Inorganic Solid Film Lubricants

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A GENERAL classification of solid lubricants as well as a discussion of properties, application, and theories has been the subject of numerous investigations (*3, 5, 6, 8, 9, 12*). Methods for utilizing solid film lubricants for ball bearing applications (*7*) have also been investigated. Experimental data on organic resin-bonded solid films indicated that film stability decreases with increase in temperature, resulting in the loss of the solid film function of reducing friction and separating metal bearing surfaces. Furthermore, some inorganic solid films must be cured at temperatures that damage many bearing materials. A new system of solid film lubricants was sought. The following characteristics were proposed for the binder fraction: capability of being deposited in the form of a binding film, ability to retain hardness and chemical stability at elevated temperatures, capability of forming a tenacious bond at temperatures which would not produce dimensional changes in metal substrates, compatibility with a variety of lubrication solids and resistance to abrasion.

A comparison of the properties of a number of organic and inorganic materials showed the soluble metal silicates to be the most promising for use as binders. Since the resultant solid film would be inorganic, greater stability under conditions of nuclear radiation, low pressure, and extreme temperatures might be expected for lubrication applications in high performance aircraft, nuclear powered rockets, and other space vehicles. Viscosity and density data (*10*) have been presented for a number of sodium silicate solutions and potassium silicate solutions.

MoS_2 and graphite were chiefly used for the lubricant fraction of the solid film envionmental studies.

Techniques for sample preparation, bonding, and lubricating formulation were investigated. Molybdenum disulfide and sodium silicate (% ratio Na_2O to SiO_2 = 1 to 2.90) as lubricant fraction and binder fraction, respectively, were chosen for preliminary studies. It was found that poor wettability of the solid lubricant results from direct addition of MoS_2 to sodium silicate solution. Samples were prepared by first wetting the lubricant solid with water to obtain a slurry, adding the slurry to the solution of sodium silicate, and stirring to obtain a uniform mixture. This mixture can be applied in the form of a thin film by a spray application. The film contains water which must be removed to obtain effective bonding and reduce softness. The water was removed by heating with a gradual temperature increase over a period of 32 to 48 hours.

Recent work has shown that curing time may be substantially reduced. This sample preparation method was extended to a variety of solids and solid mixtures. It was observed that an immediate reaction occurred when PbO, PbI, PbS, ZrCl, or CdI_2 are added to the sodium silicate solution yielding a very thick fluid or a solid mass. A substitution of sodium phosphate and/or sodium borate for the sodium silicate binder eliminated the reaction, provided a means for solid lubricant-binder compatibility for PbO, PbI_2, PbS, ZrCl, and CdI_2, and extended the number and types of inorganic binders for solid film lubricants.

The results of lubricity studies conducted using a ball bearing life test apparatus (*4*) are shown in Table I. These data represent the results of single runs on a number of combinations of solids or solid mixtures and binders. Significance is attributed to the results of single runs, since successive tests on a limited number of samples have produced a deviation from the average of less than 10%. A graphical presentation showing the effect of the ratio of graphite to MoS_2 in a sodium silicate binder (Na_2O to SiO_2 = 1 to 2.90) on wear life in terms of cycles is shown on Figure 1. A molybdenum disulfide-graphite mixture with a sodium silicate binder has proved to be the most satisfactory lubricant film produced to date for high speed, light load, ball bearing applications wherein the bearings are fabricated from Cr alloy steel (AISI-C52100) for the races and balls and carbon steel (AISI-C1010) for the retainers. Accordingly, most of the experiments conducted to determine the effect of environment on the properties of the inorganic solid film have utilized films containing MoS_2, graphite, and sodium silicate.

EXPERIMENTAL PROCEDURES FOR ENVIRONMENT STUDIES

Experimental procedures were selected or devised to produce the extreme environments associated with the bearing systems of present and future space vehicles. The successful lubrication of such bearings requires lubricant performance over a wide range of temperature, resistance to nuclear radiation, and stability under reduced pressure. Lubrication with conventional oils and greases, if feasible, would demand a weight penalty in terms of accessory equipment such as pumps, tanks, heaters, etc.

Unless otherwise specified, the ball bearing test specimens were fabricated from AISI-C52100 steel for the races and balls and AISI-1010 for the retainers.

Liquid Oxygen Detonation. Essentially the apparatus consists of a plummet assembly weighing 20.0 pounds, a striker pin, and a test sample cup. The cup containing the solid film is slowly cooled to liquid oxygen temperature by suspending in the gaseous oxygen followed by immersion in the liquid oxygen. The cup is filled with liquid oxygen and transferred to the test apparatus. A clean striker pin, precooled by immersion in liquid oxygen, was placed in contact with the sample surface and the cup was topped with liquid oxygen prior to impact. The plummet drop distance is 50 inches.

Lubricant Performance in Liquid Oxygen. Ball bearing lubrication in the presence of liquid oxygen was studied using the following experimental procedure: Liquid oxygen was contained in a 25-liter flask and pressurized gas was used to pump the liquid oxygen through copper tubing to an insulated stainless steel beaker containing the test bearing. The solid film lubricated bearing was attached to a shaft which can be rotated at 3600 r.p.m. by means of a drill press motor. The ball bearing is encased in a bearing prior to being adapted to the test shaft. A 5-pound thrust load is applied and the drive motor is actuated.

Nuclear Radiation. Solid film-lubricated ball bearing specimens were exposed to gamma radiation in the Materials Testing Reactor Gamma Irradiation Facility at Idaho Falls. The average dose rate was 4.21×10^6 r. per hour. The total dosage was 5×10^9 r. Exposure time required to obtain this dosage was 1187 hours. Prior to exposure, the bearings were wrapped in aluminum foil and placed in an aluminum container, 3 inches in diameter and 8 inches in length. The lubricated bearings were irradiated while under a constant air pressure of approximately 9.5 p.s.i.g. After irradiation, the performance life was evaluated using the standard test spindle (*4*). The test was conducted at 10,000 r.p.m. and 350° F.

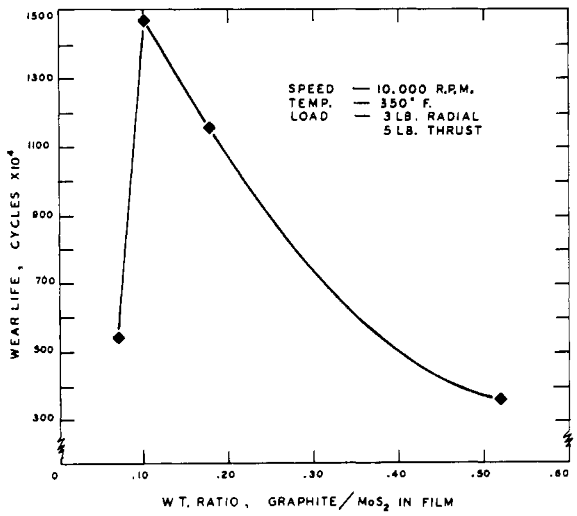

Figure 1. Wear life vs. graphite /MoS_2 weight ratio

Low Pressure. A vacuum evaporator (*11*) was utilized to provide pressures of less than 1 micron. A cylindrical 18-8 stainless steel pin, 1.25 inches in length and 0.25 inch in diameter having a Rockwell hardness of Rc32, was selected for the bearing specimen. The solid film-lubricated specimen was placed in a combustion boat which was subsequently wrapped with resistance wire. The assembly was placed in the bell jar of the evaporator. A preliminary degassing was accomplished by heating to 500° F. for 2 hours. The temperature was increased to 1020° F. over a period of 3 hours, while maintaining a pressure of less than 15 microns. The temperature was maintained at 1020° F. for 1 hour and 45 minutes. The pressure during this period was between 0.1 and 1.0 micron for two thirds of the time period and between 2 and 7 microns for the remainder of the period. After this treatment the temperature was returned to 300° F. and the pressure was raised to atmospheric.

Thermal Stability. Steel panels, AISI-4130, 3 × 6 × 0.036 inch were utilized as test specimens. Prior to application of the lubricant, the surface of the panel was subjected to a vapor blast pretreatment. The coated panels were then placed in a forced draft oven at 700° F. and allowed to remain at this temperature for 24 hours. The panels were then directly removed to a metal block to accelerate cooling to room temperature. The film was examined visually for color change, cracking, flaking, etc., and was scratched to determine, qualitatively, the adhesion characteristics.

Low Temperature Torque. The apparatus (*2*) used to evaluate the starting torque characteristics of the solid film consists essentially of a test bearing, a bearing housing, a side load, and a test shaft. The equipment is sufficiently compact so that it can be placed in a subzero cabinet, and tests can be conducted at controlled temperatures. Starting and running torque determinations were made at 77° and −100° F.

RESULTS OF ENVIRONMENT EXPERIMENTS

Liquid Oxygen Detonation. Twenty-five separate liquid oxygen detonation tests were conducted on the solid film lubricant composed of 71% molybdenum disulfide, 7% graphite, and 22% sodium silicate. The film thickness was approximately 0.002 inch. No detonations were observed in any of the runs. The tentative safety limit of 350 foot-pounds per square inch was exceeded in all runs.

Lubricant Performance in Liquid Oxygen. The retainer surfaces and races of the ball bearing specimen were lubricated with a solid film composed of 66% molybdenum disulfide, 11% graphite, and 23% sodium silicate. A phosphate pretreatment (*1*) was applied to the retainer surfaces prior to application of the solid film. Approximately 35 minutes were required to reach a temperature of −296° F. at the bearing race. The run was continued for 1 hour with the bearing submerged in liquid oxygen. The run was arbitrarily stopped and the bearing brought back at room temperature. After the bearing was dried, a 10,000 r.p.m. run at 350° F. was conducted for 21 hours. A duplicate determination gave the same result. The running time for the same formulation not subjected to the liquid oxygen run, but only to the 10,000 r.p.m. 350° F. test was also 21 hours. No comparison with oils, greases, or solid films having organic binders is afforded, because of the possibility of detonation in making runs with these materials in liquid oxygen. A nonlubricated bearing failed in 1 minute during the liquid oxygen test. In order to make runs at 750° F. after the liquid oxygen run, bearings with races and balls fabricated from Cr-Mo-V tool steel (SAE M-10) and retainers of 302 stainless steel were used. A running time of 6 hours was obtained at 750° F., 5000 r.p.m., with no applied load. The phosphate pretreatment used with the AISI-C1010 steel retainers could not be used for the stainless steel retainers.

Nuclear Radiation. The races and retainers of the ball bearing specimens were lubricated with a solid film composed of 71% molybdenum disulfide, 7% graphite, and 22% sodium silicate. After irradiation, the bearing performance life (*4*) at 10,000 r.p.m. and 350° F. was

Table I. Effect of Solid Film Composition on Bearing Performance Life

Apparatus. High speed bearing performance apparatus.
Specimen. 204 size ball bearing, AISI-C52100 steel balls and races, AISI-C1010 retainers.
Load. 5-lb. thrust, 3-lb. radial.
Test temp. 350° F.

Chemical Composition of Solid Film, Weight %			Test Speed, R.P.M.	Performance Life, Hr.
MoS_2	Graphite	Sodium silicate		
0	66	34	10,000	4
48	26	26	10,000	6
66	11	23	10,000	21
71	7	22	10,000	29
74	4	22	10,000	9
71	7	22	3,500	42
71	7	22	1,250	240
PbO	Graphite	Sodium phosphate		
59	29	12	3,500	14
89	0	11	10,000	0.5
PbI_2	Graphite	Sodium phosphate		
83	0	17	10,000	4
MoS_2	Graphite	Sodium phosphate		
71	7	22	3,500	88
MoS_2	Graphite	Sodium borate		
71	7	22	3,500	14
MoS_2	Graphite	Potassium silicate		
71	7	22	1,250	207
71	7	22	10,000	22

Solid film applied to races and retainers. Cure condition. Room temp. 0.5 hr.; 180° F.: 16-24 hr.; 300° F.: 16-24 hr. Retainer surfaces phosphated prior to solid film deposition. Approximate film thickness: 0.0001 inch (races), 0.0009 inch (retainers).

determined. A running time of 17 hours was obtained. An unirradiated bearing lubricated with a film of the same composition, but stored for a time equivalent to that required for the radiation exposure experiment, lasted 19 hours. Since the differences in these two running times are within repeatability limits, it is considered that no damaging effects to the solid film were produced by a gamma dosage of 5×10^9 r. Experiments are now in progress to determine the solid film stability at 1×10^{10} r.

Low Pressures. After being exposed to the conditions previously described for the low pressure experiment, the solid film (71% molybdenum disulfide, 7% graphite, and 22% sodium silicate) lubricated specimen was visually examined for evidence of deterioration and then subjected to a Falex endurance life test. Tests were conducted with an applied load of 500 pounds at room temperature. The V-block components were AISI-1137 steel, Rockwell Rc20. The solid film lubricant was not applied to the V-blocks. An endurance life of 271 minutes was obtained. The endurance life for the same composition not subjected to vacuum-temperature conditions was 228 minutes.

Thermal Stability. A comparison of the thermal stability characteristics of the inorganic solid film (71% molybdenum disulfide, 7% graphite, and 22% sodium silicate), a commercial solid film containing molybdenum disulfide in a phenolic resin binder, and an extreme high temperature grease, MIL-G-25013A, was made. After 24 hours at 700° F, no breakdown of the experimental film was observed, while the two organic lubricants were degraded within several hours. An 800° F. test was also conducted on the same inorganic film. No breakdown was observed after 24 hours at this temperature. At 900° F. approximately 20% of the film surface was white indicating that MoS_2 was being converted to MoO_3.

Low-Temperature Torque. The retainer surfaces and races of the ball bearing specimen were lubricated with a solid film composed of 71% molybdenum disulfide, 7% graphite, and 22% sodium silicate. The solid film produced a starting torque of 472 gram-cm. at -100° F. and of 118 gram-cm. at 77° F. Test results for a low temperature grease designed for -100° F. operation (MIL-G-7421 grease) showed that the grease produced a starting torque of 4764 gram-cm. at -100° F. and 177 gram-cm. at 77° F. Running torque characteristics were approximately the same for both lubricants.

MECHANISM STUDIES

Solid Film Structure. The typical solid film lubricant is composed of lubricating solids and binder solids. The lubricating solids and binder solids are each composed of one or more constituents. Figure 2 illustrates a cross section of a solid film lubricant bonded to a metal surface. The film thickness is exaggerated in order to show a probable gradient of lubricating solids in a continuous binder medium. The ratio of lubricating solids to binder solids is one of the factors determining lubricity for solid film lubricants. Experiments to study the comparative properties of potential lubricating solids should not be based on a direct weight substitution, since density and/or particle size differences exist. The more important volume factor should be considered. The work conducted in phase I was aimed at producing a satisfactory solution to the problem of substitution of lubricating solids in a binder such that the volume of the lubricating solids remains essentially constant.

The technique devised provides an adequate approximation for equal volume substitution. In the following outline of the procedure for a sample of given weight, the per cent by weight of lubricating solid initally employed is selected on the basis of the maximum number of wear cycles obtainable by estimation from a curve of number of wear cycles *vs*. per cent of lubricating solids.

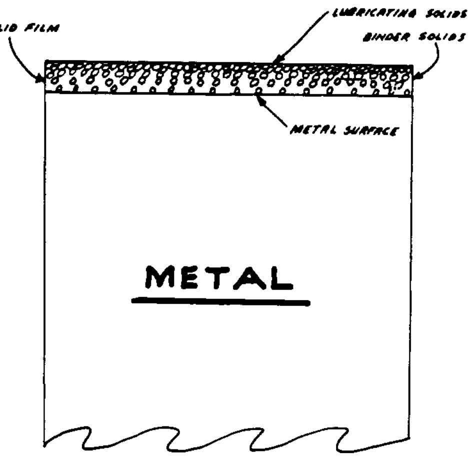

Figure 2. Section of Bonded film

The weighed solid is placed in a graduated cylinder and packed by tapping until a constant volume reading is obtained, and is centrifuged (1800 r.p.m., 7.5-inch radius) for 1 hour.

The final volume of the cylinder is noted.

The initial weight divided by the final volume represents the apparent density of the lubricating solid.

The weight of lubricating solid B required to give a volume equal to lubricating solid A was calculated on the basis of the following equation:

$$W_B = \frac{D_B \times W_A}{D_A}$$

where W_B = weight of solid B (to be calculated)
W_A = weight of solid A (in solid film formulation)
D_B = apparent density of solid B
D_A = apparent density of solid A

Table II presents apparent density data for a number of lubricating solids of interest for future research.

Wear Life. The utilization of solid film lubricants in high speed ball bearing applications is a relatively recent advance in the science of lubrication. Accordingly, not enough is yet known about the wear pattern encountered with such lubricants in ball sliding and rolling. Oxidation or other chemical degradation of liquid lubricants is a frequent cause of failure of oils and greases; however, at equivalent temperature and operating times, the inorganic lubricating solid present in the solid film under investigation is, by comparison, more oxidation resistant and thermally stable. Therefore, it is hypothesized that ball bearing failure is due to the removal of the solid film by the continual rubbing

Table II. Apparent Density of Selected Inorganic Solids

Solid, 5.5 G.	Final Volume, Cc.	Apparent Density[a]
MoS_2, 5 g., graphite, 0.5 g.[b]	3.25	1.7
MoS_2, 5 g., graphite, 0.5 g.[c]	5.35	1.0
PbO	1.5	3.6
Pb	1.1	5.0
Ag	2.2	2.5
AgI	2.05	2.7
PbI_2	2.65	2.0
Pb, 5 g., graphite, 0.5 g.	1.5	3.6
Ag, 5 g., graphite, 0.5 g.	2.2	2.5

[a] Laboratory techniques for preparation of samples may affect apparent density. [b] Av. particle size, 7μ. [c] Av. particle size, $< 1\mu$.

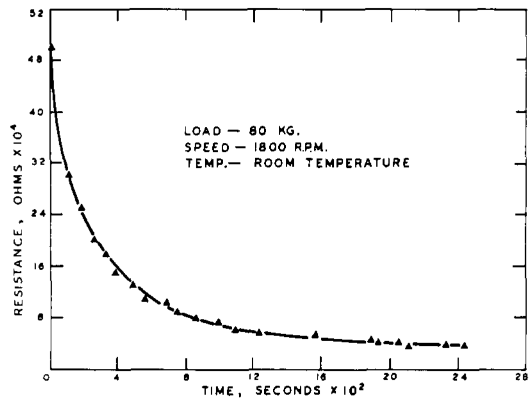

Figure 3. Resistance vs. time

Resistance reading at time zero > 1,000,00 ohms

action of the ball in contact with the lubricated surfaces. Table III presents the average results of initial runs covering the total wear cycles for two solid films at 10,000, 3500, and 1250 r.p.m. Experimental details and solid film constituents are contained in Table III. These data indicate that the mechanism of failure under the conditions described is a mechanical removal of film by the rotating balls. Furthermore, it appears that bearing life (hours) may be directly related to speed for this wear process, provided that the conditions of loading and temperature, etc., are held constant.

Wear Rate. During wear experiments it was observed, although not measured, that the rate of removal was not constant, since the rate during the beginning of the wear process was higher than during the latter. Present work covers a study of wear rate of the solid film under dynamic conditions. During the wear process, the thickness of the solid film decreased, resulting in a loss of weight. These two factors can be utilized to measure the rate of wear. However, experimental techniques for measuring these factors are cumbersome and do not yield a continuous measurement of wear rate. The approach developed consisted of placing a ball which can be rotated in contact with fixed metal specimens lubricated with solid films. The specimen-ball combination is placed in an electrical circuit of a Weston Model 785 Type 4B ohmmeter. Since the resistance of the solid film will be high by comparison with a substrate, the rate of film removal can be obtained by measuring electrical resistance as a function of time, while the ball is rotating against the loading specimen coated with a solid film. The apparatus consisted of a Shell 4-ball lubricant apparatus with a modification permitting the substitution of three fixed flat metal specimens for the three fixed ball specimens. The bearing surfaces separated by the solid film were placed in the circuit of an ohmmeter.

A load of 80 kg. was applied to the specimens in contact with the ball and the drive motor was actuated. Resistance readings in ohms were recorded prior to and during the run. The ball was M-10 tool steel and the flat specimens were 301 stainless steel. The solid film consisted of AgI (85 weight %), graphite (1 weight %), and sodium silicate (14 weight %).

The curve (Figure 3) for an initial run shows that the wear rate is rapid during the first phases, indicating the removal of loosely held surface particles. The wear then decreases, approaching a nearly constant rate. Various factors—film thickness, increased contact area with increasing depth of ball penetration, and orientation of solid crystals—are considered important to the interpretation of the report data. Accordingly, no additional conclusions can be drawn without additional experiments.

Table III. Comparison of Total Wear Life (Cycles) with the Rotary Speed

Apparatus. High speed bearing performance apparatus.
Specimen. 204 size ball bearings, AISI-C 52100 steel balls and races, ASIS-C 1010 steel retainers, radial clearance 0.0003 –0.0008 inch.
Load. 5-lb. thrust, 3-lb. radial.
Temp. 350° F.

Solid Film Lubricant	Wt. %	Test Speed, R.P.M.	Total Cycles × 10^4	% Dev. from Av.
MoS_2	71	10,000	1470	+11
Graphite	7	3,500	1113	−15
Sodium silicate	22	1,250	1373	+4
MoS_2	66	10,000	1170	+17
Graphite	11	3,500	953	−4
Sodium silicate	23	1,250	870	−13

SUMMARY

Inorganic solid film lubricants, derived from $Na_2O:SiO_2$ type binders and a variety of lubricating solids such as MoS_2, graphite, AgI, etc. have been investigated for extreme environmental conditions. Further, a means was derived to utilize such lubricants in high speed ball bearing applications. Results of studies show the inorganic solid film to possess the following characteristics:

Thermal stability from −300° to + 750° F.
Compatibility with liquid oxygen.
Resistance to nuclear radiation (gamma dosage = 5×10^9 r.)
Lubrication of ball bearings for periods up to 240 hours.
No deterioration when pressure is reduced to 1 micron at 1000° F.

Initial mechanism studies show that wear life in terms of hours can be estimated for the design under investigation on the basis of speed (providing load, temperature, and pretreatment are constant); electrical resistance can be used as a means of continuously measuring wear rate; and potential lubricating solids can be effectively studied on the basis of a technique which provides for equal volume substitution.

ACKNOWLEDGMENT

The authors thank J.P. Cerini, R.J. McCartney, J.F. Danovich, H.G. Mowery, and Arch Regn for their help in various phases of the experimental work.

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RECEIVED for review March 8, 1960. Accepted September 22, 1960.