Frictional Properties of Some Solid Lubricant Films under High Load

A. J. HALTNER and C. S. OLIVER
General Electric Research Laboratory, Schenectady, N. Y.

IN PRACTICE, solid lubricants are usually applied as films on one or both of two mating, moving, metal surfaces. Their purpose is to prevent metal-to-metal contact and possible seizure as well as to provide a low coefficient of friction. Generally they are used under high loading conditions. Since much fundamental knowledge about solid lubricant films is still needed, the authors have carried out a study of such films under extreme conditions. The program was directed at clarifying the factors which determine the ultimate properties of such films on metal surfaces and at discovering the limits on the coefficient of friction, μ, the load-carrying ability, and durability of such films.

EXPERIMENTAL

Apparatus and Procedures. The friction studies were carried out with the aid of a dynamometer based on a design developed by Hull (8). In this apparatus, the bearing surfaces consist of a metal disk and a rider. The disk is rotated with the pivoted rider held against it by a dead weight. Therefore, the rider continuously retraces the same circular path over the surface of the metal disk. In the studies reported here, the speed of rotation of the disk was 100 r.p.m., and relative travel of the rider over the disk surface was at a speed of 65 cm. per second. The apparatus allows continuous measurement of frictional force.

The riders employed in these studies were of two types. The first type consisted of cylindrical pellets compressed from powders (sufficiently fine to pass −200-mesh) of solid lubricants. The pellets were $\frac{5}{16}$ inch (0.762 cm.) in diameter, and were formed in a mold under a pressure of 70,000 p.s.i. (49.3 kg. per sq. mm.), without addition of a binding agent. In most cases, such pellets display adequate cohesion, and can be used as riders over a period of several hours under loads up to 2 kg. before wearing away completely.

Pellets of lubricants which successfully lubricate the metal disk rapidly deposit an adherent film of lubricant on the disk surface during the course of a run. Since some of these films displayed surprising durability under extreme loading conditions, a more detailed investigation of the frictional properties of such films was performed.

For frictional studies of the films, the riders were chrome alloy steel hemispheres $\frac{1}{8}$ inch in diameter. The riders had a measured Knoop hardness number (KN) of 670 ± 70 kg. per sq. mm. which is equivalent to 59 ± 3 on the Rockwell C scale. This equals or exceeds the hardness values for the various metal disk specimens used in this work. The apparent area of contact between the hemispherical rider and the lubricant film is small, and consequently even under fairly modest loading conditions the apparent pressures achieved are high. These tests employed a standard experimental procedure in which the load was increased by 50- to 100-gram increments as μ was measured. The load at which μ increased discontinuously to that typical of the rider sliding against the underlying metal surface was noted as the maximum load carried by the film. This procedure is similar to the measurement of a seizure load.

The surface hardness of each of the metal disks employed in this study was measured with a Kentron microhardness tester. A diamond pyramid indenter was customarily employed so that a Vickers diamond pyramid hardness number (DPN) in kilograms per square millimeters was obtained. In most cases, DPN is close to KN.

Materials. All metal specimens used were given superficial cleaning to remove any gross surface contamination. No attempt was made, in this work to obtain ultrapure surfaces. Therefore the surfaces of the metal disks are expected to be covered with oxide films in most cases.

Steel samples (AISI 1020 mild steel, 1090 steel, and 347 stainless steel) were cut from rolled sheets. They were carefully degreased, and the samples of 1020 and 1090 steel were cleaned with an acid solution of 2-butyne-1,4-diol to remove rust. This was followed by rinses with acetone and toluene. Some of these samples were polished with fine emery, but this had no detectable effect on subsequent experimental observations.

The disk of cast iron was fabricated from a large piece, and it had a machined surface. Specifications for this material were not available.

Disks of copper were cut from annealed cold-rolled sheets of spinning grade copper. The brass sample was Muntz metal which reportedly contains 60% copper, 39.4% zinc, and 0.6% lead. Before use, both copper and brass samples were given the standard cleaning procedure used in electroplating. Aluminum disks were cut from material having 99+% purity.

Chromium, tin, rhodium, and gold surfaces were obtained as thick electroplated deposits on 1090 steel. Chromium surfaces were conventional hard chromium plate which contains numerous cracks. Subsequent data have indicated that the somewhat softer, crack-free chromium plate may be a more advantageous substrate for lubricant films of molybdenum disulfide.

The solids used as lubricants were of the highest purity obtainable commercially. X-ray powder patterns were obtained for all of the inorganic solids studied to confirm that these solids were of the expected crystalline form and free of large amounts of impurities.

Experimental. Extensive studies have been made of molybdenum disulfide films, and some of the data obtained are summarized in Table I. Outstanding results were noted on stainless steel, chromium, and cast iron substrates. However, on soft substrates such as copper and tin, relatively low durabilities for molybdenum disulfide films were found.

The reproducibility of friction measurements between separate experiments on the same surface is of the order of ±5 to 10% for high values of μ (0.1 to 0.2). For low values of μ (<0.05), the reproducibility is somewhat poorer, as shown by duplicate runs on stainless steel and chromium (Table I). For well prepared films, the maximum load carried is generally reproduced to within 200 or 300 grams.

In some experiments, an estimate was made of the maximum apparent loading pressure obtained during the test at the point of incipient film failure. To do this the load at failure was divided by an apparent area of contact estimated as being the circle having a diameter equal to the track width produced by the steel hemisphere on the disk. This calculation is approximate, but it does give a reasonably good idea of the high magnitude of the pressures encountered. In an experiment on 1090 steel a pressure of 40 kg. per sq. mm. was estimated. The hardness value measured on this surface was 172 kg. per sq. mm., so the apparent area of contact must have been of the same order of magnitude as the real area of contact.

A number of tests were run on a variety of other lubricant films, and resulting data are collected in Table II. Of the inorganic films investigated, only tungsten disulfide and bismuth triiodide revealed outstanding lubricating properties. Bismuth triiodide showed fairly high load-carrying

Table I. Frictional Properties of MoS_2 Films

Disk Metal	Disk Hardness, DPN	Coefficient of Friction, μ	Max. Load Carried, Kg.
Mild steel	153	0.13	0.25
1090 steel	172	0.035	1.09
Stainless steel	206	0.015	3.60
Stainless steel	206	0.022	3.02
Chromium	950	0.05	>4.0
Chromium	950	0.020	2.60
Cast iron	222	0.026	>3.51
Brass	...	0.18	<0.20
Tin	...	0.07	0.28
Rhodium	...	0.06	0.80
Gold	...	0.21	<0.2

Table II. Frictional Properties of Various Lubricant Films

Film	Disk Metal	Disk Hardness, DPN	Coefficient of Friction, μ	Max. Load Carried, Kg.
ZrS_2	Copper	...	0.68	<0.20
ZrS_2	Copper	...	1.1	<0.10
Ti_2S_3	Copper	...	0.7	<0.20
WS_2	Mild steel	153	0.026	3.8
WS_2	Chromium	950	0.05	5.0
Resin-bonded MoS_2	Mild steel	153	0.16	0.26
SAE 60 oil	Mild steel	153	0.10	4.0
BiI_3	Mild steel	153	0.15	3.2
CdI_2	Aluminum	...	0.10	0.70
Indanthrene	Mild steel	153	0.090	0.70
Copper acetylacetonate	1090 steel	172	0.16	<0.20
1,5-Naphthalenedisulfonanalide	Copper	...	0.20	<0.40

ability, but the coefficient of friction was considerably higher than that obtained on films of molybdenum disulfide.

A few organic solids have been surveyed as potential solid lubricants. Most crystalline organic compounds are soft, and this is a desirable property in a solid lubricant. Some attention was given to acetylacetonates, since their known ability to chelate with metal could conceivably provide a mechanism for producing tenaciously attached films on metal surfaces. Copper acetylacetonate is typical of this group, and its frictional behavior (Table II) is not outstanding.

Large organic molecules which contain condensed ring systems have major portions of the molecule lying in a single plane. Such a high degree of planarity in the molecules might produce some layering of the molecules in the crystal, resulting in some similarity in physical properties to the lamellar inorganic solids such as molybdenum disulfide and tungsten disulfide. The authors have studied 1,5-naphthalenedisulfonanalide (Figure 1) and 6,15-dihydro-5,9,14,18-anthrazinetetrone (Figure 2). The first of these structures produced a film with indifferent frictional properties. The second structure is a blue dye available commercially under the trade name Indanthrene. Its behavior on mild steel (Table II) is comparable to that of molybdenum disulfide. This material is reported to be stable to temperatures as high as 500° C. Therefore, its chemical properties coupled with its promising frictional behavior indicate that this substance warrants further consideration as a solid lubricant.

The frictional properties of solid lubricant films display interesting effects with varying loads. Typical results for a molybdenum disulfide film on chromium (Figure 3) show that μ decreases as the load increases, and hence, that Amonton's law is definitely not obeyed by these films. It is possible to rationalize this dependence of μ on load as a heating effect, but such an explanation does not appear to be adequate. Available data indicate that the coefficient of friction of molybdenum disulfide has little dependence on ambient temperature up to about 350° C. in air (*5*). However, there do not appear to be friction data available at pressures as high as those encountered in this study. If μ does decrease as the result of heating, one would expect that changes in speed would have similar effects. In Figure 4 data are shown for the dependence of μ on speed. At the highest load studied, 6 kg., μ is essentially independent of speed over a range of from 15 to 55 cm. per second.

The variation of the coefficient of friction with load is qualitatively similar to that observed with thin coatings of soft metals, such as indium, on hard metal surfaces (*2*). The mechanism that Bowden and Tabor have advanced to

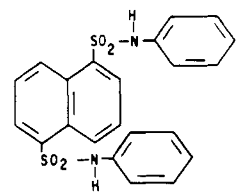

Figure 1. 1,5-Naphthalenedisulfonanilide

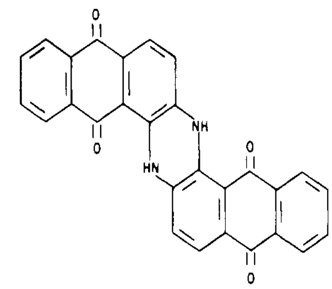

Figure 2. 6,15-Dihydro-5,9,14,18-anthrazinetetrone

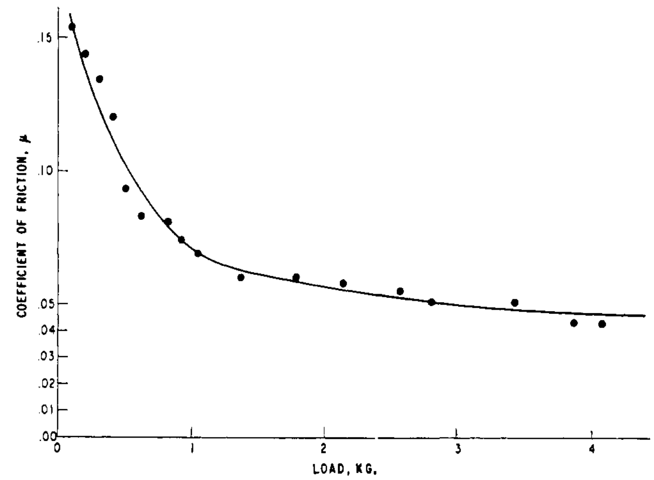

Figure 3. Variation of μ with load for MoS_2 on chromium

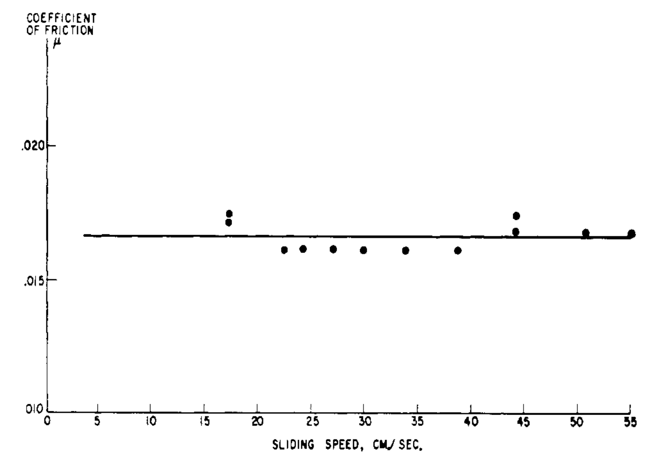

Figure 4. Coefficient of friction vs. speed for a steel hemisphere sliding against a MoS_2 film on chromium

Temperature. 25° C. Pressure. 20,000 p.s.i.
Load. 6.06 kg. Atmosphere. Nitrogen

account for this behavior has also been used by Bowers, Clinton, and Zisman (3) to account for low friction of thin films of plastics on hard metal backings. A similar mechanism may be operating in the case of thin films of solid lubricants which are softer than the underlying substrate. Solid lubricants such as molybdenum disulfide are generally considered to be soft materials. However, they are probably significantly soft in only one direction. Other directions in the crystal may be comparatively hard. Therefore, an important question to be further clarified is whether or not the mechanical properties of these crystalline solids allow them to behave as thin-film lubricants in a manner analogous to the behavior of soft metal films.

Transients in μ have been observed in experiments with pellets of molybdenum disulfide sliding against metals (9), and similar effects have now been found in these experiments under high pressure with films of molybdenum disulfide. It is found typically that μ is higher when sliding is resumed after it has been stopped for a while. The friction then gradually decreases to its previous low value.

The behavior of films of bismuth triiodide (Figure 5) is in marked contrast to that of molybdenum disulfide films. At a load of 500 grams μ passed through a maximum and then decreased to a low stable value of about 0.16. This limiting value of μ is considerably higher than the value of 0.13 (Table I) observed on molybdenum disulfide films; however, the maximum load carried by the bismuth triiodide film is significantly greater than that carried by a molybdenum disulfide film on the same substrate. Microscopic examination indicated that the bismuth triiodide film was reasonably continuous and that metal-to-metal contact was being prevented.

Microscopic examination was made of most of the riders and tracks after the experiments had been terminated. On relatively soft surfaces such as mild steel, the tracks were polished grooves, but on the harder chromium surface no depression could be observed.

No systematic investigation has been made of the effects of atmosphere and particularly of moisture on the lubricating behavior of these films. Most of the experiments were carried out under ambient room conditions at a temperature near 25° C. and a relative humidity of 30 to 40%. However, μ in dry nitrogen for a molybdenum disulfide film was about half the value found in air under similar conditions where the relative humidity was 30%. So the effect of humidity is probably similar to that reported for pellets of molybdenum disulfide sliding against a copper surface (7).

DISCUSSION

It is commonly assumed that lubrication by lamellar solids such as graphite and molybdenum disulfide occurs by means of a mechanism involving shear. These solids have planes of wide separation which should have low intermolecular cohesion and so act as planes where slipping or shearing can readily occur. This theory has recently been criticized in the work of Johnson and Vaughn (9), Finch (6), and Deacon and Goodman (5).

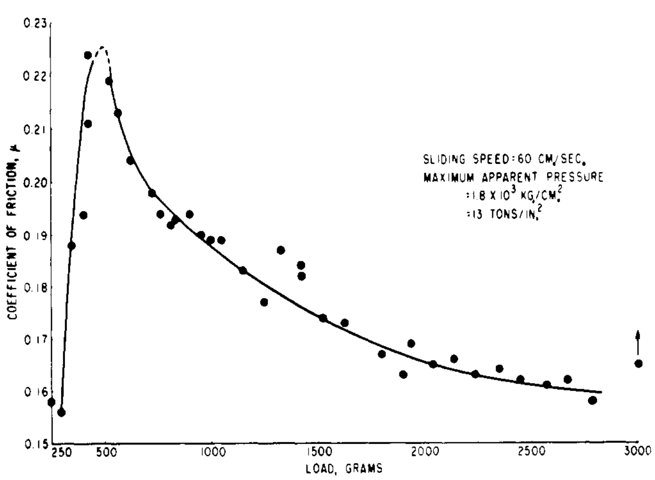

Figure 5. Coefficient of friction vs. load for a steel hemisphere sliding against a film of BiI_3 on mild steel

Since no lubrication mechanism for solid lubricants has as yet been demonstrated, it was of interest to compare the frictional behavior observed on thin films of bismuth triiodide and molybdenum disulfide with the behavior to be expected on the basis of a mechanism which involves shearing. Equations based on this theory have been given by Bowden and Tabor (2), and they permit calculation of μ, if shear strength and pressure are known. In the experiments the maximum pressure on the films was assumed to be the yield pressure of the underlying metal. Then, with this pressure an appropriate shear strength can be derived from the data of Bridgman (4). No data are given for molybdenum disulfide, but it appeared to be justified to employ the shear strength of cadmium diiodide in these calculations. Other observations on the frictional behavior of cadmium diiodide indicate that if the shear strength theory applies, then the shear strength of cadmium diiodide must provide an upper limit on the shear strength of molybdenum disulfide. In both cases the calculated values of μ were approximately one half of the observed values. For these solids the shear strength theory predicts frictional forces fairly close to those observed. Other mechanism may also produce frictional energy losses.

The decrease in friction with load has been explained by assuming a decrease in film thickness resulting in a higher proportion of the load being supported by the metal substrate. An alternative explanation based on film heating is untenable, since calculations of surface temperatures based on the treatment of Blok and Jaeger as simplified by Bowden and Tabor (2) for the experiment of Figure 4 indicate a temperature rise of approximately 30° C. at the lowest speed studied.

SUMMARY

The frictional properties and load-carrying capacities of a number of solid lubricant films on metals have been investigated. In combination with the proper metal substrate, some of these rubbed films are surprisingly tenacious.

The coefficient of friction for solid lubricant films has been shown to decrease as load increases. This behavior is similar to that reported for soft metal films—i.e., indium—on hard metal backings, and the explanation in both cases is probably the same. This suggests that to achieve low friction and high durability, solid lubricants should be used on the hardest possible metal backings, provided good adhesion between film and metal is retained.

Calculations based on a shearing mechanism predict coefficients of friction close to those observed for the films. This suggests that for lamellar solids it is energetically possible for shearing between layers to contribute to the lubrication mechanism.

LITERATURE CITED

(1) Bowden, F.P., Tabor, D., "The Friction and Lubrication of Solids," Chap. II, Oxford Univ. Press, New York, 1954.
(2) *Ibid.*, Chap. V.
(3) Bowers, R.C., Clinton, W.C., Zisman, W.A., *Modern Plastics* 31, 131 (February 1954).
(4) Bridgman, P.W., *Proc. Am. Acad. Arts Sci.* **71**, 387 (1937).
(5) Deacon, R.F., Goodman, J.F., *Proc. Roy. Soc.* **A243**, 464 (1958).
(6) Finch, G.I., *Proc. Phys. Soc. (London)* **A63**, 785 (1950).
(7) Haltner, A.J., Oliver, C.S., Abstracts, 134th Meeting, ACS, p. 5R, Chicago, Ill., September 1958.
(8) Hull, E.H., *Rev. Sci. Instr.* **29**, 1050 (1958).
(9) Johnson, V.R., Vaughn, G.W., *J. Appl. Phys.* **27**, 1173 (1956).

RECEIVED for review March 8, 1960. Accepted August 29, 1960.