N73-20537

# NASA TECHNICAL MEMORANDUM

NASA TM X- 68201

NASA TM X- 68201

# HIGH TEMPERATURE SOLID LUBRICANTS - WHEN AND WHERE TO USE THEM

by Harold E. Sliney
Lewis Research Center
Cleveland, Ohio 44135

TECHNICAL PAPER proposed for presentation at
Design Engineering Conference sponsored by the
American Society of Mechanical Engineers
Philadelphia, Pennsylvania, April 9-12, 1973

# HIGH TEMPERATURE SOLID LUBRICANTS -

# WHEN AND WHERE TO USE THEM

by Harold E. Sliney

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

E-7368

## ABSTRACT

This paper reviews the state of the art of solid lubrication for moderate to extremely high temperature lubrication (to 1600° F). Lubricating characteristics, stability in various environments, and relevant machine design considerations are discussed. Lubricating materials discussed include the layer lattice compounds: $MoS_2$, $WS_2$, graphite and graphite fluoride $(CF_x)_n$, the high temperature polyimide polymer, and calcium fluoride based coatings and composites. The scope of the information includes results from wear testers, ball bearings, and journal bearings.

## INTRODUCTION

During the last 25 years, much effort has been directed to the study of solid lubricants (e.g., refs. 1-6). Those materials have solved many unique lubrication problems. However, the misapplication of solid lubricants has not been uncommon. Solid lubricants have nevertheless gained considerable acceptance. The key to even more widespread use will be the realization that solid lubricants are specialized materials. Their properties and performance in regard to such factors as atmosphere, temperature and bearing design must be understood before a wise selection can be made. For any critically-lubricated machine element, the lubricant properties must be considered as carefully as those of any other design material. In other words the lubricant should be one of the facets of conceptual machine design.

It is the purpose of this paper to describe some of the relevant properties of various solid lubricants for use in moderate and severe environments, but with emphasis on high temperature applications.

### Advantages and Disadvantages of Solid Lubricants

When one considers the very low friction and the long life possible with oil or grease lubricated bearings, a legitimate question is, why use solid lubricants? Some of the advantages of solid lubricants are:

1. Solid lubricants can be used in severe environmental conditions where the usual fluid lubricants such as oil are not suitable. These conditions include ambient temperatures above the decomposition temperature of oils or, on the other hand, temperatures so low that oils freeze to brittle solids. Solid lubricants can also be used in chemically reactive environments such as liquid oxygen and fluorine or the molten alkali metals.

2. Sometimes design advantages are also derived. These include a reduction in weight of the mechanism: dry-lubricated bearings frequently do not require cooling; therefore recirculating oil systems, with their pumps and heat exchangers, may be eliminated - further, rotating shafts can sometimes be shortened because dry-lubricated bearings can be located closer to heat sources, or at the other temperature extreme, closer to cryogenically cooled areas. Not only is shaft weight reduced, but in high speed machinery, problems of shaft whip and critical speeds are lessened.

3. The use of dry-lubricated bearings can sometimes reduce the number of seals required in a system. In vacuum environments, for example, low vapor pressure solid lubricants need not be sealed from the vacuum to prevent evaporation. In fluid systems, seals are often required to isolate the lubricating fluid from the process fluids. These seals are not required when bonded solid lubricants that are compatible with the process fluids are used.

This is the case for solid lubricants. In order to use them intelligently, however, their disadvantages should also be discussed. Some of these are:

1. Friction coefficients are generally higher than obtained with hydrodynamic lubrication (for hydrodynamic oil-lubricated bearings, friction coefficients of 0.005 are not unusual). For the best solid lubricant, under favorable conditions, a friction coefficient of 0.05 is typical; for severe conditions of boundary lubrication, friction coefficients up to 0.20 are frequently considered to be acceptable.

2. Some wear is unavoidable because of the solid sliding contact. In hydrodynamic lubrication, wear rates theoretically can be zero.

3. When used as a bonded coating, the wear life of a solid lubricant is finite; when the coating wears out, the lubricant generally cannot be replenished except with considerable difficulty.

4. Solid lubricants cannot function as coolants while oils are effective coolants.

5. Solid lubricants have little or no damping effect. It is often overlooked that oil dampens vibrations especially in nonloaded rotating parts such as ball bearing cages. Damaging vibrational cage instabilities can occur in dry bearings running at high speeds.

This partial listing of advantages and disadvantages should indicate that the decisions to use either a solid or liquid lubricant and which specific lubricant to use can be complex and should be made early and carefully.

## SPECIFIC SOLID LUBRICANTS AND THEIR PROPERTIES

### Layer Lattice Compounds

These are materials with a hexagonal layered crystal structure. The shear properties are anisotropic with preferred easy shear parallel to the basal planes of the crystallites. This class of materials constitute the most widely used group of solid lubricating materials. Generally speaking, the friction coefficients obtained with good layer lattice solid lubricants such as $MoS_2$ or $WS_2$ are lower than those obtained with the other classes of solid lubricants to be mentioned. Therefore, they are generally preferred for applications in environments with which they are compatible.

Molybdenum disulfide ($MoS_2$). - $MoS_2$ is an excellent solid lubricating material that has gained wide acceptance. It is an intrinsically low shear strength material and, in contract to graphite does not require the presence of adsorbable vapors in order to lubricate (ref. 7). $MoS_2$ is commonly used in resin bonded coatings applied to the bearing surfaces. The maximum useful temperature of these coatings depends upon the composition of the resin binder. Thermoplastic resins such as the cellulosic or acrylic lacquers are convenient. They are easily sprayed, fast drying, and require no baking. However, their maximum recommended service temperature is only about 150° F. Some of the thermosetting resins have much better high temperature properties. The maximum service temperature for the phenolics is about 400° F; this resin has good adhesion to metal surfaces, and is quite hard. Epoxy resins also adhere well, are softer than the phenolics and are thermally stable to about 600° F. Epoxy-modified phenolics are often used in heat-cured resin-bonded $MoS_2$ formulations. Wear life of resin-bonded $MoS_2$ decreases with temperature and at the maximum recommended temperatures may be $\frac{1}{100}$ the life at room temperature.

In figure 1 the effects of temperature on the lubricating properties of a $MoS_2$ coating bonded with a mixed resin are shown (ref. 8). At about 600° F, both friction coefficients and rider wear increase sharply. This result can be attributed to failure of the resin binder. However, $MoS_2$ itself decomposes in air to form molybdic oxide and sulfur dioxide at only slightly higher temperatures. This oxidation rate is appreciable at about 750° F. To avoid the temperature limitations of an organic binder, inorganic binders such as sodium silicate have been used (ref. 9). Coatings of this type are limited by the threshold temperature for oxidation of $MoS_2$ rather than the binder. This binder may also provide some oxidation protection to the $MoS_2$ particles by, to at least a limited extent, excluding air from the lubricant particles. Enclosed bearing housings also may sometimes aid in reducing the oxidation rate. In a completely inert atmosphere such as argon, lubrication with powdered $MoS_2$ is possible up to perhaps 1500° F.

Tungsten disulfide, $WS_2$. - $WS_2$ is similar to $MoS_2$ in that it is a layer lattice type of solid lubricant and it does not require the presence of adsorbable vapors to develop low shear strength characteristics. $WS_2$ apparently has somewhat better high temperature properties in both air and nonoxidizing atmospheres (ref. 10), figure 2. Both solid lubricants are effective to higher temperatures in the nonoxidizing atmosphere. X-ray diffraction studies have shown that the significant increase in friction coefficient of both compounds in air at the higher temperatures is caused by chemical reaction of the disulfides to form the respective oxides.

Oxidation of $WS_2$ and $MoS_2$. - The influence of temperature on the oxidation rates of $WS_2$ and $MoS_2$ was determined in an X-ray diffraction furnace (ref. 11). The oxidation half-lives of the thin films of $WS_2$ and $MoS_2$ are compared in figure 3. Above about 730° F, $MoS_2$ oxidized more rapidly than $WS_2$.

The importance of oxygen availability is demonstrated in figure 4 where oxidation half-life of $MoS_2$ is given for two air flow rates. Oxidation was significantly more rapid at the higher air flow rate. The dependence of oxidation rate on oxygen availability to the reacting surface is therefore clear.

For vacuum application the maximum useful temperature is a function of the thermal dissociation rates rather than the oxidation rates of the lubricants. Thermal dissociation rates of molybdenum and tungsten disulfides, diselenides, and ditellurides in vacuum have been systematically studied (ref. 12). The major results are summarized in table I. The data indicate that the disulfides are the most stable to thermal dissociation, the deselenides are intermediate and the ditellurides are the least stable. However, thin films of the diselenides provided effective lubrication in vacuum to a higher temperature (1400° F) than the disulfides. The diselenides, because of their higher densities, evaporate more slowly than the disulfides and apparently, for the very thin films used, the evaporation rates were the controlling factor in determining the maximum temperatures for effective lubrication.

Graphite. - Graphite was perhaps the first widely used inorganic solid lubricant. It is industrially important as a parting compound for molds, and as a lubricant in metal-working processes such as wire-drawing and extrusion.

Because of its importance as a lubricant, it is interesting that pure graphite has severe deficiencies as a lubricant. It has been demonstrated that graphite must adsorb gas, moisture, or hydrocarbon vapors before it develops the property of low shear strength required of a solid lubricant (ref. 13). The presence of some oxides and other extraneous materials is also important in the formation of adherent films of graphite on solid surfaces and in reducing the shear strength of the graphite structure. It has been suggested that this is due to the formation of interstitial or intercalation compounds by reaction of these materials with graphite (ref. 14, for example). The gases and water vapor present in the normal atmosphere are usually sufficient to insure an adequate supply of adsorbable material. However, at high altitudes or under vacuum conditions, desorption occurs and graphite does not function as a lubricant. The effect of temperature on the friction coefficient for lubrication with graphite powder is shown in figure 5 (ref. 15). The friction coefficient is quite low at room temperature, but increases at temperatures above about 200° F. The friction coefficient remains high then shows a marked reduction at temperatures above approximately 800° F, and graphite is again an effective lubricant at 1000° F (probably associated with oxidation of the lubricated metal).

In air, the threshold temperature for long duration uses of graphite is determined by the oxidation rate. Graphite powder of small particle size begins to oxidize at an appreciable rate at about 850° F (ref. 16). Graphite can be used to higher temperatures if it can be replenished because the oxidation products are gases and no solid residues are produced. Considerable advantages in the development of adherent lubricating films can often be gained by the addition of metallic salts or oxides to graphite. The lower curve of figure 5 shows that, by mixing cadmium oxide (CdO) with graphite, a low friction coefficient can be obtained over the entire temperature range.

Graphite is perhaps more frequently used for high temperature applications in the form of self-lubricating, carbon graphite materials than in the form of powders or coatings. Because the oxidation of graphite involves the chemical reaction of carbon with oxygen in the air to form carbon dioxide, the oxidation of carbon-graphite bodies can be inhibited by high temperature surface treatments or by impregnating the carbon-graphite structure to exclude air. Carbon-graphites, impregnated with copper or silver, are reportedly useful to about 900° F while some of the relatively new types of ceramic-impregnated carbon-graphites are reportedly good for service at 1200° F (ref. 17).

Graphite Fluoride. - Some of the limitations of graphite are absent in a new solid lubricant, graphite fluoride ($CF_x$), which is prepared by the direct chemical combination of graphite powder and fluorine gas under carefully controlled conditions. The stoichiometry range is broad with x from 0.3 to about 1.1 depending upon the completeness of the chemical reaction. $CF_x$ is a so-called intercalation compound of graphite; some of the features of the parent graphite crystal structure are retained. However, the spacing distance between the layers of carbon atoms or basal planes in graphite are expanded from 3.4 to 7.5 ±1.5 Angstroms. In general, lubricating ability and thermal stability improve with increasing x and the best results have been obtained with $CF_{1.1}$. However, good lubrication has been obtained with x as low as 0.3.

One of the chief advantages of $CF_x$ compared to graphite is that it does not require adsorbed vapors or adjuvant impurities in order to lubricate.

Figure 6 compares the wear lives in dry air (<20 ppm $H_2O$) of $CF_x$ and $MoS_2$ films as measured on a pin on disk wear tester (ref. 18). Results for rubbed-on or burnished films and resin-bonded coatings of both lubricants are given. The resin is a heat cured polyimide (PI) varnish which is thermally stable in air to about 750° F (400° C).

$CF_{1.1}$ does not oxidize when heated in air. The maximum service temperature is determined by thermal decomposition to finely divided carbon soot, carbon tetrafluoride, and higher fluorocarbons (ref. 19). In vacuum, the onset of slow thermal decomposition occurs at about 800° F (420° C). The thermal stability is a bit better at atmospheric pressure and as indicated in figure 6, $CF_{1.1}$ can provide lubrication for some time up to 1040° F (550° C).

## Polymer Lubricating Materials

Polyimide thin film lubrication. - Polyimide varnish without any lubricating fillers is of interest as a solid lubricant coating. Friction coefficients and wear lives for PI films, PI-bonded $CF_x$, and PI-bonded $MoS_2$ are compared in figure 7. There is an interesting transition temperature in the friction and wear life properties of PI thin films between 25° and 100° C (77° and 212° F). Above this transition, PI thin films performed very well as lubricating films; below the transition, friction was high and wear life short. Adding $CF_x$ or $MoS_2$ greatly improved room temperature performance. Above the transition, no lubricant additives were needed for low friction; however, $CF_x$ additions increased wear life at all temperatures.

Polymeric bearing materials. - We have so far discussed solid lubricant coatings. We have seen that polymers or resins are used as binders for solid lubricating pigments. In one case cited, polyimide varnishes, the resin alone is an effective solid lubricant under some conditions. Polytetrafluoroethylene (PTFE) and other polymers have also been used as lubricating coatings but at lower temperatures than PI is serviceable.

A large variety of polymers are also used with and without fillers as self-lubricating bearing materials. Some well known examples are polyamides (e.g., nylon), acetals, polyethylene, and fluorocarbons. The first three are low cost materials with good processability: they can be injection molded or extruded. PTFE fluorocarbon has the lowest friction coefficient of any known solid. All are limited for high temperature applications.

Some polyamides melt at about 400° F. PTFE reinforced with glass fibers is used as a lubricating liner for highly loaded aircraft control surface bearings to a maximum of about 325° F. Thermal stability extends to 500° F but cold flow is a problem above 325° F for high load applications.

Here again PI is of interest for higher temperatures. PI retains nearly full room temperature mechanical strength almost indefinitely at 500° F and retains useful strength for hundreds of hours at 600° F. PI is available unfilled or filled with graphite or $MoS_2$ powders to improve lubricating characteristics. It can also be strengthened by reinforcement with graphite fibers. It has been reported that strong void-free molded parts can be made with a graphite fiber reinforced addition type polyimide. In contrast to the more conventional condensation polymers, the addition type undergoes the final stages of polymerization without the release of volatile reaction products; this eases the processing problem of achieving void-free moldings with thick sections (refs. 20, 21).

Graphite fiber-reinforced polyimide bearings. - We have investigated fiber-reinforced addition type PI as a heat-cured molded bearing material (ref. 22). This material is of interest for aircraft control surface bearings with higher temperature capabilities than PTFE-lined bearings. The increased aerodynamic heating of aircraft at Mach numbers of 3 or higher can result in control surface temperatures well above 325° F.

In order to minimize the weight of the thermal protection system, airframe structural members may be allowed to get as hot as mechanical strength considerations will allow. Creep limitations, for example, dictate a maximum of about 650° F for the titanium alloys which are replacing aluminum in some advanced high speed aircraft. Increased airframe temperatures, therefore, dictate that control surface bearings and other airframe bearings with capabilities well above current practice will be needed.

The design of the test bearings is shown in figure 8. The spherical element of the bearing is graphite fiber-reinforced PI. The fibers are chopped fibers about 1/4-inch long and 0.0003 inch diameter. The spherical element was not fastened to the oscillating journal. Therefore, the bearing is essentially a self-aligning plain cylindrical bearing with journal oscillation in the cylindrical bore and self-alignment provided by the spherical surface. Graphite fiber content of 15, 25, 45, and 60 w/o were evaluated.

We performed tests on oscillating plain spherical bearings at temperatures from room to 650° F and at unit loads to 5000 psi. Oscillation was ±15° at 60 cycles/minute. The tests were performed in an air atmosphere with a relative humidity of about 50 percent.

The best combination of friction, load carrying capacity and good thermal conductivity were observed with the 45 w/o graphite-PI composite. An example of the temperature and friction time profiles in a typical temperature cycling test are shown in figure 9. The temperature profile is our estimate of the thermal history for the control surface bearings in a shuttle orbiter during re-entry from orbit and the subsequent landing approach. The 650° F temperature is the maximum anticipated re-entry temperature for titanium alloy airframe kept "cool" with an insulator/ablator thermal protection system.

The friction temperature characteristics of all four graphite/polyimide compositions are summarized and compared to the results for a standard PTFE-lined airframe bearing in figure 10. Duration of bearing tests and bore deformation due to wear and plastic yielding are given in table II.

The friction coefficients of the polyimide composites decreased in a regular manner with increasing graphite content. The 15 and 25 w/o graphite fiber composite deformed, then fractured at 600° F and a 5000 psi unit load. The 60 w/o graphite fiber composite failed by brittle fracture under the same conditions. However, the 45 w/o graphite fiber composite did not fail under a 5000 psi unit load up to 650° F and for a short duration of 675° F.

The nature of the composites, therefore, changes in a regular manner from plastic to brittle behavior with an apparent optimum load capacity between 25 and 60 w/o graphite fiber and with 45 w/o the best composition of those evaluated in this preliminary study.

The standard PTFE-lined bearing had very low torque to 400° F but the PTFE liner extruded out of the bearing at 450° F.

Graphite additions substantially improve thermal conductivity as well as reducing friction. Heat generation at the sliding surfaces is therefore reduced substantially. This is of great practical significance especially with bearing materials containing polymers. For example, the commonly used design criterion for plastic bearings, which is termed limiting "PV" refers to the maximum product of unit load and velocity to which the bearing can be subjected before the surface temperature reaches the thermal degradation temperature of the polymer. Within the limits of load carrying capacity dictated by mechanical strength considerations, improved thermal conductivity will therefore increase the limiting PV of the bearing material.

## Extreme Temperature Solid Lubricants

For lubrication at 1000° F or higher, calcium fluoride ($CaF_2$) and barium fluoride ($BaF_2$) have shown considerable promise. These compounds have been tested in a number of coating compositions and as the lubricating material in fluoride/metal composites.

Coatings of $BaF_2$ and $CaF_2$ are applied by spraying (essentially painting) a suspension of the fluoride solids in water on to the metal surface. The metal is pre-heated to about 180° F to cause almost instantaneous evaporation of the water thus leaving a film of fluorides on the surface. Next, bond is developed by heating the coated part in argon or in hydrogen up to either the sintering point or the melting point of the coating material. Upon cooling, a bonded solid film coating is obtained. The sintered coatings, of course, require a lower firing temperature but they are more porous than the fused coating. Coating thicknesses from about $2x10^{-4}$ to $2x10^{-3}$ inches can be achieved by controlling the thickness of the coating during spraying. Therefore, no subsequent machining of the fired coatings is required.

Fluoride-lubricated composites are prepared either by infiltrating porous sintered metal bodies with molten fluorides or by plasma-spraying a mixture of fluorides and powdered metal. Plasma sprayed coatings are usually thicker and rougher than conventionally sprayed and fused coatings. Plasma sprayed coatings therefore often do require subsequent machining to provide a surface finish that is satisfactory for a bearing application. Plasma spraying has a tremendous advantage in that the coated parts are not heated severely in the process.

Fused fluoride coatings. - The friction and wear properties in air of fused fluoride coatings of the composition 38 percent $CaF_2$ - 62 percent $BaF_2$ are given in figure 11. The rider wear and friction coefficients of uncoated specimens are included for comparison. Separate 1-hour experiments were conducted to obtain each of the data points shown over a range of temperatures from 75° to 1500° F and at two sliding velocities, 455 and 2000 feet per minute. Rider wear is expressed as wear per foot of sliding so that wear at the two sliding velocities can be directly compared.

Over the entire temperature range and at both sliding velocities, the coatings were responsible for very significant reduction in friction and wear relative to the uncoated metals. At a sliding velocity of 455 feet per minute, the friction coefficient of the coated specimen was high (0.4) at 75° F, but rider wear was very low; from about 500° to 1500° F the friction coefficients were less than 0.20. At 2000 feet per minute, the friction coefficients were 0.10 to 0.22 over the entire temperature range 75° to 1500° F.

Significantly, the coatings did not wear through to failure in any of the experiments in an air atmosphere. One hour represents 52 200 cycles with no failure at the lower speed and 229 000 cycles with no failure at the higher speed. Because of their excellent chemical stability, these coatings are also suitable for use in strong reducing environments such as hydrogen or even liquid sodium.

Fluoride metal composites. - Composite materials which are suitable for use at high temperatures in such reactive environments as air, hydrogen and liquid metals have been reported (ref. 23). The composites consist of a porous metal matrix impregnated with barium fluoride-calcium fluoride eutectic composition. As already indicated, bonded coatings of this eutectic were shown to be effective solid lubricants in severe environments such as liquid sodium, air (to 1200° F), and hydrogen (to 1500° F).

The microstructure of a composite with 60 w/o nickel-chromium alloy - 40 w/o fluoride eutectic is shown in figure 12. The effects of temperature on the friction and wear of the composites are given in figure 13. Low wear of the composite and the dense metal rider were observed in all cases. Friction coefficients decreased with increasing temperature, and were reduced appreciably when a thin fluoride overlay was bonded to the surface of the composite.

The friction and wear of composites in a hydrogen atmosphere are given in figure 14. Very low wear was observed at all temperatures; disk wear rate was nearly constant for all temperatures. With an overlay, friction coefficients were 0.20 at 80° F and decreased with temperature to 0.06 at 1500° F. The wear lives of composites in air and in hydrogen are given in table III.

In air the endurance life of the composites exceeded one million cycles at 500°, 1000°, and 1200° F. At 80° F, the friction coefficient was greater than 0.30 and a zero wear life is indicated. However, the low wear rate (fig. 15) at 80° F indicates the composite could be used at 80° F in applications where a low friction coefficient is not essential. At 1500° F, the wear life was 850 000 but severe oxidation occurred. The wear life of a $BaF_2$-$CaF_2$ eutectic coating on dense nickel-chromium alloy was 389 000 cycles at 1000° F. The wear life of the composite was almost three times greater.

In hydrogen, the experiments were terminated after about 1 1/2 million cycles if the friction coefficient had not yet increased to 0.30. Results were similar to those obtained in air with the exception that the friction coefficient at 80° F was lower in hydrogen than in air and the composite was run a full 1 1/2 million cycles at friction coefficients below 0.30.

At 1000° F wear life of the composite was far superior to the wear life of the coating bonded to a dense metal substrate.

## Ball Bearing Tests

Fluoride solid lubricants were tested in ball bearings at 1200° F and 1500° F. The bearing test head and an exploded view of the test bearing are shown in figure 16. The bearing cages were made from self-lubricating composites of sintered Inconel impregnated with a eutectic fluoride (38 w/o $CaF_2$ - 62 w/o $BaF_2$) composition.

Some typical test data are shown in figure 17. The torque of an unlubricated bearing is shown for comparison. The data show that fluoride-lubricated ball bearings can run for useful periods of time at 1200° and 1500° F. Bearing torque was steady at about 1 to 3 inch ounces compared to erratic torque between 3 and 10 inch ounces for the unlubricated bearing. The 1 to 3 inch ounces torque was comparable to the torque of grease-packed bearings run at lower temperatures (100° - 400° F) but under otherwise identical conditions.

The failure mode was not due to excessive wear. In all cases, failure was caused by a gradual swelling of the composite cage material due to oxidation which eventually caused the cage to jam against the outer race. This experience prompted a study to develop improved oxidation resistance in the fluoride-metal composites. This was accomplished by introducing specially-formulated glasses into the composition; these glasses acted as oxidation barriers or inhibitors.

## Plain Cylindrical Bearings With Oxidation-Resistant Self-Lubricating Liners

Recent tests of the subject bearings have been very encouraging. The test bearings are similar to figure 8 except the entire bearing is of nickel chromium alloy. The bore of the spherical element is lined with a 0.010-inch plasma-sprayed and machined composite layer of nichrome, $CaF_2$, and glass. Friction coefficients from room temperature to 1600° F were on the order of 0.2 to 0.3. Less than $2 \times 10^{-4}$ inch of combined journal and bore wear occurred in a 6-hour oscillating test at a bearing unit load of 5000 psi.

## CONCLUDING REMARKS

1. Solid lubricants are available which can be used over a wide temperature range. Layer lattice materials such as $MoS_2$ and $WS_2$ lubricate to maximum temperatures of 700° to 800° F, but oxidize at higher

temperatures. Graphite is useful to about 850° F but requires adsorbed moisture or solid additives to lubricate. Graphite fluoride, an intercalation compound of graphite does not require adsorption or additives and lubricates 100° to 200° F higher than $MoS_2$ in a given application. $CaF_2$-based coatings and composites can be used in most atmospheres to at least 1600° F.

2. Machine design should include consideration of the lubricant from the conceptual stage of design. Bearing systems should be matched to the properties of solid lubricants. A bearing design suitable for oil lubrication is not necessarily appropriate for solid lubrication.

## REFERENCES


1. Campbell, W. E., "Solid Lubricants," Boundary Lubrication: An Appraisal of World Literature, F. F. Ling, E. E. Klaus, and R. S. Fein, eds., ASME, New York, 1969, ch. 10.
2. Campbell, M. E., Loser, J. B., and Sneegas, E., "Solid Lubricants," SP-5059, 1966, NASA, Washington, D.C.
3. Barry, H. F., "Solid Lubricants Section, Friction and Wear Topic," Lubrication Review - A Digest of the Literature for 1967, J. H. Rumbarger, ed., Journal of Lubrication Technology, Vol. 91, No. 2, Apr. 1969, pp. 239-240.
4. Johnson, R. L., "A Review of the Early Use of Molybdenum Disulfide as a Lubricant," NLGI Spokesman, Nov. 1968, pp. 298-305.
5. Campbell, M. E., "Solid Lubrication Technology - A Review," Mechanical Engineering, Vol. 90, No. 2, Feb. 1968, pp. 28-36.
6. Peace, J. B., "Solid Lubricants," Lubrication and Lubricants, E. R. Braithwaite, ed., Elsevier Publ. Co., 1967, pp. 67-118.
7. Bryant, P. J., Gutshall, P. L., and Taylor, L. H., "A Study of Mechanisms of Graphite Friction and Wear," Wear, Vol. 7, No. 1, Jan.-Feb. 1964, pp. 118-126.
8. Sliney, H. E., and Johnson, R. L., "Bonded Lead Monoxide Films as Solid Lubricants for Temperatures up to 1250° F," RM E57B15, 1957, NACA, Cleveland, Ohio.
9. Devine, M. J., Lamson, E. R., and Bowen, J. H., Jr., "Inorganic Solid Film Lubricants," Journal of Chemical and Engineering Data, Vol. 6, No. 1, Jan. 1961, pp. 79-82.

10. Johnson, R. L., and Sliney, H. E., "Ceramic Surface Films for Lubrication at Temperatures to 2000° F," American Ceramic Society Bulletin, Vol. 41, No. 8, Aug. 1962, pp. 504-508.

11. Sliney, H. E., "Decomposition Kinetics of Some Solid Lubricants Determined by Elevated-Temperature X-Ray Diffraction Techniques," Proceedings of the U.S.A.F. Aerospace Fluids and Lubricants Conference, P. M. Ku, ed., Southwest Research Inst., Sept. 1963, pp. 350-367.

12. Brainard, W. A., "The Thermal Stability and Friction of the Disulfides, Diselenides, and Ditellurides of Molybdenum and Tungsten in Vacuum ($10^{-9}$ to $10^{-6}$ Torr)," TN D-5141, 1969, NASA, Cleveland, Ohio.

13. Savage, R. H., "Graphite Lubrication," Journal of Applied Physics, Vol. 19, No. 1, Jan. 1948, pp. 1-10.

14. Lipp, L. C., and Klemgard, E. N., "Graphite Lubricant Combinations for High Temperature Applications," Lubrication Engineering, Vol. 22, No. 5, May 1966, pp. 187-195.

15. Peterson, M. B., and Johnson, R. L., "Friction Studies of Graphite and Mixtures of Graphite with Several Metallic Oxides and Salts at Temperatures to 1000° F," TN-3657, 1956, NACA, Cleveland, Ohio.

16. Peterson, M. B., and Johnson, R. L., "Solid Lubricants for Temperatures to 1000° F," Lubrication Engineering, Vol. 13, No. 4, Apr. 1957, pp. 203-207.

17. Carson, R. W., "Selecting High-Temperature Sleeve Bearings," Product Engineering, Vol. 6, No. 1, Jan. 4, 1965, pp. 76-82.

18. Fusaro, R. L., and Sliney, H. E., "Lubricating Characteristics of Polyimide Bonded Graphite Fluoride and Polyimide Thin Films," Preprint 72LC-7C-3, Oct. 1972, ASLE, Park Ridge, Ill.

19. Kuriakose, A. K., and Margrave, J. L., "Mass Spectrometric Studies of the Thermal Decomposition of Poly (Carbon Mono-Fluoride)," Inorganic Chemistry, Vol. 4, No. 11, Nov. 1965, pp. 1693-1641.

20. Hanson, M. P., and Serafini, T. T., "Effects of Thermal and Environmental Exposure on the Mechanical Properties of Graphite/Polyimide Composites," TN D-6604, 1971, NASA, Cleveland, Ohio.

21. Kaplan, S. L., Helford, D., and Hersch, S., "P13N Polyimide Molding Compounds," Proceedings 27th Annual Conference on Reinforced Plastics/Composites Institute, Society of the Plastics Indsutries, Inc., New York, Feb. 1972, pp. 1-6, Sect. 2-A.

22. Sliney, H. E., and Johnson, R. L., "Graphite-Fiber - Polyimide Composites for Spherical Bearings to 340° C (650° F). TN D-7078, 1972, NASA, Cleveland, Ohio.

23. Sliney, H. E., "Self-Lubricating Composites of Porous Nickel and Nickel-Chromium Alloy Impregnated With Barium Fluoride-Calcium Fluoride Eutectic," ASLE Transactions, Vol. 9, No. 4, Oct. 1966, pp. 336-347.

TABLE I. - RESULTS OF THERMAL STABILITY AND FRICTIONAL EXPERIMENTS IN VACUUM OF $10^{-9}$ TO $10^{-6}$ TORR

| Compound | Probable onset of thermal dissociation as (detected by TGA) °F | Dissociation products first detected by mass spectrometry, °F | Maximum temperature at which burnished films provided effective lubrication, °F |
|---|---|---|---|
| $MoS_2$ | 1700 | 2000 | 1200 |
| $WS_2$ | 1600 | 1900 | 1350 |
| $MoSe_2$ | 1400 | 1800 | 1400 |
| $WSe_2$ | 1300 | 1700 | 1400 |
| $MoTe_2$ | 1300 | 1300 | 1000 |
| $WTe_2$ | 1300 | 1300 | (a) |

[a]Friction coefficient greater than 0.2 at all temperatures.

TABLE II. - BORE WEAR AND DEFORMATION IN GRAPHITE FIBER-POLYIMIDE SPHERICAL BEARING ELEMENTS

[Oscillation at 60 cpm, ±15°, unit loads to 5000 psi ($3.5 \times 10^7$ $N/m^2$) maximum variable temperature, ambient to 650° F (350° C).]

| Graphite content, w/o | Total journal oscilla-tions, kilocycles | Increase in bore diameter | | Appearance of transfer film on journal |
|---|---|---|---|---|
| | | Parallel to load | 90° to load | |
| | | in. | in. | |
| 15 | 5 | 0.0785 | 0.0263 | powder, non-adherent |
| 25 | 4 | .0478 | .0035 | thick, patchy, adherent |
| 45 | 32 | .0030 | .0016 | complete coverage with very thin adherent film |
| 60 | 11 | a | a | barely visible in-complete film |

[a]Fracture too extensive to allow accurate measurements.

TABLE III. - COMPARATIVE WEAR LIFE OF COMPOSITES AND COATINGS IN AIR AND HYDROGEN

| Specimen temperature °F | Cycles at which friction coefficient increased to 0.30[a] | | | |
|---|---|---|---|---|
| | Air | | Hydrogen | |
| | Composites | Coatings | Composites | Coatings |
| 80 | (b) | (c) | [d]1,560,000 | (c) |
| 500 | 2,750,000 | 115,000 | [d]1,490,000 | (c) |
| 1000 | 1,150,000 | 389,000 | [d]1,610,000 | 275,000 |
| 1200 | 1,370,000 | (c) | [d]1,370,000 | (c) |
| 1500 | 850,000 | (c) | 570,000 | (c) |

[a]Based on single runs.

[b]Low wear rate but friction coefficient of 0.30 to 0.35.

[c]No test.

[d]Experiments terminated before failure. (Friction coefficient did not increase to 0.3 during number of cycles indicated.)

E-7368

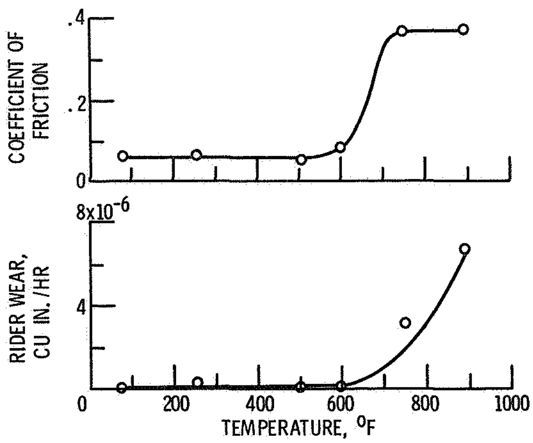


Figure 1. - Lubricating properties of resin-bonded molybdenum disulfide.

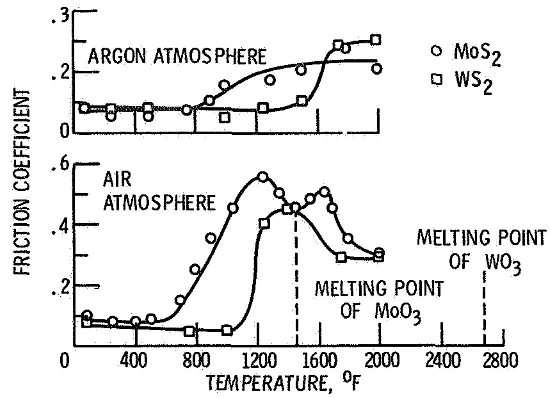


Figure 2. - Friction characteristics of $MoS_2$ and $WS_2$ in air and in argon. Sliding velocity, 6 ft/min; load, 6 kg.

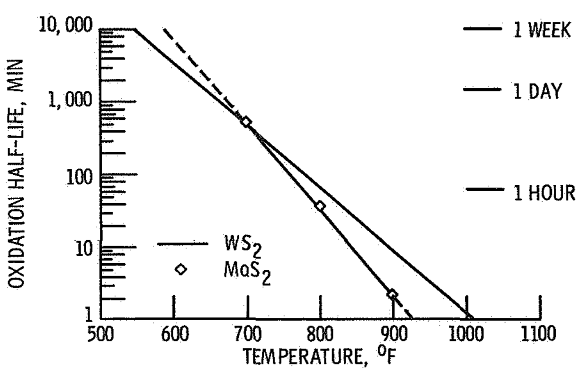


Figure 3. - Comparative oxidation of $WS_2$ and $MoS_2$ average particle size, ~1.0μ; compact density 50% of maximum air flow rate, 1/3 L/min.

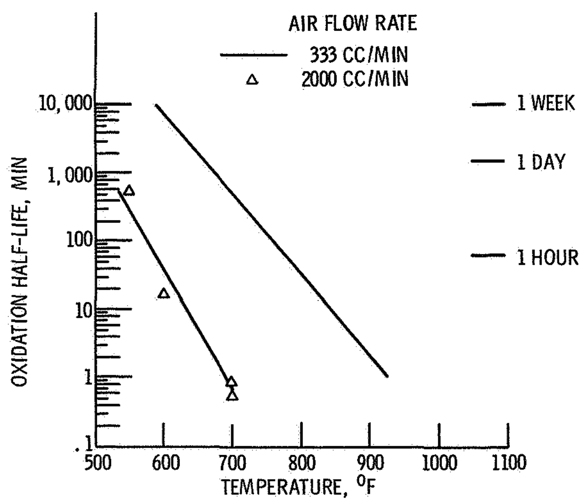


Figure 4. - Oxidation characteristics of $MoS_2$ at two air flow rates. Average particle size, ~1.0μ; compact density, 50% of maximum.

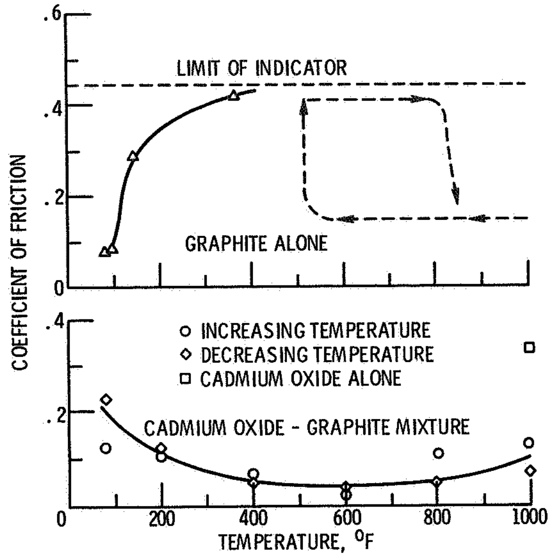


Figure 5. - Lubrication with graphite and with graphite - cadmium oxide mixture.

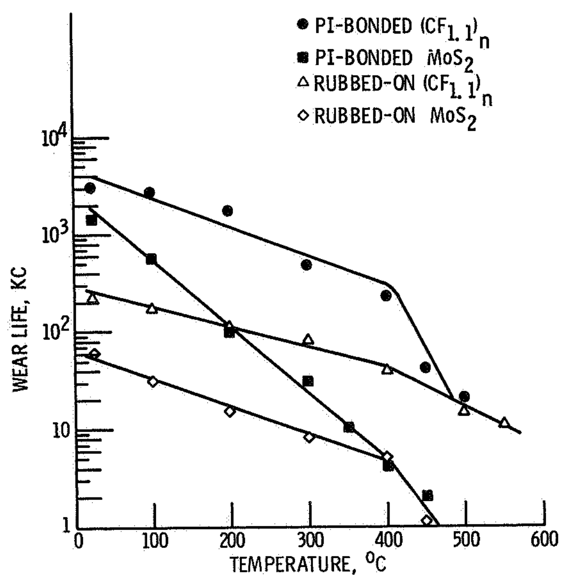


Figure 6. - Wear life vs temperature. Exp cond: load, 1 kg; speed, 2.6 m/sec (1000 rpm); dry air atm (20 ppm $H_2O$); failure criterion, friction coeff of 0.30.

E-7368

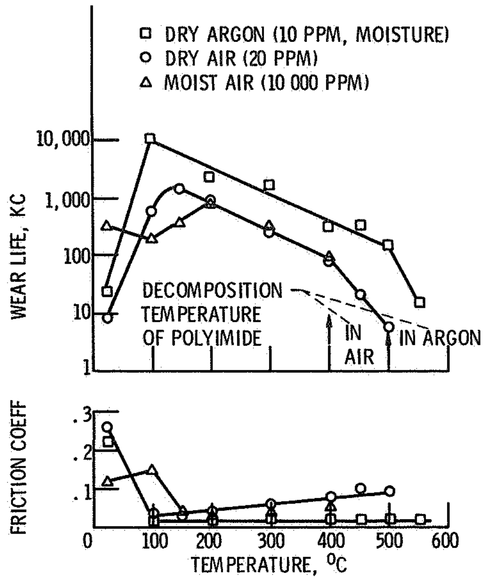


Figure 7. - Effect of temperature and atmosphere on the wear life and friction coefficient of polyimide films. Experimental condition: load, 1 kg; speed, 2.6 m/sec; failure criterion, friction coefficient of 0.30.

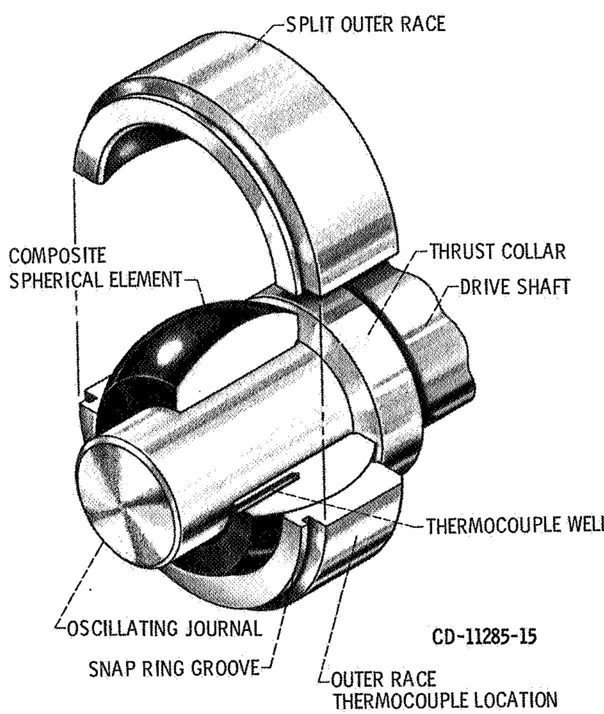


Figure 8. - Self-aligning plain Spherical Test Bearing.

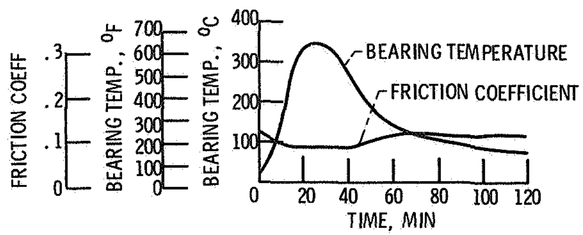


Figure 9. - Temperature and friction profile of bearing with 45 wt.% graphite-fiber-reinforced - polyimide composite during simulated re-entry test.

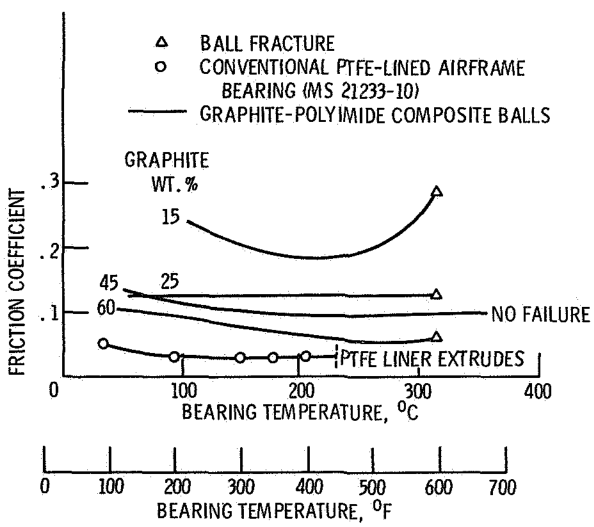


Figure 10. - Summary of friction of spherical bearings with polyimide - graphite-fiber composites of various fiber contents. Stellite 6B journal; radial unit load, $3.5\times10^{7}$ N/m$^{2}$ (5000 psi); journal oscillation in cylindrical bore at 1 hertz, $\pm15^{0}$.

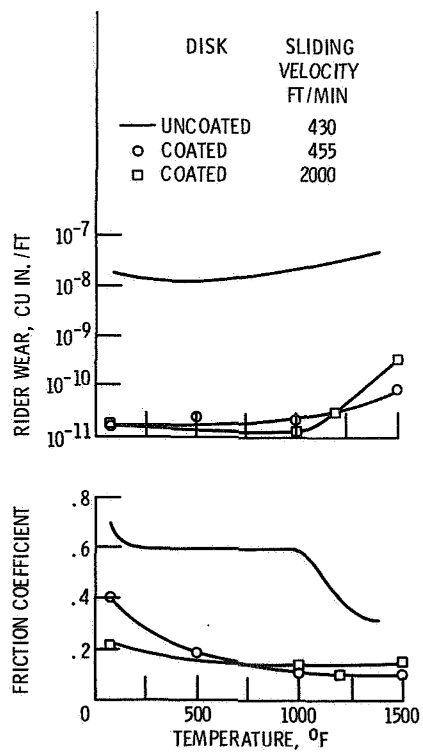


Figure 11. - Lubricating properties of fused fluoride coating composition in air.

E-7368

PHOTOGRAPH OF FLUORIDE-INCONEL COMPOSITE

35 V% $BaF_2$-$CaF_2$ EUTECTIC, 65 V% SINTERED INCONEL-X

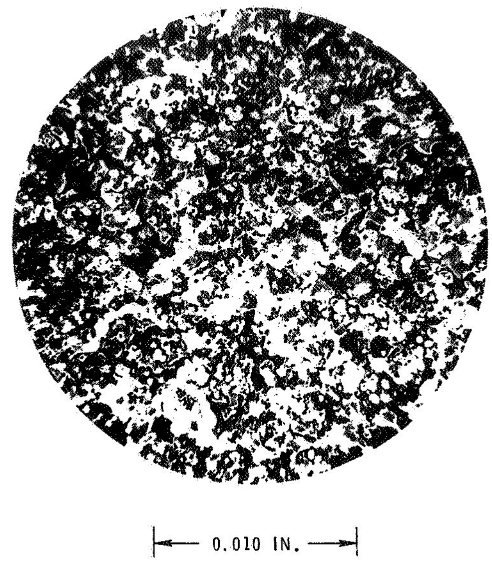


Figure 12.

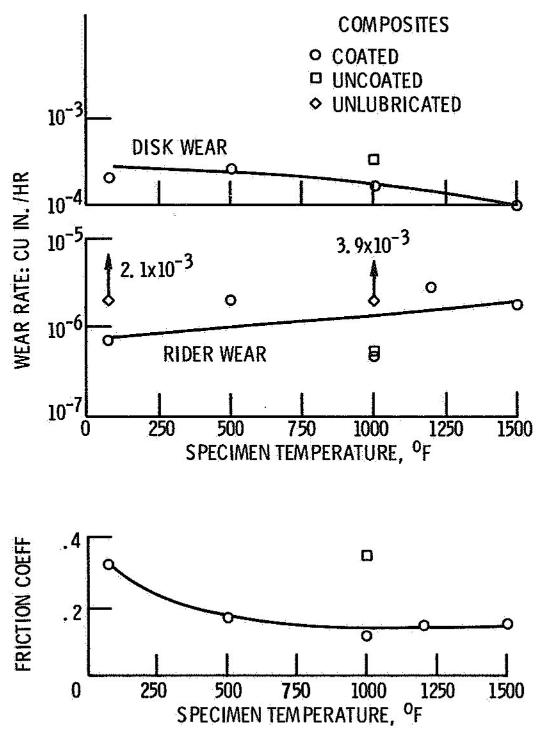


Figure 13. - Friction and wear of fluoride-Inconel composite disks and cast Inconel riders in air. (35 V% $BaF_2$-$CaF_2$ eutectic, 65 V% sintered Inconel; 7/8-in.-radius riders, 500-gm load, 2000 ft/min.)

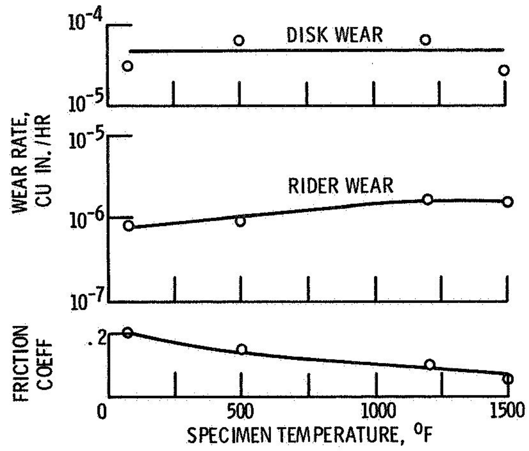


Figure 14. - Lubricating properties of fluoride-Inconel composite disk and cast Inconel riders in hydrogen. 35 V% $BaF_2$-$CaF_2$ eutectic, 65 V% sintered Inconel-X; 7/8-in.-radius riders, 500-gm load, 2000 ft/min.

LOAD-BEARING SURFACE OF FLUORIDE-INCONEL COMPOSITE

35 V% $BaF_2$-$CaF_2$ EUTECTIC, 65 V% INCONEL; 1200° F HYDROGEN, 2000 FT/MIN, 500-GM LOAD, 6 HR

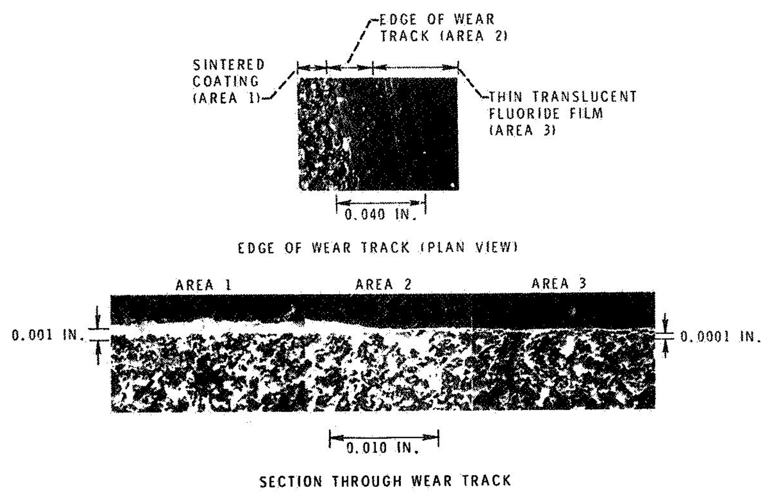


Figure 15.

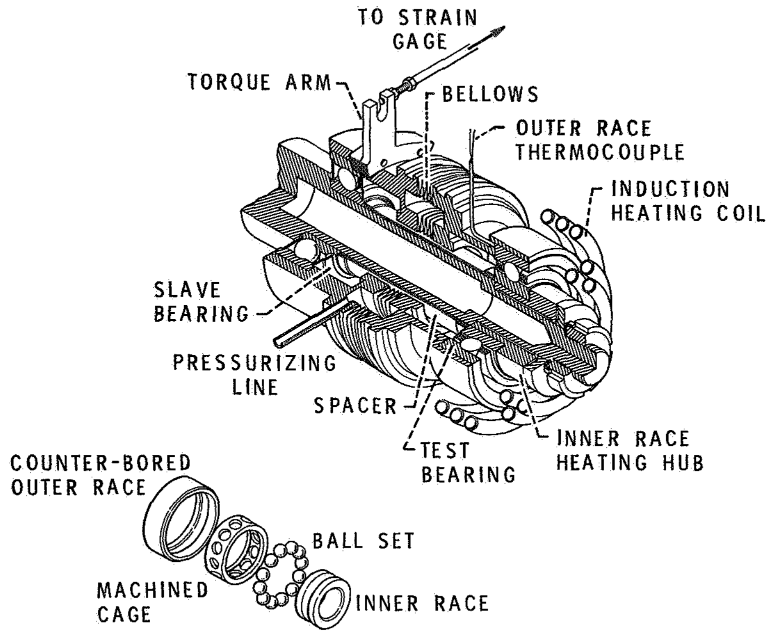


Figure 16. - Bearing test head and test bearing.

E-7368

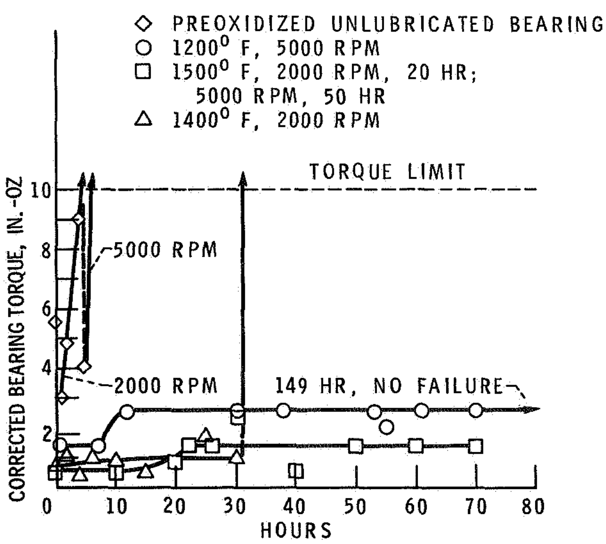


Figure 17. - Influence of temperature and speed on bearing performance. Composite cages, 30 lb thrust load, 0.020-in. cage-race clearance.