MOLYBDENUM DISULFIDE AS A LUBRICANT: A REVIEW OF THE FUNDAMENTAL KNOWLEDGE*

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SUMMARY

This report consists of a review and evaluation of the work presented in the literature over the past 40 years on the behavior of MoS_2 as a lubricant. The discussion is concerned with the behavior of MoS_2 as a lubricant, its frictional characteristics, the apparent reasons for these characteristics, and the physical and chemical properties which are important to its use as a lubricant.

The low friction and easy cleavage of molybdenum disulfide is intrinsic to the material and a result of its crystal structure. Although it is clear that the presence of condensable vapors is not required for molybdenum disulfide to exhibit low friction, as it is in the case of graphite, it is true that condensable vapors play an important role in determining the friction and wear characteristics of a lubricant film of MoS_2. The presence of oxidizing agents, particularly water vapor and oxygen, tends to reduce the wear life of the MoS_2 film. This is particularly true in the case of burnished films. Although a great deal of knowledge exists concerning the behavior of molybdenum disulfide as a lubricant, there are still voids in our understanding of this subject.

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INTRODUCTION

The use of molybdenum disulfide as a dry lubricant apparently dates back several centuries[1]. It was often mistaken for graphite because of its similar appearance and physical behavior. The use of molybdenum disulfide as a lubricant in the present technology appears in the patent records in 1927[2] where it is suggested as a component mixed with talc, mica, graphite and other materials. In 1934[2] a patent appears in which a "synthetic" molybdenum disulfide is discussed as an additive in lubricating oils or greases and in 1939[2] another patent discusses the use of molybdenum disulfide in combination with other materials including a binder to be employed as a solid-dry-film lubricant. The use of MoS_2 as a dry-film lubricant begins to appear outside the patent literature in 1941[3] where it is first employed as a lubricant in a vacuum. In spite of the fact that its frictional characteristics have been known for some years, the use of molybdenum disulfide as a lubricant has only expanded extensively since the late 1940's.

Because of the importance of molybdenum disulfide as a dry lubricant it has been the subject of considerable research both of a fundamental and applied nature. There are many articles in the literature where the behavior of MoS_2 is reviewed and discussed[4-16,113]. The list of references of original work of both applied and fundamental research with MoS_2 is of considerable length.

The intent of this report is to review and evaluate the literature concerning the behavior of MoS_2 as a lubricant. To this end about 230 publications, covering a period of over 40 years, have been read and compared. Of these, approximately 100 publications seem to contain pertinent information on the fundamental behavior of MoS_2 as a lubricant. The discussion presented here is concerned principally with the information in these publications which pertains to the behaviour of MoS_2 as a lubricant; its frictional characteristics, the apparent reasons for these characteristics, and the physical and chemical properties which are important in the use of it as a lubricant.

The applications and methods of application of MoS_2 as a lubricating medium are numerous and no attempt will be made to discuss them in detail. This type of information is available in the previously mentioned review papers[6,7,8,10,12,15,16]. Suffice to point out that there are few types of lubrication where MoS_2 has not been employed as a lubricant. It has been used alone by simply rubbing it on the surfaces to be lubricated. It has also been used as a component in dry lubricants which can be either applied singly or bonded to the surface with either an organic or inorganic binder. It is used as an additive agent in both greases and oils as well as in the form of solid compressed pellets. It can even be used as a surface coating for hydrodynamic or hydrostatic bearings thereby acting as a reserve lubricant should the intended means of lubrication fail.

MECHANISM OF FRICTION IN MOLYBDENUM DISULFIDE

Although molybdenum disulfide has long been known to exhibit a low coefficient of friction, the reason for this behavior has been the subject of much research and speculation. Because of the similarities between MoS_2 and graphite the early scientists mistook one for the other, and, in recent years, some scientists have at

times attempted to explain the behavior of one in terms of the other. This has been particularly true in trying to explain the frictional behaviour of MoS_2. To date there appears to have been three major schools of thought on the mechanism of friction in molybdenum disulfide and in two of these there appears to be a tendency to base conclusions on the behavior of graphite as much as on the known information about MoS_2. At first glance this seems to be true of the third school of thought as well. However, there is adequate documentation to show that the same conclusions were arrived at for both graphite and MoS_2 quite separately. The three mechanisms used to explain the frictional behavior of MoS_2 are, briefly, (a) the easy cleavage, and hence low friction, is intrinsic to the crystal structure of the material, (b) the low friction is dependent on adsorbed molecules between crystallites and (c) the frictional behavior is dominated by the forces acting between individual crystallites with cleavage taking place along grain boundaries as opposed to cleavage between the layers in an individual crystal. At present the mechanism which has the most experimental support is the first; namely, the mechanism which explains the friction behavior in terms of the intrinsic nature of the crystal structure.

Intrinsic cleavage mechanism

The suggestion that the easy cleavage of MoS_2, was due to its crystal structure was first made by DICKINSON AND PAULING[17] in 1923 when they investigated and reported the crystal structure of the material. The details of the crystal structure will be discussed in a later section. They noted that the crystal was made up of lamina each consisting of two layers of sulfur atoms separated by a layer of molybdenum atoms and that the distance between the sulfur atoms of one lamina and those of the next was actually greater than the thickness of the lamina itself. The distance between the sulfur layers of one lamina and the next was actually larger than would be expected by the concepts of atom packing and the known sizes of the atomic radii at that time and hence led them to state that this large distance was undoubtedly connected with the excellent basal cleavage of the molybdenite. Hence, the easy cleavage and low friction characteristics of the molybdenite were intrinsic to the crystal structure. It is interesting to note that two years later BRAGG[18] in a speech before the Royal Institution suggested that the good lubricating qualities of graphite were due to the "flaky" nature of the layered crystal structure of graphite. Hence, the relating of the crystal structure to the frictional characteristics of molybdenum disulfide and graphite was done at about the same time and independently. As will be seen, the parallel between molybdenum disulfide and graphite has at times apparently been carried to the extreme and led to misleading concepts of the behavior of molybdenum disulfide.

Those wishing to put forth some explanation of the mechanism of friction in molybdenum disulfide other than that of cleavage within the crystal often refer to FINCH[19] in support of their argument that shearing along the basal plane is unreasonable because of the forces required to shear simultaneously all the bonds between the layers. However, FINCH[19] mentions this particular point only in a footnote (p. 794), of a relatively long paper which is itself the record of a general lecture (the Guthrie Lecture) presented before the Physical Society. In this footnote he groups mica, graphite, and molybdenum disulfide together as layer-lattice solids and then draws his conclusion that the basal crystal cleavage cannot be responsible for the low fric-

tion of these materials because of the data and demonstrations mentioned "earlier in this lecture". However, the "earlier" demonstrations and data are only in connection with graphite and mica and not with molybdenum disulfide. Since the interplanar π electron binding in graphite is large[20] relative to that in molybdenum disulfide, it would seem that his conclusion ("Thus the ability of layer-lattic cleavage surfaces to slide easily over each other is due to adsorbed layers") is reasonable for these two materials but not for MoS_2. The importance of the adsorbed layers in the friction of graphite had, of course, already been demonstrated two years earlier by SAVAGE[21]. This footnote by FINCH[19] is apparently the first suggestion in the literature that the frictional properties of MoS_2 were due to adsorbed vapor layers.

A detailed description of how slip takes place within the MoS_2 crystal is given by AMELINCKX[99] in terms of dislocation theory. He indicates that two types of dislocations or stacking faults take place, the MoS-glide as well as the SS-glide. Low energy stacking faults are associated with SS-plane glide and high energy stacking faults are associated with MoS-plane glide in the crystallite; (see also ref. 108).

Adsorption mechanism theory

A second school of thought on the frictional mechanism of MoS_2 concludes that the low friction of MoS_2 is the result of adsorbed layers of some foreign material on the MoS_2 crystal surface which weakens the structure. The possibility of such a mechanism was apparently first suggested by FINCH[19] as mentioned above. It was an obvious hypothesis to investigate in view of the work of SAVAGE[21] showing the effect of adsorbed vapors on graphite and the general tendency to draw a parallel between graphite and MoS_2. However, in 1952, FENG[7] in a discussion of the friction properties of MoS_2, states that the lubricating properties of MoS_2 have been found to be independent of adsorption films by referring to a private communication from SAVAGE as the basis for the statement. Then, in 1954, SAVAGE[22] reports some experimental work on the friction of MoS_2 in a vacuum ($5 \cdot 10^{-5}$ mm Hg) and states that the behavior is independent of adsorbed films.

Although there was published information to the contrary[7,22], the adsorption mechanism as suggested by FINCH[19] was investigated[9,23]. The work, which was performed in a vacuum of 10^{-6} mm Hg with an acetone–dry ice trap and an oil diffusion pump, showed that an increase in the coefficeint of friction occurred upon resumption of sliding if the sliding surfaces were allowed to rest with no relative motion for a period. Upon resumption of the sliding, the friction force went through a transient decreasing to the same steady-state value in each case. Although this friction transient was the only observation made, the conclusion was drawn that the friction mechanism in MoS_2 was due to an adsorbed layer of amorphous sulfur which was generated during the sliding process and then desorbed by the vacuum. It was postulated that a dynamic equilibrium existed between the rate of sulfur generation due to sliding and the rate of sulfur desorption into the vacuum and that during sliding the sulfur layer was sufficient to lubricate the MoS_2 layers. However, during the non-sliding period the sulfur was desorbed and hence the high friction at the beginning of sliding. Similar behavior was observed with WS_2[24,25] and for molybdenum diselenide[26]. However, investigations employing radiotracer techniques[27] indicate that the friction transients observed were probably not the result of an amorphous sulfur layer. It has also been pointed out by BRAITHWAITE[32] (p. 163) that the amorphous sulfur layer theory

is unacceptable because free sulfur is not detected when outgassing MoS_2 even up to 1000°C.

The adsorption theory suggests that the friction of MoS_2 should increase at still higher vacuum where the contaminant layer would be desorbed. This led to the investigation of the proposed sulfur layer theory by other laboratories at higher vacuum[28,29]. They found that the coefficient of friction decreased as the vacuum was increased, and that no transients were observed at a vacuum of 10^{-9} mm Hg. They have also shown that the friction transients occur in vacuums of 10^{-6} mm Hg, as reported, but that these transients are probably due to the increase of friction caused by the adsorption of contaminants on the MoS_2 in these lower vacuums. As will be discussed later, adsorption on MoS_2 does play an important role in its frictional behavior but the adsorbed layers do not decrease the friction but rather increase it. In fact, it now seems quite reasonable[28,29] to conclude that the more contaminant-free MoS_2 is, the lower the coefficient of friction and hence the friction characteristics of MoS_2 are intrinsic to the material as was originally suggested by DICKINSON AND PAULING[17].

Intercrystallite slip mechanism

The third mechanism hypothesized to explain the friction of MoS_2 is that of intercrystallite slip. It was postulated in 1958 by DEACON AND GOODMAN[30,31], and is apparently also held by BRAITHWAITE[32]. In both cases it seems to have been based primarily on their ideas about the behavior of graphite. Briefly, this hypothesis asserts that the high energy edge surfaces of the crystallites react rapidly to form stable oxides which have weak attraction for both the low energy cleavage surfaces and other edge surfaces, and that this results in weak intercrystallite adhesion and low friction. The principal difficulty with this theory, in addition to having relatively little experimental support in general, is that it is unable to explain variation of the coefficient of friction with crystal orientation. It is known[7] that the minimum friction occurs when the basal plane is parallel to the sliding surfaces and maximum when the basal plane is perpendicular to the sliding surfaces, contrary to what would be expected from the above hypothesis. It is also unable to explain the orientation of the crystals found on the surface after rubbing as observed by electron diffraction[7]. These difficulties in the application of this theory have been pointed out elsewhere[33].

CRYSTAL STRUCTURE OF MOLYBDENUM DISULFIDE

As mentioned above, the lubricating characteristics of molybdenum disulfide are principally the result of its crystal structure, which for natural molybdenite was first investigated and reported by DICKINSON AND PAULING[17]. It is hexagonal with six-fold symmetry, a layered type of structure and two molecules per unit cell, Fig. 1. Each sulfur atom is equidistant from three molybdenum atoms and each molybdenum atom is surrounded by six equidistant sulfur atoms at the corners of a triangular prism whose altitude is 3.17 ± 0.1 Å and whose edge is 3.15 ± 0.02 Å. The distance between molybdenum atoms and the nearest sulfur atoms is 2.41 ± 0.06 Å, (Fig. 2). However, the distance between the two adjacent sulfur layers is 3.49 Å which is greater than the thickness of the layers themselves. DICKINSON AND PAULING state that "the great distance between the sulfur atoms is undoubtedly connected

with the excellent basal cleavage of molybdenite". Hence, it seemed obvious at that time that the low friction of molybdenite and, therefore, its lubricating qualities were the result of its crystal structure.

It is clear from the crystal structure why molybdenite is called a layer-lattice material. However, the layer lattice of MoS_2 is different from that of graphite with which it is often compared. In the case of MoS_2 the important layers are made up of
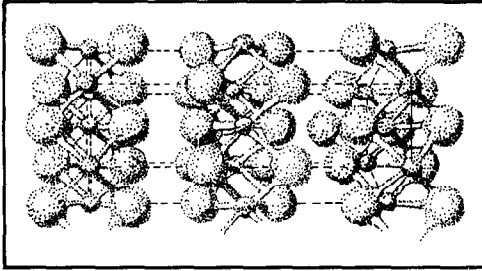

Fig. 1. The structure of molybdenite, MoS_2, (after PAULING, from Chap. 9 of KILLEFFER AND LINZ[1], p. 96). The small spheres represent molybdenum atoms, and the large spheres sulfur atoms. Each molybdenum atom is surrounded by six sulfur atoms at the corners of a triangular prism.
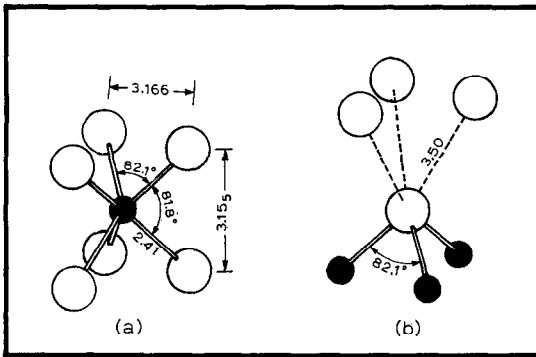

Fig. 2. Atomic coordination in MoS_2, (after TAKEUCHI AND NOWACKI[37]). (a) Configuration of MoS_6 trigonal prism; (b) surroundings of sulfur atom. Mo and S are respectively shown by solid and open circles.

the MoS_2 molecules and are three atom layers thick. Although these layers have strong covalent bonding within them, the bonding between the layers is of the weak van der Waals type. It is along this plane of weak bonding that the shearing takes place resulting in the low friction. Graphite, which also has a layered type of structure, has relatively large Coulombic attractions between the layers which are the result of the interplanar π electron pair distribution[20].

Except for some investigations confirming the findings of DICKINSON AND PAULING, little is reported on the crystal structure of the MoS_2 system until 1957 when BELL AND HERFERT[34] report finding the rhombohedral structure in a high-purity synthetic MoS_2. In this configuration the a axis is the same as that in the hexagonal form but the c axis is one-and-one-half times that in the hexagonal form resulting in three molecules per unit cell instead of two. The interatomic distances are about the same in the two crystals forms and they are both of the layer-lattice type. BELL AND HERFERT[34] interpret their X-ray diffraction patterns in a fashion which results in one
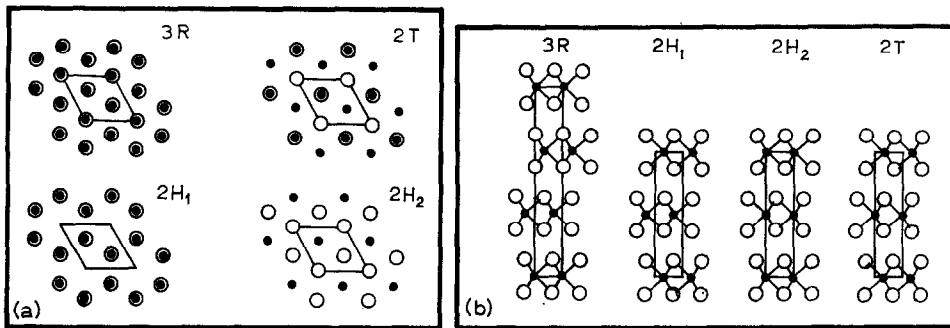
Fig. 3. Projections of MoS_2 crystal polytypes, (after TAKEUCHI AND NOWACKI[37]). (a) Structures of simple polytypes projected along the c-axis; (b) structures of simple polytypes projected along the a_2 axis. Note: Figs. 3(a) and (b) can be thought of as plan and elevation views respectively of the various MoS_2 simple polytype structures if the MoS_2 platlet were resting with its base plane on a horizontal plane. The solid circles represent the molybdenum atoms and the open circles represent the sulfur atoms. In Fig. 3(a) a solid circle inside an open circle represents the Mo and S atoms situated one above the other.

layer of sulfur atoms within an S–Mo–S layer to be rotated 60 degrees relative to the other leaving the molybdenum atom in the octahedral site between the sulfur layers. This has been shown to be incorrect independently by JELLINEK et al.[35] and SEMILE-TOV[36]. The correct structure for the rhombohedral material is shown in form 3R of Fig. 3. It is seen that the lattice is built up of the same type of layers, with trigonal–prismatic surrounding of the metal, as in the hexagonal form. However, in rhombohedral MoS_2, all layers are in parallel orientation, neighboring layers are related by translation only. This arrangement still results in the six and three-fold symmetry as well as the two and three molecule unit cells observed in the hexagonal and rhombohedral crystals forms respectively.

There have been several additional studies of the crystal structure of both natural and synthetic MoS_2; cf. WILDERVANCK AND JELLINEK[100] and TAKEUCHI AND NOWACKI[37]. The most complete and definitive of these studies appears to be that of TAKEUCHI AND NOWACKI[37] in which they report the single-crystal X-ray diffraction investigation using Fourier methods on a rhombohedral form of natural MoS_2 found in Switzerland. The crystal was found to have a trigonal prismatic coordination of the Mo atoms similar to that reported by DICKINSON AND PAULING[17]. TAKEUCHI AND NOWACKI, in the same article, report the findings of a theoretical analysis of the possible simple polytypes which should be expected in the molybdenite system. Polytypism in crystal structures is the phenomenon of different stacking orders of the layers within a given crystal system and has been found to be common in inorganic systems. They report[37] that there should be four simple polytypes in the MoS_2 system, all of which have the trigonal prismatic coordination of the molybdenum atom between the sulfur layers with the polytypism resulting from the different stacking of these S–Mo–S lamina. The four polytypes consist of a rhombohedral (3R), two hexagonal (2H₁, 2H₂) and one trigonal (2T)*. The projections of the atoms for these

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* R, H, and T stand for the basic crystal structures rhombohedral, hexagonal, and trigonal respectively. The coefficient represents the number of molecules per unit cell and the subscript is used to distinguish between different arrangements within the same class of crystal structures. For example the 3R is a rhombohedral structure which has three MoS_2 groups in the unit cell or fundamental repeating unit of the crystal lattice.

four polytypes along the c axis and a_2 axis are shown in Figs. 3(a) and (b) respectively. To date, only two of the possible simple polytypes have been definitely identified. They are the 3R and 2H₁. The 2H₁ is the hexagonal form ordinarily found in nature and the 3R is the rhombohedral form which has been found both in synthetic material by BELL AND HERFERT[34], JELLINEK et al.[35,100], RODE AND LEBEDEV[44], and in nature by TRAILL[38] in the Mackenzie District of Canada, GRAESAR[39] in Switzerland and CLARK[40] in Portugal. The sample studied by TAKEUCHI AND NOWACKI[37] was found and reported by GRAESAR[39]. The hexagonal form 2H₁ has been found in synthetic materials as well as in nature[41-44,100]. The existence of polytypism in the MoS_2 system was suggested by SEMILETOV[36] and ZELIKMAN et al.[43] in their work on both natural and synthetic MoS_2.

STUBBLES AND RICHARDSON[42] have synthesized MoS_2 and have observed the hexagonal structure which had previously been found only in the natural MoS_2. They claim to have seen the hexagonal pattern appearing when the material was heated to 400°C, but upon heating to 1200°C the material showed complete hexagonal structure. RODE AND LEBEDEV[44] in studying the decomposition of MoS_3 to MoS_2, state that the crystallization of the MoS_2 takes place in two stages. First, the rhombohedral structure appears and then as the temperature is increased to 600°C for five days the hexagonal structure begins to appear. JELLINEK[101] has also extensively studied the rhombohedral and hexagonal forms and has observed that the direct decomposition of MoS_3 leads to the hexagonal form of MoS_2 (with considerable stacking disorder) even at temperatures as low·as 425°C. He indicates that synthetic hexagonal MoS_2 generally possesses considerable stacking disorder as well as a texture different from natural molybdenite which has mislead some investigators.

SEMILETOV[36] states that the MoS_2 he synthetized below 900°C gives X-ray powder diffraction patterns with broad peaks and that, in general, the lower the temperature of synthesis the broader are the peaks. These broad poorly defined peaks do not fit either the hexagonal form or the rhombohedral form and are, in general, similar to those associated with mixed or disordered stacking in layered structures. Above 900°C the peaks become relatively sharp and show the hexagonal pattern. Once the hexagonal form is reached in the synthetic material it appears to be stable and does not change to the rhombohedral structure or any intermediate form even with prolonged heating up to the decomposition temperature.

MORIMOTO AND KULLERUD[45] believe that the rhombohedral form is metastable throughout the entire temperature range and that the hexagonal structure is the stable form of the system. However, the question of which sequence of stacking is the stable one in a system displaying polytypism is not resolved[46]. In fact, if the sequence of stacking is not unique, an infinite number of polytypes is possible in the theoretical sense[37]. Because of the known existence of two polytypes, the possible existence of many, and the fact that each polytype will give a different diffraction pattern, the interpretation of X-ray diffraction data should be approached with great caution by the investigator lacking a thorough training in this field.

Although these different polytypes give different diffraction patterns, the macroscopic physical properties of the various forms would not be expected to be significantly different because of the common layered structure. TAKEUCHI AND NOWACKI[37] report similar densities of the two known types. WILDERVANCK AND JELLINEK[100], in discussing the mechanism of crystal growth, indicate that when

obtaining MoS_2 from a melt preparation the initially formed crystallites are relatively isolated from each other. In such a circumstance these crystallite germs are planar and tend to grow only in the plane. By a simple screw dislocation the foil can grow on top of itself in a spiral fashion with parallel orientation (*i.e.* rhombohedral structure). Accordingly, the crystals of the rhombohedral form are, in general, more perfect and larger than the hexagonal crystals grown under the same conditions. This allows the rhombohedral form to be separated from the hexagonal by sieving[100]. BELL AND HERFERT[34] also report similar densities and state that their investigations showed no detectable differences in the lubricating properties of the synthetic rhombohedral and natural hexagonal MoS_2. The similarity of the frictional characteristics of the synthetic and natural forms of MoS_2 is also reported by several other authors [43,47–49,57,58]. This would be expected from considerations of the crystal structure alone, but, because the importance of surface chemical phenomena on the film-forming characteristics of MoS_2 on metal substrates, it is not surprising that differences between the natural and synthetic materials are reported in at least two instances. In studying the frictional behavior of a hexagonal form of synthetic MoS_2, it is reported that[41] the synthetic material is inferior to the natural MoS_2 where the lubricating film is formed by burnishing on a steel surface but that they have similar frictional behavior when used in an oil or grease. In studies of the frictional behavior of MoS_2 in vacuum, FLOM[50] states that the friction of synthetic MoS_2 (the same material as that produced and studied by BELL AND HERFERT) at atmospheric pressure and 10^{-6} mm Hg is the same as that of the natural material but that the friction of the synthetic material is as much as three times that of the natural material at 10^{-9} mm Hg. These differences warrant, and are receiving, further investigation.

THE BEHAVIOR OF MOLYBDENUM DISULFIDE AS A LUBRICANT

In the following part of the report, the lubricating behavior of MoS_2 as a function of the various physical and chemical aspects of its environment will be discussed. The physical and chemical properties of MoS_2 which are of importance to its application as a lubricant will also be discussed. The order of presentation is not significant but is based to some extent on the importance of the various influences to lubrication. Unless otherwise specified the information reported in this section was obtained with natural MoS_2.

The effect of water vapor and other condensable gases
As stated earlier, the low friction of molybdenum disulfide is intrinsic to the crystal structure and, unlike graphite, not dependent on the presence of condensable vapor. In fact, it has been shown that the friction of MoS_2 decreases when condensable vapors are removed from the atmosphere. Nevertheless, condensable vapors, and, in particular, water vapor have a significant effect on the functioning of MoS_2 as a lubricant. The first report of the effect of relative humidity on the friction and wear of MoS_2 is that of PETERSON AND JOHNSON[51]. An investigation of this was logical because of the earlier work of SAVAGE[21] showing the dependence of low friction in graphite on condensed water vapor. SAVAGE[22] reported that the frictional behavior of MoS_2 was not dependent on the presence of water vapor.

In their work, PETERSON AND JOHNSON[51] show that, with increasing relative

humidity, the friction between metal surfaces lubricated by MoS$_2$ increased up to 65% R.H. and then decreased. They found substantially the same results for either bonded or unbonded films. Since the time of these investigations considerable effort has been expended to more fully understand the role of condensed vapors in the frictional behavior of MoS$_2$. MIDGLEY[47] reports the results of a study of the effect of humidity, temperature, and rubbing time on the friction of a natural MoS$_2$ powder rubbed on surfaces. He observed the same effects that others had observed for natural MoS$_2$ and suggests that the frictional resistance of MoS$_2$ is largely controlled by the moisture content of the film. He shows that the friction decreases with increasing temperature and decreasing relative humidity as well as with rubbing time in an atmosphere with a given relative humidity. He interprets the results on the basis of decreasing moisture content in the film which causes a reduction in the coefficient of friction. He also suggests that this type of interpretation can be used to explain the observations of PETERSON AND JOHNSON cited above and those of JOHNSON et al.[52] who found that the friction decreased with increased sliding speed and those of BAR-WELL AND MILNE[53] who observed that the friction decreased with increasing load.

MIDGLEY's interpretation has now been substantiated by the work of GÄNS-HEIMER[54] and BARRY AND BINKELMAN[55]. GÄNSHEIMER has shown that the effect of load on the friction of a burnished film is really the effect of moisture content of the film which changes because of the frictional heating of the film. His results, Fig. 4, show that the effect of load on the coefficient of friction is essentially nonexistent when the relative humidity of the atmosphere is low. GÄNSHEIMER's work was on steel surfaces and he reports similar results were obtained with "organic vapors such as those of alcohols, acetones or hydrocarbons".

BARRY AND BINKELMAN[55] investigated the effects of speed, load and relative humidity on the friction characteristics of MoS$_2$ on substrates of several metals
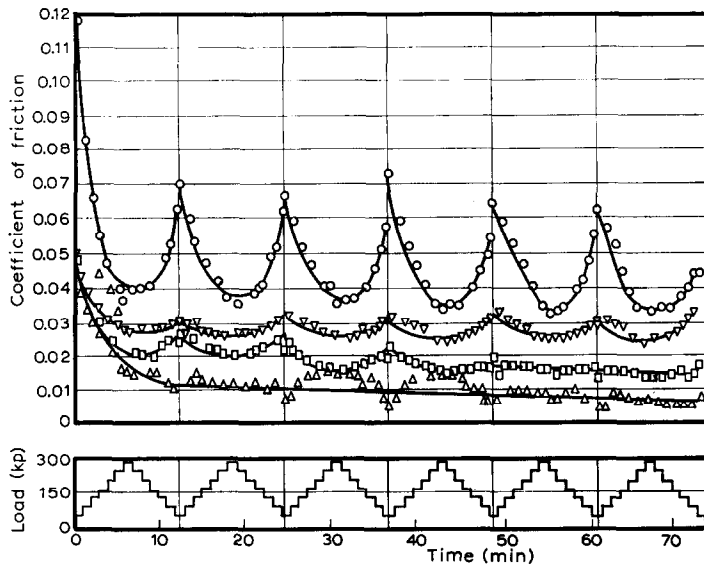

Fig. 4. Effect of humidity and load on the coefficient of friction of molybdenum disulphide, (after GÄNSHEIMER[54]). Relative humidity (%): ○ = 16.2; ▽ = 6.5; □ = 0.12; △ = 0.

varying in hardness from 99 to 882 on the Vickers Diamond Hardness scale. The speed range investigated was from approximately 0.012 to 2.35 in./sec and the load range from 50 to 250 lb. for an average pressure of from 220 to 1085 p.s.i. The metals also represent both reactive and nonreactive surfaces. Their results show that the friction of the MoS_2 film decreases with both increasing load and increasing speed only when moisture is present, and that in a dry atmosphere the variation of friction with speed, load, or substrate hardness is virtually nonexistent in the range of variables investigated. A summary of their results is shown in Fig. 5. These results of both GÄNSHEIMER and BARRY AND BINKELMAN are for rubbed-on films of natural MoS_2.

The essential conclusion of the above is that the absence of a condensable vapor reduces the friction of an MoS_2 film. This has been shown by other methods as well. HALTNER AND OLIVER[56,109] have shown that water vapor in a nitrogen atmosphere caused an increase in the coefficient of friction of compressed pellets of MoS_2 rubbing against the transferred film of MoS_2 on a metal surface. Changing the atmosphere to dry nitrogen causes a sudden drop in the coefficient of friction. Toluene and n-heptane in a nitrogen atmosphere had the same effect except the decrease of friction upon changing to dry nitrogen was not as sudden. In two papers, FLOM, HALTNER AND GAULIN[28] and HALTNER[29] have shown that the coefficient of friction of MoS_2 films formed from compacts rubbed on copper surfaces decreases with increasing vacuum. They have clearly shown that the presence of condensable vapors only serves to increase the intrinsically low coefficient of friction of MoS_2.

SALOMON et al.[57,58] have studied the behavior of rubbed MoS_2 films in various atmospheres with particular emphasis on the wear life of the film. They have studied the wear life of rubbed films of MoS_2 on the surfaces of glass and steel. By following a consistent procedure for the application of the film they were able to obtain consistent reproducibility of the wear life of the film. They define the wear life of the film as the "smooth running period" which occurs between the end of run-in and the beginning of failure as indicated by an erratic friction force. They find that the wear life of the film defined in this manner is also a function of the relative humidity at the surface of the specimen.

In these studies motion pictures were taken of the MoS_2 film which show the formation of blisters in the film. The film failure (end of smooth running period) is accompanied by the breakup of these blisters which leave the bare metal exposed. Long periods of smooth running and no wear were obtained with MoS_2 on steel and glass surfaces. The length of the periods depends on the oxygen and water vapor content of the atmosphere. The film life in dry oxygen was about three hours compared to six hours in dry air and more than a week in dry argon. Even 2% oxygen was found to decrease the wear life considerably.

It has been found that both oxygen and water vapor react instantaneously with the mechanically activated surface[56,57]. In a neutral atmosphere (nitrogen or argon) with water vapor present, hydrogen sulfide is given off and molybdenum oxides and oxide hydrates are formed. However, in an atmosphere containing both

Fig. 5. The effects of load, speed, and moisture on the friction of burnished MoS_2 films on various substrates, (after BARRY AND BINKELMAN[55]). (a) Effect of speed on MoS_2 friction coefficient; (b) effect of speed on MoS_2 friction coefficient; (c) effect of load on MoS_2 friction coefficient; (d) effect of load on MoS_2 friction coefficient. TZM is an alloy containing 0.5% titatinum, 0.08% zirconium and the balance of molybdenum. Based on the geometry of the test specimen, the range 1–200 rev./min represents an average speed of approximately 0.012–2.35 in./sec.
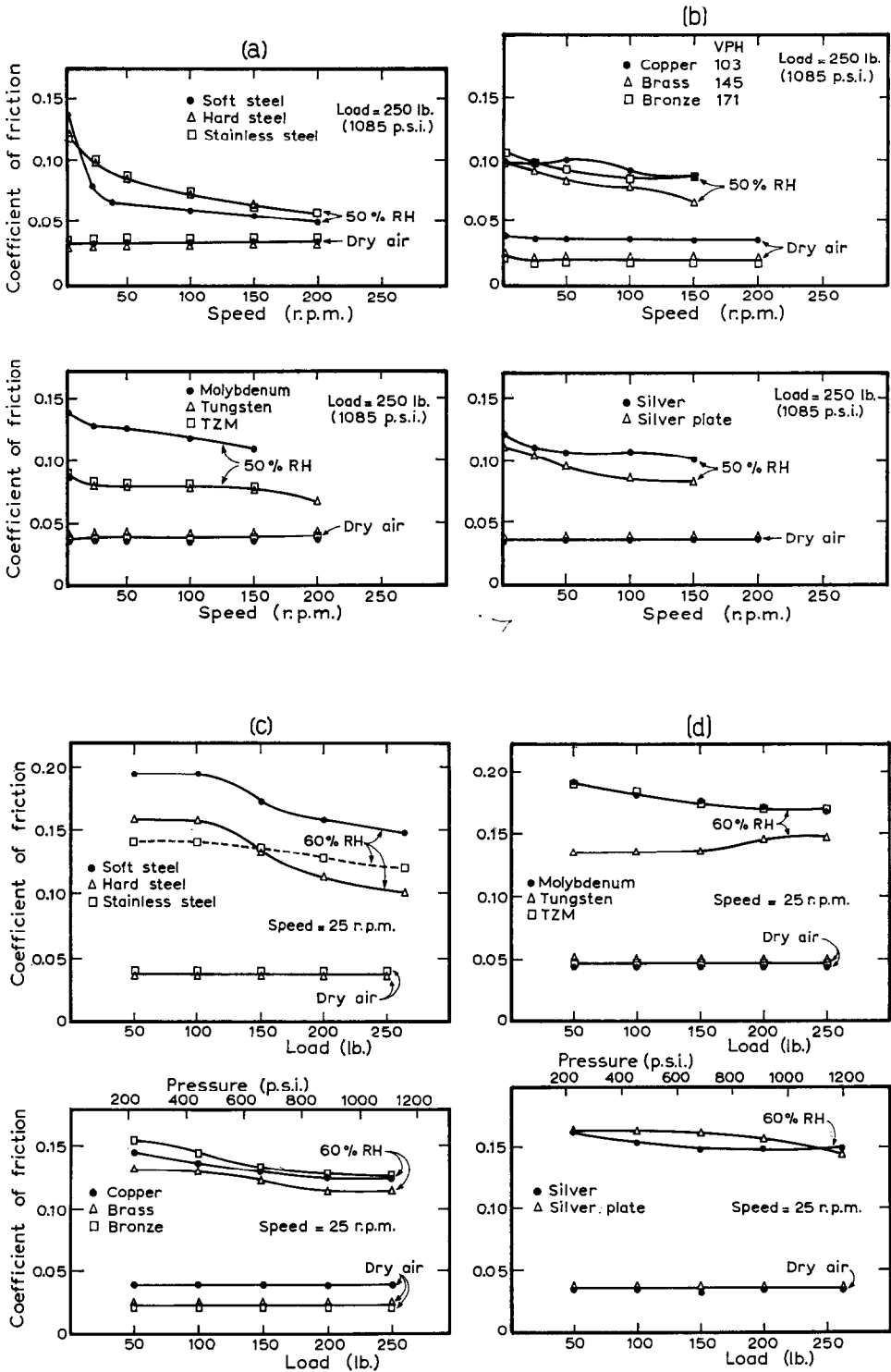
water vapor and oxygen, no H_2S is formed; the principal products are molybdenum oxides and elemental sufur. In a dry atmosphere no H_2S is given off[57].

A recent investigation reported by JOHNSTON AND MOORE[59] on the effect of water vapor on the density of burnished MoS_2 films should have significant influence on future work with rubbed-on films of MoS_2. They studied the burnishing of MoS_2 films on copper surfaces under controlled conditions, measured the film density by X-ray fluorescence techniques, and found that the density of the film increased with relative humidity, surface roughness, load on the burnisher, and the number of of strokes. Changing the relative humidity of the atmosphere from 6 to 85% could increase the film density by a factor of seven or eight with the other variables remaining constant. Hence, the relative humidity at the time of film formation could have a significant effect on the wear life and friction of unbonded films and should be taken into consideration in all future investigations.

The adsorption of benzene and water vapor by MoS_2 has been studied by BALLOU AND ROSS[60]. They found that MoS_2 powder which has been heated to 110°C was covered with a layer of MoO_3. The MoO_3 was found to be hydrophilic and when this layer was removed by a treatment with ammonium hydroxide the oxide-free surface of the MoS_2 was hydrophobic. The amount of water vapor adsorbed is proportional to the extent of surface oxidation. Apparently no work has been done on the frictional characteristics of MoS_2 if the surface oxide layer is removed. In the light of this and the above cited work, an interesting question can be raised. Namely, how important is the surface oxide of MoO_3 to the friction and wear of unbonded films of MoS_2? Apparently no work has been done along these lines. (The possible role of a surface oxide layer should not be confused with that of bulk oxide content in the film which is known to reduce the effectiveness of the MoS_2 lubricating qualities (cf.[102]).)

There is little doubt, in the light of the above, that the effect of moisture content in the film accounts for much of the conflicting friction data in the literature.

The effect of reducing (hydrogen) and inert (nitrogen) environments at 1200°F on the lubricating ability of MoS_2 with several substrate materials was studied by AMATEAU, KRAUSE et al.[61]. No significant difference in either the sliding friction or wear was detected. The stability of MoS_2 in hydrogen and nitrogen environments at high temperature has been studied by ECKERT[62]. He defines a "critical temperature" as that temperature at which 1% of the MoS_2 is decomposed after exposure to a stream of the gas for 30 min. The critical temperatures are 715°C in hydrogen, 870°C in hydrogen–nitrogen (20:80 vol.%), and 985°C in hydrogen–nitrogen (12:88 vol. %).

BRAITHWAITE[32] (p. 156–57) indicates that MoO_2 is formed when MoS_2 is heated in the presence of carbon dioxide. This reaction is very slow for temperatures between 200 and 500°C. In sulfur dioxide at temperatures from 800°C to 1100°C MoS_2 reacts to form MoO_2 and elemental sulfur. Below 800°C only a trace of MoO_2 can be detected on the particle surfaces. GRATTAN AND LANCASTER[111] have shown that MoO_2 is very abrasive.

The effect of load (or pressure) and sliding speed

The effect of load or film pressure and sliding speed on the friction of MoS_2 has been studied by several people and, as stated above, it is now thought that changes in friction with load or speed are actually the result of a changing moisture content in the film. This seems to be clear from the work cited above where the coefficient of

friction in a dry atmosphere remained constant for changes of load, speed, and substrate hardness.

The coefficient of friction of MoS_2 as a function of load was first measured by BOYD AND ROBERTSON[63] in an opposing anvil-type device. They found that the coefficient of friction of MoS_2 decreased with increasing load up to a pressure of 600,000 p.s.i. (40,000 atm.) at which pressure it was 0.032 and had the lowest coefficient of friction of any material tested. HYDE[64] measured the coefficient of friction of Molykote Z (principally MoS_2) in an opposing anvil-type device and found that the coefficient of friction at low pressures was 0.06 and then, with increasing pressure, it decreased to 0.04 and remained constant to a pressure of 70,000 atm. JOHNSON et al.[52] reported the change of coefficient of friction of MoS_2 films with a change of load. They found a slight increase of the coefficient of friction with load at low loads and then a constant value with continually increasing load. They employed a hemispherical slider on a flat plate, which, it is suggested by MIDGLEY[47], will cause an increase of the shearing area with increasing load. This increase of shear area in turn causes the increase in friction, a relation which was shown by PETERSON AND JOHNSON[51]. The fact that the effect of load on the coefficient of friction was actually related to the moisture content of the film was first suggested by MIDGLEY[47] in 1956 but this relationship was not established conclusively until the independent work of GÄNSHEIMER[54] and BARRY AND BINKELMAN[55] in 1964 and 1965 respectively.

The effect of sliding velocity on the coefficient of friction of MoS_2 has a history similar to that of load discussed above. However, the data are not as extensive in this case. The decrease of friction with increasing speed was first observed by JOHNSON et al.[52] in 1948 and the suggestion that it is tied to the moisture content of the film via frictional heating by MIDGLEY[47] in 1956. The relationship was established by BARRY AND BINKELMAN[55] in 1965. In the absence of condensable vapors the friction is constant with varying sliding speed. The fact that the friction variation with sliding velocity is related to the presence of condensable vapors is also shown by the work of HALTNER[29].

The effect of load and sliding speed on the life of rubbed unbonded films of MoS_2 is discussed by SALOMON et al.[58]. They state that in the range of their investigations the wear life was not greatly affected by the load–speed product over a wide range of loads and speeds. The wear life was affected only at very low loads and high speeds, when the wear life seemed to increase, and at high loads and very low speeds in which case the wear life is reduced because of the reactivity of the atmosphere. The wear life discussed here is based on the "distance traveled" by the slider on the disk and not in time as mentioned previously.

The effect of temperature

The effect of temperature on the frictional characteristics of MoS_2 can be roughly divided into three categories from the standpoint of applications. They are cryogenic, normal, and high temperature applications. For the purposes of discussion, these three temperature ranges can be established as being from absolute zero to zero centigrade, from 0°C to 100°C and above 100°C respectively.

In the 0°C–100°C range the friction of the MoS_2 film is affected by temperature via the moisture content of the film as discussed above, the coefficient of friction decreasing with increasing temperature because of the decreasing moisture

content of the film. The decrease of friction with the increase of temperature has been observed by several investigators including PETERSON AND JOHNSON[65] and MIDGLEY[47]. The range of temperatures where the temperature affects the moisture content of the film, and hence the friction, would be expected to be different for different condensable vapors. DEACON AND GOODMAN[31] also report a decreasing friction with increasing film temperature but they report the effect is observed up to a temperature of 400°C. However, as MIDGLEY suggests, it is unlikely that they had equilibrium conditions in their films during the observations because the films were applied by rubbing from a water solution and then, while continually recording the friction, the films were heated to 400°C in less than 10 min. Hence, the entire experiment probably represents the change of friction in the film while it is drying.

For the cryogenic temperature range very little basic data exist. However, there are reports of the use of MoS_2 as a lubricant in cryogenic systems (cf. ref. 67). One additional consideration for cryogenic applications is the LOX sensitivity of the lubricant. LOX sensitivity, the tendency of the material to detonate when impacted in the presence of liquid oxygen, is measured under specified conditions with the material bathed in liquid oxygen. ZAEHRINGER[66] has reported that MoS_2 is not LOX sensitive and therefore acceptable as a material in cryogenic systems. However, care must be taken to insure that the binder used when forming a resin-bonded MoS_2 film for cryogenic applications is also LOX insensitive. DEVINE, LAMSON, AND BOWEN[67] have shown that films consisting of 71% MoS_2, 7% graphite, and 22% sodium silicate as binder are compatible with liquid oxygen.

With respect to the high temperature application of MoS_2, there is considerable confusion in the literature. Unfortunately, there are publications as recent as 1964 which are still quoting incorrect data on the melting and sublimation temperatures of MoS_2 which date from work done at the turn of the century; work which has been superseded by several other investigators. Probably the best indication of the upper temperature limit for the use of MoS_2 can be seen from the work of SCHOLZ, DOANE, AND TIMMONS[68]. They found that molybdenum metal can be obtained from MoS_2 by direct thermal dissociation by heating the sulfide in a vacuum to 1600°C at which temperature dissociation occurs with the sulfur being evolved as gas and pumped off, leaving the molybdenum. They state that this method can be used for the commercial production of molybdenum. They also state that the dissociation was detected at 1370°C but occurred at a very slow rate. CANNON[69] observes that the sublimation of MoS_2 begins to occur at 1050°C and in attempting to determine the melting point of the material arrives at an estimate of 2375°C. This conclusion seems unlikely in light of the above quoted work of SCHOLZ et al. ZELIKMAN AND BELYAEVSKAYA[70] report that upon heating MoS_2 in a graphite tube under 30 kg/cm² pressure they observe melting accompanied by dissociation at temperatures above 1700°C. Therefore, in the absence of oxygen or water vapor, the upper temperature limit for the use of MoS_2 as a lubricant would be about 1300°–1400°C. The work of AMATEAU, KRAUSE et al.[61] has shown that MoS_2 can be used as a lubricant to temperatures of 650°C (1200°F) in either nitrogen or hydrogen atmospheres.

At high temperatures in the presence of oxygen or water vapor the MoS_2 film will oxidize. ROSS AND SUSSMAN[71] show that, in static tests, in the presence of air and water vapor the outermost S–Mo–S layer of the MoS_2 crystal is oxidized at temperatures as low as 85°C and that this outer layer of oxide protects the crystal from
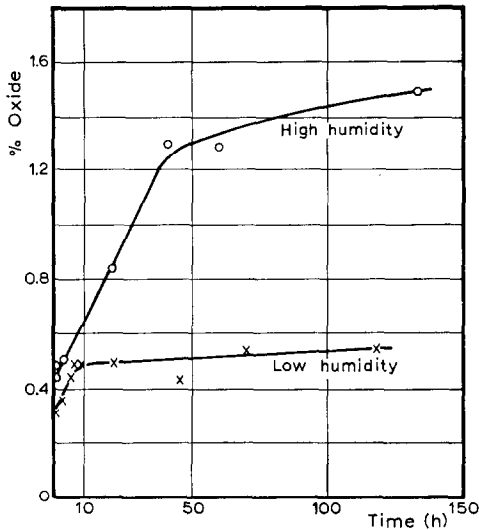
Fig. 6. Rates of oxidation of pulverized molybdenum disulphide at 100° (low humidity) and 85° (high humidity), (after Ross AND SUSSMAN[71]). The lower curve was obtained from analyses of an undisturbed sample in an open dish; the upper curve from a sample constantly tumbled inside an open, wide-mouth bottle. The calculated oxidation of a monolayer is 3.92% MoO_3.

further oxidation at room temperature and greatly reduces the rate of oxidation at 100°C. They show that the oxidation rate in the 85–100°C temperature range is very low and that even in a humid atmosphere at 85°C the oxidation has not proceeded to as much as 50% of the surface layer even after 100 h (Fig. 6). BISSON et al.[72] state that in the presence of air the rate of oxidation of MoS_2 is low at temperatures below 370°C(700°F) and increases with temperature above 370°C. However, they point out that the lubricating effectiveness of the film is not lost because of this oxidation as long as there is some unoxidized MoS_2 in the film. SLINEY[73] investigated the chemical reaction kinetics of powder compacts of MoS_2, WS_2, and several other solid lubricants in air. The oxidation rates of thin layers were estimated at the temperature of interest by X-ray diffraction. The results of his work on MoS_2 compacts with a density of 25% of maximum are shown in Fig. 7. It was found that the oxidation rate followed an Arrhenius type relation with temperature and was also a function of initial particle size of the compacted material and the availability of air as shown. Bulk oxidation rates were determined by analyses of the volatile reaction products. Both MoS_2 and WS_2 oxidized very slowly in air at 315°C (600°F). Below 390°C (730°F) MoS_2 oxidizes more slowly than WS_2 whereas above 390°C (730°F) MoS_2 oxidized more rapidly than the WS_2 of comparable particle size. In static tests the average powder particle sizes within a range of 1–8 μ did not appreciably affect oxidation rates, but submicron powders oxidized more rapidly than did the coarser powders. Although much of the work on oxidation temperatures and oxidation rates of MoS_2 refers to the particle size as the primary variable, it would appear from the work of Ross AND SUSSMAN[71] and BRAITHWAITE[32] (p. 155) that the specific surface, or surface area, is a more important variable affecting the oxidation of MoS_2. In general MoS_2 particles are solid particles with only an external surface, but as a consequence of previous history, porous aggregates can be formed. Therefore there will normally be a one-to-one relation between surface area and particle size.
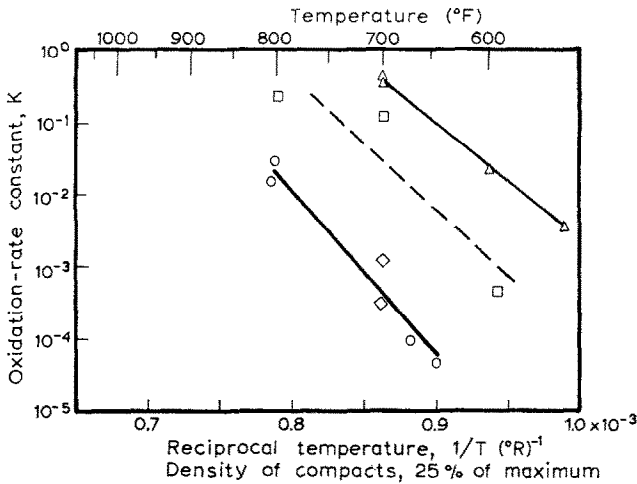
Fig. 7. Arrhenius plot showing effect of particle size and air flow rate on X-ray (surface) layer oxidation-rate constant for MoS₂ power compacts, (after SLINEY[73]).

	△	□	◇	○
Particle size (μ):	0.98	0.98	8	8
Air flow rate (l/min):	2	1/3	2	1/3

The effect of a vacuum environment

One of the first reports of the use of MoS₂ as a lubricant is that of BELL AND FINDLAY[3]. They report the use of MoS₂ as a lubricant in vacuum on the rotating anode of an X-ray tube. Considerable effort has been directed toward studying the frictional behavior of MoS₂ in vacuum since that time. SAVAGE[22] reports that at $5 \cdot 10^{-5}$ mm Hg the friction of MoS₂, unlike that of graphite, is still low and exhibits wear rates comparable to graphite when in the presence of water vapor, where graphite performs the best. JOHNSON, VAUGHN, LAVIK, *et al.*[23-26] report the frictional behavior of MoS₂, MoSe₂, and WS₂ in a vacuum of 10^{-6} mm Hg. They report that the coefficient of friction decreases with rubbing time and after a period of no relative motion the friction, upon resumption of sliding, is again high and again decreases with rubbing time. Their interpretation of this behavior has been discussed in an earlier section of this report. It now seems clear that although their data are valid, their interpretation is incorrect. HALTNER, FLOM AND GAULIN[28,29] have shown that the transients observed are due to the condensation of contaminants from the vacuum system on the MoS₂ film and with continued rubbing these are again desorbed or worn away with the resultant reduction of the friction force. They have shown that in sufficiently high vacuum (10^{-9} mm Hg) the transients do not occur because the time required for the condensed film of contaminants to form is very long. These results are what is expected based on the discussion above concerning the effects of condensed vapors in normal atmospheres. FLOM[50] has indicated that in their work the friction of synthetic MoS₂ (that produced by BELL AND HERFERT[34]) and synthetic WS₂ both exhibit higher friction at 10^{-9} mm Hg than at 10^{-6} mm Hg. These measurements were made on a film of the material transferred on to copper surfaces from compacts. In light of the above discussion of the film-forming abilities of the MoS₂ as a function of relative humidity and the relation between the adsorption of water vapor to the surface oxi-

dation of the crystal, it is possible that the findings of FLOM may eventually be explained in terms of the surface chemistry of MoS_2. This work is continuing.

Some work has been done on the life of a bonded film of MoS_2, graphite, and sodium silicate by DEVINE et al.[74] and CRAIG[75] to vacuums of 10^{-6} mm Hg and 10^{-8} mm Hg respectively. DEVINE et al. report that the lubricant performed satisfactorily at temperatures to 540°C (1000°F) for up to five days at which time the test was terminated. CRAIG reports that in the temperature range of from −90° to 95°C (−130°–200°F) the lubricant behaved satisfactorily for up to five months with no sign of failure.

The effect of radiation environment

Considerable work has been directed toward determining the radiation stability of solid film lubricants. Most of the work has been performed with compounded bonded films. DEVINE et al.[67] have shown that a MoS_2–graphite–sodium silicate bonded film is resistant to a gamma dosage of $5 \cdot 10^9 R$, (average dosage rate of $4.2 \cdot 10^6 R/h$ for an exposure time of 1187 h). McDANIEL[76] has recently studied the effects of reactor radiation on the high temperature wear life of three bonded solid film lubricants containing MoS_2. The three films contained PbS–MoS_2–B_2O_3 on SAE 4620 steel, PbS–MoS_2–B_2O_3 on nickel-base alloy, and MoS_2–graphite–sodium silicate on nickel-base alloy. The proportions of the compositions were not given. These films were irradiated with gamma and neutron radiation and then the film life was tested at 315°C (600°F), 650°C (1200°F), and 815°C (1500°F). The results indicate that the irradiation caused no significant effect on the wear life of either of the first two films and on the third the irradiation caused a fivefold decrease of wear life at room temperature but an increase of wear life at 315°C (600°F) and 650°C (1200°F). It should be pointed out that the film on which McDANIEL reports a change of wear life due to irradiation is composed of the same materials as the film for which DEVINE et al. report no effect of gamma radiation.

The effect of the substrate

The effect of the substrate on the lubricating behavior of MoS_2 can be divided into several categories, surface finish, surface pretreatment, surface hardness, and surface chemistry.

The effects of surface finish were first discussed by PETERSON AND JOHNSON[51] in 1954. They found that the coefficient of friction of a rubbed film of MoS_2 on a disk whose surface was obtained by grinding varied from 0.1 to 0.25 depending on the direction of sliding relative to the grind marks on the surface. The high value occurred when the slider was moving perpendicular to the grind marks and the low value was observed when the slider was moving parallel to the grind marks. They attribute this to the differing shear areas in the two directions. That is, when the slider is moving perpendicular to the grind marks there is a large shear area because the MoS_2 tends to fill the crevasses and when the slider is moving parallel to the grind marks the shear area is limited to the peaks of the grind marks which are covered with MoS_2. The rubbing parallel to the grind marks does not have a tendency to fill in the crevasses. They have also shown that with constant load, speed, and humidity, and a controlled shear area the friction coefficient increases with shear area. When the relative humidity was less than 6% the coefficient of friction was directly proportional to shear area.

SONNTAG[77] also reports that the surface finish can have considerable influence on the wear life of a bonded-film solid lubricant (although he unfortunately gives no indication of what the lubricant is), and states that a surface finish of 20 μin. r.m.s. will give the optimum wear life for any method of film preparation. SALOMON et al.[58] state that the wear life with a wet-blasted surface to a surface finish of 0.3–0.4 μm center line average (c.l.a.) (i.e., 13–17·10^{-6} in. r.m.s.) was about 13 h for their standard conditions but if the surface finish was improved by a factor of one hundred to 0.004 μm c.l.a. (i.e., about 0.7·10^{-6} in. r.m.s.) the wear life was generally only a few minutes.

From the work of JOHNSTON AND MOORE[59] on the burnishing of MoS_2 films on soft copper surfaces as a function of surface finish, it is clear that at any relative humidity the film density is proportional to the surface finish for the same number of strokes of the burnisher. They have worked in the range 6–100 μm c.l.a. for surface finish and have shown that an increase of one order of magnitude in surface roughness causes an increase in the resultant film density of two in a humid atmosphere (R.H. 84–89%) and an increase of about three in a relatively dry atmosphere (R.H. 4–10%). These conclusions are true only when the number of strokes of the burnisher exceeds 100 and the difference is greater when the number of strokes of the burnisher is less than 100. The difference in relative humidities stated causes a difference in film density of about five times with the more dense film for the higher relative humidity. It is quite possible that this difference in film density with different surface finishes will explain much of the difference in wear life with surface finish reported by SALOMON et al. Although, apparently, no work has been done on the subject, it would seem reasonable to expect that the effects of varying the surface finish will themselves be a function of the particle size of the MoS_2 used.

The effect of surface pretreatment has been studied to some extent in addition to the surface finish work discussed above. MILNE[78] shows that sulfating and phosphating pretreatments of the surfaces are beneficial in that they increase the wear life of bonded MoS_2 films. SONNTAG[77] shows that a combination of sandblasting to a surface finish of 20 μin. r.m.s. followed by a phosphate treatment will give the maximum film life for bonded solid films. DEVINE et al.[79] have shown that "microreservoirs" can be designed into the surface of the substrate for the storage of the solid lubricant and suggest that this is essentially what is happening in the cases of optimum surface finish and phosphate coating described above.

The effects of substrate hardness and surface chemistry on the lubrication with MoS_2 were not well understood. At first sight the information in the literature is often conflicting but upon further study it seems that in all cases the conditions are sufficiently different that it is impossible to compare results and hence impossible to draw any general conclusions. Certainly, further work on the physical and chemical interactions of the substrates and MoS_2 films is desirable in the case of many substrates. In the case of burnished films, SALOMON et al.[58] report most of their work is with a steel pin on a steel disk giving good reproducible wear life and low friction. In tests with a titanium pin on a glass disk with rubbed-on MoS_2, low friction and smooth running was maintained in a dry argon atmosphere for several hours. When the test was repeated with a titanium disk, and in other runs with a molybdenum disk and titanium pin, seizure occurred in less than five seconds. They also state that rubbing a 60/40 brass pin against a MoS_2 covered steel disk gave irregular friction from the

beginning and the experiment only lasted for a short time. They state, "Obviously, such scoring pairs of metals, which have a very short dwell period, cannot be parted effectively by an MoS_2 film for any considerable length of time". Dwell time is that period between the initiation of the test and the first indications of wear. In the case of steel on steel with a burnished MoS_2 film, they report that if the hardness of the pin is reduced below 200 kg/mm^2 or increased above 800 kg/mm^2 the film life is reduced about 30%, but that this effect is small compared to the effect of surface finish. BARRY AND BINKELMAN[55] have also reported work on burnished films with various substrate hardnesses (Fig. 5). In each case both of the rubbing surfaces are of the same material. The test specimens used were washer shaped and loaded in a direction normal to the flats with average pressures to 1100 p.s.i. The hardness varied from 99 to 882 on the Vickers Diamond Hardness scale and the materials represented several different surface reactivities. In a dry atmosphere they observed virtually no difference in friction with hardness and very little difference in a moist atmosphere. Included in the series of metals were brass, bronze, and copper, all of which were lubricated successfully for test durations of two minutes. However, they also tried titanium and aluminum whose hardness values were 163 and 224 respectively, and were unable to eliminate seizure with burnished MoS_2 films. Babbit metal and lead were also tried (VPN hardness values of 37 and 10 respectively) and could not be lubricated. As they point out, the failure of MoS_2 to lubricate aluminum and titanium is related to the poor adhesion of the MoS_2 to these materials and the results reported for unbonded films are not applicable to the case of bonded films on these materials.

Recently KARPE[80] has attempted to study the effects of load and substrate hardness on the friction of MoS_2 films. He attempts to explain his results in terms of substrate deformation but there is reason to doubt his conclusions because of the added effects of film moisture content and crystallographic orientation, both of which are covered in the "discussion" of this paper[80] by GÄNSHEIMER, and SALOMON AND DE GEE

For the behavior of compressed pellets of MoS_2 rubbing on various metals the works of HALTNER AND OLIVER[81] and LANCASTER[102,110,111] are of value. HALTNER AND OLIVER[81] report very good friction and wear behavior of the MoS_2 pellets on substrates of stainless steel, chromium and cast iron but relatively low durability on soft substrates such as copper and tin.

More recently LANCASTER[102,110] has reported extensive work on the behavior of compressed pellets of various solid lubricants rubbing against several metallic substrates representing a wide range of hardnesses. He indicates, as have others, that the effective reduction in wear with MoS_2 pellets on metal surfaces is dependent on the formation of a transferred layer of MoS_2 on the metal. He shows that the formation of the transferred film appears to be primarily a mechanical process with three distinct processes; (a) direct embedding of the solid into a softer surface, (b) deposition of the solid into surface depressions generated in the substrate during sliding by the abrasive action of the solid itself, (c) deposition of the solid into the surface depressions characteristic of the original surface finish of the substrate. Thus, being a mechanical process, the formation of the transferred film is dependent on the hardness of the metal to be lubricated relative to the maximum hardness of the MoS_2 crystal which, due to its crystal structure, is strongly anisotropic. He concludes that the hardness of the MoS_2 crystallites in a direction parallel to the basal planes is about 800–1000 VPN

(7–8 Mohs) compared to 20–30 VPN[39] in a direction perpendicular to the basal planes. Therefore because of this anisotropic hardness MoS_2 is, depending on crystallographic orientation, intrinsically abrasive. The amount of wear and surface damage produced by MoS_2 on a metal during sliding depends on metal hardness relative to the maximum hardness of MoS_2 and the degree of preferred orientation present, or induced, in the surface layers of the MoS_2 pellet.

The work of DEVINE et al.[74] reports a study of the effect of various substrates on the wear life of a bonded film containing 71% MoS_2. They show that a molybdenum substrate gives better wear life than steel; also, alloys whose major constituent is molybdenum give good wear life with MoS_2.

VINEALL AND TAYLOR[82], in an attempt to answer the criticism that MoS_2 will not effectively lubricate brass–steel combinations, show the results of their tests with MoS_2 added to mineral oil and grease as a lubricant for brass on brass and brass on steel. Their results indicate that it was successful in lubricating these combinations. It should be noted that the statement by SALOMON, mentioned above, concerning the inability of MoS_2 to lubricate 60/40 brass on steel was referring to rubbed-on MoS_2, i.e. not MoS_2 in suspension or as a bonded film.

The reaction of MoS_2 with a substrate which reacts with sulphur has often been suggested. The suggestion is that under some conditions the MoS_2 and the metal substrate will react forming a metal sulphide and thereby giving rise to a lubrication mechanism similar to that postulated in classical extreme-pressure additive lubrication. A recent claim along this line has been made by KNAPPWOST[112]. He indicates that the reaction between MoS_2 and Fe occurs at temperatures above 720°C to form FeS. Therefore the "hot spots" in the conjunctive region are coated with an interface of FeS which prevents seizure. There is very little work presented in the literature on this subject, and therefore may be an area worthy of further examination. However, in the light of what is known of the behavior of MoS_2, this mechanism probably does not play a major role in determining the effectiveness of MoS_2 as a lubricant.

The effect of particle size

As mentioned above, a relation between particle size and surface finish should probably be expected to affect the wear life of burnished films although this relationship apparently has not been studied to date. The effect of particle size has been considered for the addition of MoS_2 to diester greases by DEVINE et al.[83]. They studied the effect of particle size on load capacity of the grease and oxidation stability using MoS_2 powders of three different average particle sizes (0.3, 0.7, and 7 μ). No significant differences in load-carrying capacities were found for the 0.7 and 7 μ particles but the load-carrying capacity of the same grease modified with the 0.3 μ average particle size MoS_2 was significantly lower. In tests to determine the oxidation stability of the MoS_2-modified greases they found the greases containing the 0.3 and 0.7 μ particles had a reduced oxidation resistance compared to the base grease during the 500 h test but, based on the repeatability of the tests, the difference in oxidation stability of the base grease and the base grease modified with the 7 μ MoS_2 was slight. VINEALL AND TAYLOR[84] have also shown that the oxidation resistance of MoS_2-containing greases and oils decreases with increasing micronization of the MoS_2 and that excessive micronization should be avoided especially if the materials are to be used in a moist atmosphere. The increase of oxidation with decreasing particle size should be expected because of

the increasing surface area. ROSS AND SUSSMAN[71] have shown that the oxidation rate increases with greater surface area and hence finer subdivision.

BARRY AND BINKELMAN[55] investigated the effect of MoS$_2$ added to a mineral oil (0–10 wt.%) on the coefficient of friction and scoring characteristics of several metals rubbing against themselves. They used MoS$_2$ powders of two average particle sizes (0.7 μ and 7.0 μ). Although not without exception, the results tend to indicate that the 7 μ size had greater antiscoring abilities.

The effect of impurities and the presence of molybdenum trioxide (MoO$_3$)

Virtually all molybdenite used as a lubricant is a mined natural ore. Considerable processing and purification is required to obtain lubricant-grade MoS$_2$. The predominant materials occurring with the natural molybdenite are feldspar and quartzite (silica). PETERSON AND JOHNSON[65] have shown that a silica content of 0.5% by weight does not affect the frictional characteristics of MoS$_2$ but can adversely affect the wear. There is 0.7–1.0% carbon in commercially pure MoS$_2$. The influence of this impurity is not clearly understood but there are indications[58] (pp. 90 and 98) that the addition of small quantities of amorphous carbon black greatly reduce the life expectancy of burnished MoS$_2$ films.

It is very difficult to avoid the presence of some molybdenum trioxide (MoO$_3$) in MoS$_2$. However, there is considerable confusion as to the role of the MoO$_3$ present. ROSS AND SUSSMAN[71] have shown that in the presence of air or water vapor MoS$_2$ surface layers will oxidize at temperatures as low as 85°C. They have shown that the oxidation corresponds to the outer MoS$_2$ layers on the particles and that this oxide layer protects the MoS$_2$ from further oxidation at room temperature and greatly reduces the oxidation at 100°C. They have studied the oxidation rates of clean MoS$_2$ powder and state that the oxidation rate at 85°C shows significant increases with high relative humidity, finer degree of subdivision and greater ease of access to moist air. BALLOU AND ROSS[60] have shown that the MoO$_3$ layer is strongly hydrophilic and is responsible for the adsorption of water vapor. The MoS$_2$ itself was shown to be hydrophobic. JOHNSTON AND MOORE[85] have also investigated the adsorption of water on MoS$_2$ with oxidation products (sulfate and MoO$_3$) on the surface. Employing a silica helix balance, they measured weight losses while heating the MoS$_2$ at various temperatures up to 1000°C under a vacuum. Water vapor isotherms at 30°C were then determined in the same apparatus. They found that physical adsorption of water occurred on the MoS$_2$ as received, but not on MoS$_2$ previously heated to 350°C under vacuum (about 10^{-5} torr) when the sulfuric acid would have been removed. Chemisorption of water still occurs and is associated with the MoO$_3$ still present. This chemisorption was reduced on MoS$_2$ heated under conditions in which the MoO$_3$ would have been volatilized (900°C in vacuum). In the light of the importance of relative humidity on the formation and life of burnished films it is likely that the surface oxide layer plays an important and possibly useful role. ROSS AND SUSSMAN[71] also discuss the desirability of removing the surface oxide layer to obtain the hydrophobic MoS$_2$ surface if the material is to be suspended in oil. They state that the hydrophobic sulfide particles would not tend to flocculate whereas the oxidized and hence hydrophilic particles would tend to flocculate. This seems to be indicated by the work of BRAITHWAITE[86] who shows that washing the oxidized MoS$_2$ with ammonia causes the powder to be more easily dispersed in oil. BALLOU AND ROSS[60] showed that

the surface oxidation could be removed with ammonium hydroxide.

As stated previously, the bulk oxidation of MoS_2 in air is low below 370°C (700°F), (GODFREY AND NELSON[87]) and increases with temperature to a rather rapid rate at 560°C (1050°F) and above. They have also shown that, although MoO_3 is a poor lubricant (at room temperature), the bonded MoS_2 film will maintain low values of friction during oxidation as long as a subfilm of MoS_2 remained. The bulk oxidation of rubbed-on films has a greater effect on the frictional characteristics of the film. It is often stated that the reason for the failure of an oxidized MoS_2 film to lubricate is the abrasiveness of MoO_3 (cf. BRAITHWAITE[32] pp. 159, 161). This is an error in nomenclature* for, although MoO_3 is not a lubricant at normal temperatures, it is not an abrasive. McCABE[10] indicates that according to a standard ASTM Abrasion Test (D-1367) pure MoO_3 is less abrasive than many materials including technical and technical fine grades of MoS_2, WS_2, ZnO, mica, and natural and synthetic graphite. VINEALL AND TAYLOR[84] also conducted tests to determine the extent to which MoO_3 was abrasive and found that both in the case of resin-bonded films and oil suspensions the presence of MoO_3 caused no increase in wear and in no way could the material be considered an abrasive. Their tests on resin-bonded films were carried out with films containing 80% MoO_3 and 20% binder compared to the film of resin binder only. The oil suspension tests were performed with an SAE 30 mineral oil containing 3% MoO_3 on Timken, Shell 4-Ball, and Falex testers. The result in each case showed that the MoO_3 caused no abrasive action. LANCASTER[102] has also shown that compressed pellets of pure MoO_3 against steel are not abrasive.

A few additional comments on MoO_3 itself are in order because of the importance of it in MoS_2 lubrication. MoO_3 has been suggested as a possible lubricant for high temperature applications[88]. PETERSON[88] found that it gave low friction and prevented surface damage at 1300°F in air even though it exhibits high friction at lower temperatures. Both BRIDGEMAN[89] and HYDE[64] have conducted shearing experiments at high pressure on MoO_3. BRIDGEMAN found that the behavior of MoO_3 was similar to that of graphite but HYDE found that the coefficient of friction of MoO_3 was about 0.4 whereas that of graphite was 0.02 at low pressures and 0.1 from 30,000 to 60,000 atm. Extensive discussions of the physical and chemical properties of the oxides of molybdenum will be found in KILLEFFER AND LINZ[1] and WELLE[103]. They point out that MoO_3 is the most important and common oxide of molybdenum and is a white crystalline powder which is obtained commercially by the roasting of molybdenum disulfide in air. Sublimation of MoO_3 begins at 700°C with its melting and boiling points 795°C and 1155°C respectively. Its density is about 4.7. Molybdenum also forms complex oxides[103] of the general formula Mo_nO_{3n-x}. These oxides can form deeply colored hydrates[107] one of which is molybdenum blue which is used as a dye and can be used as an extreme-pressure lubricant additive (cf. ref 32 p. 156).

The effect of crystallographic orientation

Because of the preferential cleavage along the basal plane of the MoS_2 crystal, a preferential orientation of the MoS_2 powder should be expected when the material is rubbed on a surface. This preferential orientation upon rubbing has, in fact, been shown. GODFREY AND BISSON[90] have shown by electron diffraction that rubbing

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* E. R. BRAITHWAITE, private communication, Nov. 1965.

MoS_2 films produces a distinct preferred orientation of the basal plane of the crystal parallel to the surface whether the films are formed by dusting, rubbing, or resin bonding. FENG[7], using X-ray diffraction, also studied the effect of rubbing pressure on the orientation of the film. His results indicate that the higher the rubbing pressure the greater the orientation of the film. He also showed that, as would be expected, the coefficient of friction of an MoS_2 crystal is anisotropic. With a specimen cut from a natural crystal he found that the coefficient of friction varied from 0.1 with basal plane parallel to surface to 0.26 with the basal plane perpendicular to the surface when rubbed on 1020 steel in ordinary atmosphere. Because of the anisotropy of the coefficient of friction and the increased orientation with rubbing, an initial transient would be expected in the friction measurements of any MoS_2 film in addition to the transient which is due to the change in moisture content of the film from some initial value to the new steady-state value determined by the particular test conditions. These initial transient effects probably account for the initial transient shown in the work of GÄNSHEIMER (Fig. 4). They also may account for much of the data observed by KARPE[80] since his test conditions are very similar to those used by FENG[7] in demonstrating the orientation phenomena. JOHNSTON AND MOORE[59] have also shown that the orientation occurs when burnishing the MoS_2 films onto a surface. They employed X-ray diffraction and showed that the degree of orientation is related to the humidity of the atmosphere in which the burnishing takes place with greater orientation occurring at higher relative humidities. At present no information is available as to the relative contributions to the friction transient from the effects of crystallographic orientation and changing humidity in the film. BARRY AND BINKELMAN[55] allowed their test specimens to come to equilibrium with the test atmosphere before conducting the experiment and hence any transient observed should only be the result of crystallographic orientation. Unfortunately they reported only the steady state friction values.

ADDITIONAL PERTINENT PROPERTIES OF MOLYBDENUM DISULFIDE

Because of the tendency to employ electrical contact resistance measurements in lubrication research, a few comments of the existing knowledge of the electrical properties of MoS_2 are in order. The literature indicates that the electrical properties are not well understood and appear to be erratic. The use of electrical contact resistance measurements with MoS_2 studies in lubrication should be approached with great caution. KILLEFFER AND LINZ[1] state that the electrical resistance is high at low potential but drops as the potential increases. As the temperature approaches red heat MoS_2 becomes a fairly good conductor. Wide differences of the electrical properties are measured on different parts of the same specimen as well as on different pieces of the mineral. They also state that it is diamagnetic as well as photoelectric. Its photoelectric behavior and bimetallic thermoelectric behavior between the mineral and copper or lead are both as erratic as its electrical resistivity. MIKHAILOV[91] states that pure MoS_2 is conducting and has more positive electrode potential than most other sulfide minerals. He also states that the oxidation between the laminae results in the semiconductor properties often ascribed to MoS_2. Also according to MIKHAILOV, the electrical resistivity varies greatly with the degree of oxidation and values given in the literature differ by as much as ten orders of magnitude. He gives the resistivity

of fresh unoxidized specimens as about 10^{-2}–10^{-1} ohm m parallel to the cleavage planes and 10–50 times greater in the direction perpendicular to the cleavage planes. BOES[92] reports the electrical resistivity of MoS_2 as 8.5 ohm m. The measurements were made on a pellet of MoS_2 which was synthesized from the elements and hot (200°C) pressed at a pressure of 30,000 p.s.i.

The hardness of MoS_2 is generally reported as being from 1 to 1.5 on the Moh's hardness scale but apparently few measurements of the hardness have ever been made. GRAESER[39] reports hardness measurements made with a GKN Micro Hardness tester on the basal planes of specimens of natural hexagonal and rhombohedral MoS_2 obtained in Switzerland as well as natural hexagonal WS_2 found in the north of Italy. He reports the hardness values on the Vickers hardness scale as shown in Table I.

TABLE I

	Mean	Range
Hexagonal MoS_2	29.1	24.3–31.9
Rhombohedral MoS_2	20.7	18.2–23.2
Hexagonal WS_2	15.5	14.6–15.6

The tungstenite was definitely the softest of the three. He was unable to obtain hardness measurements on planes perpendicular to the cleavage planes because the size of the specimens prohibited preparing a surface suitable for indentation. Because of the anisotropic nature of the crystal the hardness on surfaces other than the basal plane would be expected to be different. LANCASTER[102], by an indirect method, has estimated the hardness of MoS_2 on the plane perpendicular to the basal plane to be from 800 to 1000 on the Vickers hardness scale. Direct micro-hardness measurements by diamond indenters have been made on 127 minerals including MoS_2 by ROBERTSON[104]. These measurements show the existence of anisotropy. ROBERTSON reports that the hardness of MoS_2 on the Knoop hardness scale is 12 on the plane perpendicular to the basal plane and 60 on the basal plane itself. Although, at first, these data seem to be the opposite to what would be expected from considerations of the behavior of MoS_2 as a lubricant, it must be remembered that a normal hardness measurement on the plane perpendicular to the basal plane of an MoS_2 crystallite is greatly influenced by the easy cleavage of the basal plane ahead of the indenter and may not reflect the behaviour of the laminae of an MoS_2 crystallite when it is constrained in the conjunctive region of a lubricated contact.

Upon examining his minerals by X-ray fluorescence analysis, GRAESER found that the rhombohedral MoS_2 contained 0.7% tungsten and the hexagonal WS_2 contained 6.0% molybdenum. This may indicate that a solid solution exists between MoS_2 and WS_2.

The optical properties and photoconductivity of thin crystals of MoS_2 have been studied by FRINDT AND YOFFEE[105]. Crystals less than 100 Å thick were prepared by cleavage. The optical absorption spectra are similar for crystal thickness ranging from several μm to less than 100 Å. Absorption coefficients were measured and the absorption bands observed with thin crystals are associated with bulk rather than surface properties.

FORMATION OF MOLYBDENUM DISULFIDE "IN SITU"

The *in situ* formation of a lubricating film of MoS_2 has been reported by several investigators (BOWDEN[93], ROWE[94], FENG *et al.*[95] etc.). Although it is clear that they observe effective lubrication by the formation of a film, it is not, in general, as clear that the film is MoS_2. ROWE[98] indicates, however, that the material in his experiments was generated in sufficient quantity to enable him to obtain X-ray powder patterns which were compared with the molybdenite pattern (ASTM Card 6-0097). FENG *et al.*[95] studied the possibility of forming a lubricant *in situ*, by reaction of components in the oil and not involving the substrate. When a molybdenum complex and zinc dialkyl phosphorodithionate are added to the oil they find, by electron diffraction, MoS_2 "and some other unidentified crystalline material" on the surface. SPENGLER AND WEBER[96] also studied the behavior of mineral oils supplemented with organic molybdenum compounds in the presence of sulfur and concluded, from thermal decomposition studies, that molybdenumoxysulfide (MoOS) is more probable than MoS_2. They also studied the lubricating properties of molybdenumoxysulfide and found it to be a good lubricant.

A patent has been issued to BROPHY *et al.*[97] for the formation of a lubricating film on the surface of a metal component by electroplating the surface with molybdenum and then treating the surface with a sulfur-containing gas. They make no claims as to the presence of MoS_2 or any other material, just to the fact the resulting film has good lubricating qualities. Subsequently the patent was sold and further research work by the new patent holders has led to further information concerning the nature of the resulting film[106]. In this work the X-ray diffraction analysis was made of the bearing surface directly, as well as on the deposit subsequently scraped off the surface. The X-ray diffraction analysis was carried out on the bearing surfaces before and after running. The equipment used consisted of a Norcelo X-ray Diffraction Unit with high-intensity copper target tube $\lambda = 1.5401$. The unit was fitted with a General Electric film camera of 143 mm diam. The $1\frac{1}{2}$ in. bearing surface was aligned in the beam at grazing incidence and was not rotated during the three hour exposure. The copper target tube was operated at 40 kV and 35 mA.

The data obtained on three bearing samples are shown in Table II where (a) = new bearing not plated or friction tested, (b) = bearing plated, but not friction tested and (c) = two bearings plated and run-in on friction tester. The samples (a) and (b) exhibit lines due to α-Fe and steel similar to austenite. In (c) the 6.15 Å diffuse band was attributed to MoS_2.

TABLE II

d (Å)			
(a)	(b)	(c)	MoS_2 ASTM 6-0097
		6.0–6.8	6.15
		2.67	2.67
2.06	2.06	2.06	
2.03	2.03	2.02	
1.79	1.79	1.78	
1.43	1.43	1.43	
1.27	1.27		

The above bearings were then scraped and the small amount of material removed from the surface was placed into a wedge-type sample holder prepared with a 1/32 in. diam. notch which had been machined into the edge to receive the sample powder. These samples were then run in the conventional manner, rotating through an arc of 30° to reduce orientation effects.

The bearing (b) which had been plated but not run-in exhibited a very hard coating and sufficient material could not be scraped off for test. Data on the new bearing (a) and the friction-tested bearing (c) are shown in Table III.

TABLE III

d ($\overset{\circ}{A}$)		
		MoS_2
(a)	(c)	ASTM 6-0097
2.03	6.0 –6.6	6.15
	2.64–2.74	2.67
	2.03–2.06	2.03
	1.54–1.58	1.54

The reflections obtained on (c) were attributed to formation of MoS_2, except for the 2.03 Å line which was very weak and is probably α-Fe. The broadness of the lines of MoS_2 would seem to indicate that the particle size is quite small, perhaps less than 100 Å.

ACKNOWLEDGEMENTS

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