC POWER ATTN: AMCPM-MEP-TM 7500 BACKLICK ROAD SPRINGFIELD VA 22150	1	CDR US ARMY WATERVLIET ARSENAL ATTN: SARWY-RDD WATERVLIET NY 12189	1
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CDR US ARMY RESEARCH OFC ATTN: SLCRO-EG (DR MANN) SLCRO-CB P O BOX 12211 RSCH TRIANGLE PARK NC 27709-2211	1	PROJ MGR, LIGHT ARMORED VEHICLES ATTN: AMCPM-LA-E WARREN MI 48397	1
DIR AMC PACKAGING, STORAGE, AND CONTAINERIZATION CTR ATTN: SDSTO-TE-S TOBYHANNA PA 18466-5097	1	CDR US ARMY ORDNANCE CENTER & SCHOOL ATTN: ATSL-CD-CS ABERDEEN PROVING GROUND MD 21005	1
		CDR AMC MATERIEL READINESS SUPPORT ACTIVITY (MRSA) ATTN: AMXMD-MO (MR BROWN) LEXINGTON KY 40511-5101	1

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US ARMY FOREIGN SCIENCE & TECH
CENTER
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AIAST-MT-1 1
FEDERAL BLDG
CHARLOTTESVILLE VA 22901

PROJECT MANAGER, LIGHT COMBAT
VEHICLES
ATTN: AMCPM-LCV-TC 1
WARREN, MI 48397

HQ, US ARMY T&E COMMAND
ATTN: AMSTE-TO-O 1
AMSTE-CM-R-O 1
AMSTE-TE-T (MR RITONDO) 1
ABERDEEN PROVING GROUND MD
21005-5006

CDR
US ARMY ARMAMENT RESEARCH
& DEVELOPMENT CTR
ATTN: AMSMC-LC 1
AMSMC-SC 1
DOVER NJ 07801-5001

CDR, US ARMY TROOP SUPPORT
COMMAND
ATTN: AMSTR-ME 1
AMSTR-S 1
AMSTR-E 1
AMSTR-WL (MR BRADLEY) 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
CONSTRUCTION ENG RSCH LAB
ATTN: CERL-EM 1
CERL-ES (MR CASE) 1
CERL-EH 1
P O BOX 4005
CHAMPAIGN IL 61820

TRADOC LIAISON OFFICE
ATTN: ATFE-LO-AV 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
US ARMY NATICK RES & DEV CENTER
ATTN: STRNA-YE (DR KAPLAN) 1
STRNA-U 1
NATICK MA 01760-5000

CDR
US ARMY QUARTERMASTER SCHOOL
ATTN: ATSM-CD 1
ATSM-TD 1
ATSM-PFS (MR ELLIOTT) 1
FORT LEE VA 23801

HQ
US ARMY TRAINING & DOCTRINE CMD
ATTN: ATCD-SL-5 1
FORT MONROE VA 23651-5000

DIRECTOR
US ARMY RSCH & TECH ACTIVITIES
(AVSCOM)
PROPULSION DIRECTORATE
ATTN: SAVDL-PL-D (MR ACURIO) 1
21000 BROOKPARK ROAD
CLEVELAND OH 44135-3127

CDR
US ARMY TRANSPORTATION SCHOOL
ATTN: ATSP-CD-MS (MR HARNET) 1
FORT EUSTIS VA 23604-5000

PROJ MGR, PATRIOT PROJ OFFICE
ATTN: AMCPM-MD-T-C 1
U.S. ARMY MISSILE COMMAND
REDSTONE ARSENAL AL 35898

HQ, US ARMY ARMOR CENTER AND
FORT KNOX
ATTN: ATSB-CD 1
FORT KNOX KY 40121

CDR
101ST AIRBORNE DIV (AASLT)
ATTN: AFZB-KE-J 1
AFSB-KE-DMMC 1
FORT CAMPBELL KY 42223

CDR
US ARMY WESTERN COMMAND
ATTN: APLG-TR 1
FORT SCHAFTER HI 96858

CDR
COMBINED ARMS COMBAT
DEVELOPMENT ACTIVITY
ATTN: ATZL-CAT-E 1
ATZL-CAT-A 1
FORT LEAVENWORTH KS 66027-5300

CDR
US ARMY LOGISTICS CTR
ATTN: ATCL-MS (MR A MARSHALL) 1
ATCL-C 1
FORT LEE VA 23801-6000

PROJECT MANAGER
PETROLEUM & WATER LOGISTICS
ATTN: AMCPM-PWL 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

CDR
US ARMY FIELD ARTILLERY SCHOOL
ATTN: ATSF-CD 1
FORT SILL OK 73503-5600

CDR
US ARMY ENGINEER SCHOOL
ATTN: ATZA-TSM-G 1
ATZA-CD 1
FORT BELVOIR VA 22060-5606

CDR
US ARMY INFANTRY SCHOOL
ATTN: ATSH-CD-MS-M 1
FORT BENNING GA 31905-5400

CDR
MILITARY TRAFFIC MANAGEMENT
COMMAND
ATTN: MT-SA (MR DOWD) 1
WASHINGTON DC 20315

DIR
US ARMY MATERIALS TECHNOLOGY
LABORATORY
ATTN: SLCMT-M 1
SLCMT-EM (DR FOPIANO) 1
WATERTOWN MA 02172-2796

CDR
US ARMY MISSILE CMD
ATTN: AMSMI-U 1
AMSMI-RR 1
REDSTONE ARSENAL AL 35898-5242

CDR
US ARMY ARMOR & ENGINEER BOARD
ATTN: ATZK-AE-AR 1
ATZK-AE-LT 1
FORT KNOX KY 40121

CDR
US ARMY MEDICAL BIOENGINEERING
R&D LABORATORY
ATTN: SGRD-USG-M (MR EATON) 1
FORT DETRICK, MD 21701

CDR
US ARMY AVIATION CTR & FT RUCKER
ATTN: ATZQ-DI 1
FORT RUCKER AL 36362

PROG MGR, TANK SYSTEMS
ATTN: AMCPM-GCM-SM 1
AMCPM-M60 1
WARREN MI 48397

CDR
6TH MATERIEL MANAGEMENT CENTER
19TH SUPPORT BRIGADE 1
APO SAN FRANCISCO 96212-0172

CHIEF, U.S. ARMY LOGISTICS
ASSISTANCE OFFICE, FORSCOM
ATTN: AMXLA-FO (MR PITTMAN) 1
FT MCPHERSON GA 30330

CDR
US ARMY SAFETY CENTER
ATTN: PESC-SSD (MR BUCHAN) 1
FORT RUCKER AL 36362

DEPARTMENT OF THE NAVY

CDR
NAVAL AIR PROPULSION CENTER
ATTN: PE-33 (MR D'ORAZIO) 1
PE-32 (MR MANGIONE) 1
P O BOX 7176
TRENTON NJ 06828

CDR
NAVAL SEA SYSTEMS CMD
ATTN: CODE 05M4 (MR R LAYNE) 1
WASHINGTON DC 20362-5101

CDR
DAVID TAYLOR NAVAL SHIP R&D CTR
ATTN: CODE 2830 (MR SINGERMAN) 1
CODE 2759 (MR STRUCKO) 1
CODE 2831 1
ANNAPOLIS MD 21402-5067

JOINT OIL ANALYSIS PROGRAM -
TECHNICAL SUPPORT CTR
BLDG 780
NAVAL AIR STATION
PENSACOLA FL 32508

CG
FLEET MARINE FORCE ATLANTIC
ATTN: G4
NORFOLK VA 23511

CG
FLEET MARINE FORCE PACIFIC
ATTN: G4
CAMP H.M. SMITH HI 96861

CDR
NAVAL SHIP ENGINEERING CENTER
ATTN: CODE 6764
PHILADELPHIA PA 19112

PROJ MGR, M60 TANK DEVELOPMENT
ATTN: USMC-LNO
US ARMY TANK-AUTOMOTIVE
COMMAND (TACOM)
WARREN MI 48397

DEPARTMENT OF THE NAVY
HQ, US MARINE CORPS
ATTN: LPP (MAJ LANG)
LMM/2 (MAJ PATTERSON)
WASHINGTON DC 20380

CDR
NAVAL AIR SYSTEMS CMD
ATTN: CODE 53645 (MR MEARNES)
WASHINGTON DC 20361

CDR
NAVAL AIR DEVELOPMENT CTR
ATTN: CODE 60612
WARMINSTER PA 18974

CDR
NAVAL RESEARCH LABORATORY
ATTN: CODE 6170
CODE 6180
CODE 6110 (DR HARVEY)
WASHINGTON DC 20375-5000

CDR
NAVAL AIR ENGR CENTER
ATTN: CODE 92727
LAKEHURST NJ 08733

1 CDR
NAVAL FACILITIES ENGR CTR
ATTN: CODE 1202B (MR R BURRIS)
200 STOVAL ST
ALEXANDRIA VA 22322 1

1 COMMANDING GENERAL
US MARINE CORPS DEVELOPMENT
& EDUCATION COMMAND
ATTN: DO74 1
QUANTICO VA 22134

1 OFFICE OF THE CHIEF OF NAVAL
RESEARCH
ATTN: OCNR-126 (MR ZIEM) 1
CODE 432 (DR MILLER) 1
ARLINGTON, VA 22217-5000

1 CHIEF OF NAVAL OPERATIONS
ATTN: OP 413 1
WASHINGTON DC 20350

1 CDR
NAVY PETROLEUM OFC
ATTN: CODE 43 (MR LONG) 1
CAMERON STATION
ALEXANDRIA VA 22304-6180

DEPARTMENT OF THE AIR FORCE

1 HQ, USAF
ATTN: LEYSF (COL LEE) 1
WASHINGTON DC 20330

1 HQ AIR FORCE SYSTEMS CMD
ATTN: AFSC/DLF 1
ANDREWS AFB MD 20334

1 CDR
US AIR FORCE WRIGHT AERONAUTICAL
LAB
ATTN: AFWAL/POSF (MR CHURCHILL) 1
AFWAL/POSL (MR JONES) 1
AFWAL/MLSE 1
AFWAL/MLBT (MR SNYDER) 1
WRIGHT-PATTERSON AFB OH
45433-6563

1 CDR
WARNER ROBINS AIR LOGISTIC
CTR
ATTN: WRALC/MMTV (MR GRAHAM) 1
ROBINS AFB GA 31098

CDR
SAN ANTONIO AIR LOGISTICS
CTR
ATTN: SAALC/SFT (MR MAKRIS) 1
SAALC/MMPRR 1
KELLY AIR FORCE BASE TX 78241

CDR
HQ 3RD USAF
ATTN: LGSF (CPT HEWITT) 1
APO NEW YORK 09127

CDR
USAF 3902 TRANSPORTATION
SQUADRON
ATTN: LGTVP (MR VAUGHN) 1
OFFUTT AIR FORCE BASE NE 68113

CDR
DET 29
ATTN: SA-ALC/SFM 1
CAMERON STATION
ALEXANDRIA VA 22314

OTHER GOVERNMENT AGENCIES

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION 1
LEWIS RESEARCH CENTER
CLEVELAND OH 44135

DEPARTMENT OF TRANSPORTATION
FEDERAL AVIATION ADMINISTRATION
ATTN: AWS-110 1
800 INDEPENDENCE AVE, SW
WASHINGTON DC 20590

US DEPARTMENT OF ENERGY
ATTN: MR ECKLUND 1
MAIL CODE CE-151
FORRESTAL BLDG.
1000 INDEPENDENCE AVE, SW
WASHINGTON DC 20585

1 ENVIRONMENTAL PROTECTION
AGENCY
AIR POLLUTION CONTROL 1
2565 PLYMOUTH ROAD
ANN ARBOR MI 48105

END

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