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U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, ***Secretary***
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ABSTRACT

Studies have been carried out to determine certain basic properties of the complex metal sulfide, $SbSbS_4$, that pertain to its use as a solid lubricant and lubricant additive material. Past research had demonstrated that this material exhibited superior extreme pressure (EP) performance, antiwear properties, and high temperature stability. The present research has verified the performance under EP conditions as an additive to a base grease. However the performance of $SbSbS_4$ as a solid lubricant (in the form of a powder) was not found to be effective at temperatures below about 225°C. It was noted though that, when used as a dry powder lubricant, the compound did produce a thick adherent film on steel surfaces in sliding contact. Six different types of wear and friction tests were carried out under various conditions of load, sliding speed, contact geometry, temperature, and time, in order to fully explore the potential of $SbSbS_4$ as a lubricant on several different metals. In a number of cases, its performance was compared with MoS_2 and with other sulfur containing additives in lubricants. Electron microscopy studies on film material removed from the sliding contact surfaces have shown that the interaction of sulfur released from $SbSbS_4$ with the steel surface, presumably at locally elevated temperatures, is a principal mechanism. However, the physical characteristics of the $SbSbS_4$ film in the contact zone probably also have a significant role in its overall performance.

I. Introduction

This report will describe results obtained in a project concerned with evaluation and characterization of the wear properties of metal surfaces lubricated with certain inorganic solid sulfur compounds.* Several of those materials, such as $SbSbS_4$, have been shown to exhibit superior extreme pressure (EP) performance, antiwear properties, and high temperature stablility, under laboratory test conditions (1-4). It was important in the present work to determine more fully the conditions under which these compounds were effective, to compare their performance with other known lubricants, and to improve the understanding of the mechanisms by which they function.

The study thus far has concentrated on one compound, $SbSbS_4$, antimony thioantimonate. That material had been studied before (1-4) and was found to possess very good EP lubricating characteristics. It was thought that this compound could serve as a high quality solid lubricant material, and that it might offer improved performance in bearing applications involving metals such as stainless steels and titanium alloys. Navy requirements for lubricants, both as additives to oils and greases, and in dry film applications, are varied and involve a wide range of contact loads, speeds, and environments. The development of new lubricant materials with improved EP and other characteristics would be of significant value in many Navy applications, particularly if bearing maintenance intervals could be lengthened as a result, or if more corrosion resistant metals could be employed in bearings without compromising the wear performance. The availability of proven, tested alternatives to presently used materials, such as graphite and molybdenum disulfide, would also contribute to Navy program needs.

*Commercial products are identified in this report in order to fully describe the materials used and the testing conditions involved. Endorsement of such materials by NBS is not implied.

The present study has examined the performance of $SbSbS_4$ under dry sliding conditions and as an additive to oils and to grease. Six different tests have been carried out at temperatures from 20°C to 500°C. Several different metallurgical combinations have been studied with wear and friction data obtained. An important aspect of this work has been the attempt to identify the mechanisms by which the $SbSbS_4$ compound functions.

II. Background

In 1968 a paper by Devine (1) et al. reported on "New Sulfide Addition Agents for Lubricant Materials." Arsenic and antimony sulfides were added (5% by weight) to a base grease, and evaluated using the four-ball EP test. The compounds studied significantly increased the seizure load* and the weld load** over that measured for the base grease. Certain sulfides ($AsSbS_4$, $AsAsS_4$, Sb_2S_3, and Sb_2S_5) increased the weld load to greater than 400 kg compared with 80 kg for the base grease and 200 kg for a 5% MoS_2 addition. Based upon these promising results further studies of the mixed metal sulfides were conducted by the Naval Air Development Center (2-4). A variety of these sulfides including $SbSbS_4$ were evaluated as grease additives using the four-ball EP test. They gave approximately the same seizure load as obtained with MoS_2-containing greases but gave much higher weld loads. However, most of these compounds did not

*Seizure load: load in the four-ball EP test at which a rapid increase in wear scar diameter is noted.

**Weld load: load in the four-ball EP test at which welding occurs between the balls.

pass the ASTM copper corrosion test, except for the $SbSbS_4$ compound. That compound was also effective as a lubricant additive with stainless steel whereas MoS_2 as an additive was not. Good endurance lives were also obtained when these compounds were used as dry film lubricants in a phenolic binder. However, when used as dry solid lubricants they were not as effective as MoS_2 in the press fit test where a cylindrical pin is pressed into a bushing. Further investigations of $SbSbS_4$ as a grease additive were conducted by King and Asmerom (5). Using the ASTM standard four-ball test (D2596) they showed dramatic increases in the weld load and seizure load (Table 1) over that for the lithium base grease (RM81) and the MoS_2 additive in grease.

Other greases were studied with the same additives and showed essentially the same effect. It was also found that only small concentrations of $SbSbS_4$ in the grease were needed to significantly increase weld load capacity and that there was a strong concentration effect (Fig. 1). These results generated considerable interest in $SbSbS_4$ and raised the question as to the mechanism responsible for the enhanced performance imparted by $SbSbS_4$.

Although a great deal of work has been reported on the behavior of soluble additives such as sulphur, phosphorous, and chlorine-containing molecules, there has been relatively little work reported on solid additives other than MoS_2. Gansheimer (6) investigated solids such as inorganic phosphates, oxides, hydroxides, and sulfides. He reported four-ball O.K. loads* on the materials shown in Table 2.

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*Gansheimer (6) does not define O.K. load. However, it usually refers to a load which is a small constant increment (e.g. 10 kg) below the weld load.

Additional studies were conducted (7,8) afterward to determine the mechanism of lubrication by such solids when added to oils and greases. It was shown that below the seizure load, MoS_2 formed a film on the contact surfaces even though the surfaces were effectively lubricated in boundary conditions by the oil. Above the seizure load reaction occurred between the MoS_2 and the metal surface to form iron sulfide. It was also discovered that molybdenum diffuses into the steel and hardens the surface. The formation of Mo_2C was suggested. In the case of $Zn_2P_2O_4$ it was shown that the process did not involve film formation but rather a reaction to form FeP in the contact region. The reactions involved can be quite complex. When $Ca(OH)_2$ was added to fluorosilicone oil a reaction occurred at the metal surface to form CaF_2 which was stated to be responsible for improved lubricating properties.

Another investigator (9) added a number of different solid oxides to mineral oil and found large increases in both the load wear index and the weld load (Table 3). The increase in the weld load could be directly correlated with oxide hardness: softer oxides gave higher weld loads. It should also be noted that extremely high weld loads were obtained with B_2O_3 and Sb_2O_3, both of which are low melting (577°C and 656°C respectively) glassy oxides. Unfortunately the authors did not define the conditions under which the weld load was obtained so that direct comparisons with $SbSbS_4$ are not possible.

Thus it can be seen that when a solid is used in conjunction with a fluid lubricant it may improve the wear behavior by two different mechanisms:

1. The solid may form a film on the surface, such as was found with MoS_2 and the oxides. This takes place primarily in the low load region. This film reduces wear only slightly with an effective lubricant but has a major effect on the seizure load. The softer the film the greater the increase in seizure load that occurs.
2. The solid may participate in a reaction with the surface to form another film. This effect is most noticable in region II at higher loads (Fig. 2) where it significantly reduces wear and significantly increases the weld load.

The mechanism of action of solid additives seems clear. In region II (Fig. 2) the film that is formed prevents metal welding. The weld load is effectively increased by replacing metal welding by film failure.

The mechanism by which a solid film increases the seizure load is somewhat more complicated. However some guidance is available from the work reported in reference 10 concerning the mechanism of boundary lubrication with oil. From a detailed study of the seizure process it was concluded that failure was dependent upon the temperature reached during run-in. If the temperature did not reach the "lubricant desorption temperature T*", low wear would result with surface polishing. For temperatures greater than T*, local seizure will result producing a high wear rate. Thus the seizure load is determined by the condition T = T* where T is the actual surface temperature. Higher seizure load will result from lower surface temperatures. The principal means of accomplishing lower surface temperatures is to lower the friction coefficient at the contact. In cases where friction coefficients were measured

(11), the highest seizure loads were found with the lowest friction additives.

Thus it can be postulated that the solid films laid down in region I (low loads - Fig. 2) increase the seizure load by lowering friction. Almost any soft solid could perform in this way if it remained firmly attached to the surface. However good adhesion is difficult in the presence of surface active lubricating molecules.

In dry contacts a large number of compounds have been found which lower friction and prevent wear and surface damage at a rubbing contact. The general types of solid lubricants along with examples are listed in Table 4. One common property of all these materials is that they are relatively soft. Many compounds which do not lubricate at room temperatures become more effective at higher temperatures. This is illustrated in Fig. 3 from (12) where friction coefficients for a variety of materials are plotted against temperature. The reduction in friction is due to the lower shear strength in the solid film at higher temperatures. The conclusion drawn from such studies is that almost any compound will behave as a solid lubricant as the operating temperature approaches the melting point of the compound. However to be effective it has been shown that a layer of the solid must be firmly attached to the metal surface. Soft solids which did not adhere do not perform well as solid lubricants.

Available data on sulfides used as solid lubricants are limited other than for MoS_2 and WS_2. Some values for coefficient of friction are given in Table 5. It can be seen that many sulfides are at least partially effective as solid lubricants within a specified temperature range. An interesting result with solid sulfide additions has been reported by Haltner and Oliver (13). In that work 10% of a variety of metal sulfides were added to MoS_2 and films of the mixtures were then formed on steel surfaces. The load capacity of the film was then measured. Increases in load capacity by a factor of 20 over MoS_2 alone was found for Sb_2S_5. It was suggested that the most effective additives are those which have the lowest thermal stability. That is, a chemical interaction of the sulfide and the metal surface was suggested. It was also stated that sulfides, especially stannic sulfide, form stable, adherent films.

$SbSbS_4$ is a newly developed material and many of its properties are unknown. It can be characterized as a soft amorphous or glassy solid. Thus it would be expected to have potential as a solid lubricant. Glasses are particularly effective at high temperatures where they are used as metal working lubricants (see also B_2O_3 in Fig. 3). The temperature range of effectiveness of $SbSbS_4$ has not been determined yet.

One important question to be asked concerns the mechanism (deposited film or reactive film) that applies to $SbSbS_4$. There can be no firm answer based upon the published literature. However it should be noted that the primary effect of $SbSbS_4$ according to published data is in region II where much lower wear rates and higher weld loads are reported. Furthermore, this compound contains large quantities of sulfur which is well known for showing strong EP effects. Thus one might suspect a reactivity effect involving sulfur.

The effect of sulfur on wearing contacts has been the subject of a large number of studies (references 14 to 20). In the work of Davey (14-18) and the later work of Forbes (19) using soluble organic additives the following mechanisms were proposed. At low loads (region I - Fig. 2) the sulfur molecule is either physically or chemically adsorbed on the steel surface of interest. The sulfur atom is attached with the chain oriented perpendicular to the surface. At higher loads (region II), cleavage of the sulfur-sulfur bonds occurs and a sulfur-metal reaction can occur. The actual effectiveness of an organo-sulfur compound is related to the ease of splitting the S-S bond necessary for adsorption and the sulfur-iron interaction. Obviously the first step for reaction to take place involves adsorption at the surface. In region II the actual film does not appear to be pure sulfide (21) but some mixture of metal oxide and sulfide. As the weld load is approached, a higher percentage of oxide is found. This is understandable since Buckley (22) has shown oxygen replaces sulfur in a metal sulfide compound. In later work Sakurai (23) confirmed the sulfur reactivity role and found that an optimum sulfur concentration existed. This optimum concentration is that needed to give a critical film thickness for minimum wear. A direct correlation (15) is found between wear and reactivity in region II as shown in Fig. 4. It should be noted that the maximum load carrying capacity is obtained with sulfur additions.

In summary a number of explanations can be proposed to account for the effective lubrication characteristics found for $SbSbS_4$:

(1) It can form an effective solid film lubricant, both dry and when contained in a fluid lubricant.

(2) It can serve as a source of sulfur which improves both dry and fluid lubrication especially in the high load region.

(3) Upon decomposition under EP conditions, antimony is liberated which can act as a lubricant or which can contribute to the formation of a lubricating film.

(4) Lubrication reactions can be more complicated; the $SbSbS_4$ may be involved in reactions with the lubricant itself or with oxygen present at the contact.

In the present study a series of experiments were carried out to consider the feasibility of these different explanations.

III. Test Methods and Materials

Testing procedures involving six different machines were used to evaluate the friction and wear characteristics of $SbSbS_4$ both in the dry powder form and when blended as an additive with base lubricating fluids. The same procedures were also applied to other lubricating materials for comparison purposes. Three of the test machines, the four-ball EP machine, the pin and V-block (Falex) machine, and the block and ring (LFW-1) machine are widely used for lubricant testing. Two other wear test machines, the 3-pin on disk machine, and the reciprocating linear sliding high temperature machine were special laboratory designs. The sixth machine, a ring compression apparatus was, strictly speaking, not a wear test machine but an application of a commercial compression-tension testing machine operating in the compression mode. All tests were conducted in laboratory air (21-23°C). The relative humidity was monitored but not controlled; it was found to vary between 40 and 60%. In the remainder of this section a brief description of each of the test systems will be presented together with a summary of the test procedures that were applied.

A. Pin and V-block Tests

A detailed description of the pin and V-block machine (also known as the Falex machine) can be found in a paper by Faville and Faville (24) as well as in three ASTM standard test methods (D2627, D3233, D2625) which are based on this machine. The test specimens consist of two blocks with 96° V-grooves and a cylindrical 6.35 mm diameter pin. The V-blocks are held in a lever arm mechanism and squeezed against the rotating pin. The load can be adjusted manually or increased automatically. The magnitude of the load is usually indicated by a dial gauge; however, the present machine was modified to include a strain gauge type load cell which allowed the load to be indicated electronically. The torque imparted to the V-blocks as a result of the friction force was also measured by a strain gauge type load cell. Load and friction force together with specimen temperature, which was measured by means of a thermocouple spot welded to one V-block, were continuously recorded during each test. The test specimens specified in the ASTM standards, V-blocks of 1137 steel and pins of 1335 steel,were used in many tests. To evaluate the behavior of $SbSbS_4$ with other metals, specimens of 440 stainless steel, 52100 steel, 4340 steel, and Ti-6Al-4V were also employed.

Tests were carried out with two different procedures. One was a modification of ASTM D3233, method A, which is designed to determine the load carrying capacity of fluid lubricants. In that procedure after a 5 min. run-in at 1330 N (300 lb) the load is advanced automatically until failure occurs either by fracture of the specimen locking pin, of the specimen pin itself, or by extrusion of the specimen pin. The failure event is accompanied by a marked rise in friction force when seizure and fracture occur, or by a drop in the load advance rate when pin extrusion results. The load at which the failure event occurs is designated the load carrying capacity of the lubricant according to this test. The ASTM method specifies that the specimens be immersed in a fixed volume of lubricant. A different procedure was adopted when the test was applied to greases. The V-grooves of the V-blocks were filled with grease and then squeezed against the pin. No additional grease was applied during the test.

A second test procedure was used to measure wear as well as load carrying capacity. This procedure consisted of a series of 30 min. tests starting at a gauge load of 445 N (100 lb) with each succeeding test being run at a load of 445 N (100 lb) higher than the former. The series was terminated when failure occurred before the 30 min. test period was completed. The maximum load at which the lubricant was able to survive the 30 min. test period was considered to be the load carrying capacity of that lubricant. A major difference between this procedure and the first procedure described involves the relationship between temperature and load. In the first procedure load is rapidly advanced and there is no opportunity for the achievement of steady state thermal conditions. A steep temperature gradient exists at the contact surface. In the 30 min. constant load test, the specimen temperature is allowed to rise to a steady state value; consequently, for a given load the surface temperature of the specimen may be considerably higher than in the first procedure.

Wear was determined by measuring widths (lengths were approximately constant) of the four wear scars on the two V-blocks and calculating the average wear volume. These measurements were found to be most useful when various lubricants gave large differences in wear rates. Small differences could not be resolved because of scatter in the data.

B. Block and Ring Tests

The block and ring tests were conducted with a commercial LFW-1 machine equipped with a 30:1 lever arm and a strain gauge type load cell for the measurement of friction. Grease was supplied to the rotating ring by means of a commercial grease feeder adjusted to deliver a volume of 0.5 cm^3 at 20 min. intervals. The grease was supplied directly to the rotating ring from a nozzle with a rectangular opening approximately equal to the width of the ring. During the course of a test the grease was allowed to accummulate in the vicinity of the nozzle and the entrant side of the block. One test was conducted with dry $SbSbS_4$ powder as a lubricant. In that case the powder was applied repeatedly to the ring with a small artist's brush during the test.

The test procedure employed was designed primarily to determine the wear rate under conditions of low sliding speed and high load (below seizure). Most of the tests were conducted at a load of 267 N (60 lb) and a sliding speed of 5.5 cm/s. Wear is reported here as the volume of material lost from the block. The volume was calculated from the measured width and length of the cylindrical wear scar. Surface profile traces across selected scars indicated that the scar shape conformed closely to the ring geometry. Both ring and block were of 52100 steel. The ring hardness was 62 HRC and the surface roughness across the circumference of the ring, perpendicular to the grinding direction was 0.17 μm R_a. Similarly, the block hardness and surface finish were 62 HRC and 0.25 μm R_a, respectively. Details on conducting wear tests with the LFW-1 machine are discussed in ASTM D2714.

C. Four-Ball Tests

The four-ball test was employed mainly to confirm the results of King and Asmerom (5) who first evaluated the load capacity of $SbSbS_4$ in this way. A description of the four-ball EP test machine and the test procedure employed is described in ASTM method D2596. Briefly, the test specimen configuration consists of one steel ball that is rotated in the apex of three stationary steel balls. Ten second runs are made at increasing loads until failure occurs. A new set of specimens are used at each load. The rotating speed is 1770 RPM; the ball material is SAE 52100 steel. The weld point is defined as the load at which the balls weld together or a wear scar diameter of greater than 4 mm is obtained.

D. Ring Compression Tests

A ring compression test has been developed (25) (26) previously to measure friction under typical metal working conditions. The test involves compression of a metal ring between two flat metal platens. Changes in the ring diameter at a given amount of deformation (reduction in ring thickness) can be directly correlated with friction coefficient at the ring-platen surfaces. This technique can be used to evaluate the effectiveness of solids as lubricants at high normal pressures while minimizing the temperature rise during the test. In these tests, rings of 1018 steel (1.9 cm OD x 9.5 mm ID x 6.35 mm thickness) were compressed 50% between flat plates of O-2 tool steel finished to 4-8 μm R_a. The solid or fluid lubricants were applied uniformly to the ring surfaces at the start of the test. The coefficient of friction was determined by the change in the internal ring diameter using the calibration data given in Table 6 from reference 25.

E. Three-pin on Disk Tests

For certain tests a pin-on-disk apparatus was used (Fig. 5). The specimen configuration consists of 3 hemispherical or flat ended pins sliding against a flat plate and forming a single wear track. The pins were held in a round disk which was mounted in a drill press chuck. The drill press had been modified with a variable speed motor and gear drive to operate up to a speed of 350 RPM. Alignment of the contact was achieved by means of a ball mounted between the pin holder and the chuck. The flat disk specimen was mounted on a small table below the pin holder and was supported by a ball bearing. In operation the table was restrained by a fixture to which a load cell was attached; this allowed continuous recording of the friction force during the wear test. The table also contained a cavity in which resistance heaters were inserted for high temperature wear test operation. Water cooling was provided to protect the ball bearing during heating. The load was applied through the drill press spindle. The spindle was modified to reduce vertical friction forces which might interfere with the transmission of the applied load to the specimens. Small guide vanes were attached to the upper pin holder so that the lubricants in the powder form were continuously returned to the sliding track in front of the pins during the test. The solid powders were spread on the disk with a thickness of approximately 3 mm. Hardened SAE 52100 steel balls and O-2 tool steel disks were used for most of the experiments. Tests were run at a load of 237 N (53.3 lb), a speed of 10 cm/s, and temperatures from 20°C to 250°C.

F. Reciprocating Linear Sliding Tests

For high temperature tests a reciprocating sliding rig was used (Fig. 6). It consisted of a flat ended pin (6.35 x 6.35 mm) sliding back and forth against a flat plate; the track length was 25 mm. The pin was held in an arm which was moved back and forth by an air motor. One end of the moving arm was supported by a universal joint so that it could move in both the linear horizontal and vertical directions. Load was applied by an air cylinder which was mounted directly above the specimen pin. Motion was imparted to the moving arm through strain gauges so that the friction force could be measured. The flat plate specimen was fastened to a block mounted directly under the pin. The test specimens were surrounded by a furnace. Heat was supplied to the upper and lower specimens by cartridge heaters mounted in the specimen holder blocks.

In operation, the specimens were placed in the test rig and brought to the desired operating temperature. The lubricant was applied as a powder (3 mm depth) on the flat plate and the test begun. M2 tool steel specimens (60 HRC) having a sand blasted surface finish were employed. A load of 142 N (32 lb) and a velocity of 25 mm/sec was used. Ten minute test runs were made at increasing temperature levels from room temperature to 580°C. Friction was plotted as a function of temperature.

G. Lubricant Materials

A list of the lubricants studied in this program is given in Table 7. Tests were conducted on dry powder materials and on many of the same materials blended with two different base fluids, a lithium 12-hydroxy stearate grease designated RM81 by its manufacturer and a laboratory grade of white paraffinic mineral oil. Several of the solid materials, most notably MoS_2, were selected because of their known good qualities as solid lubricants. These served to provide reference data to which results obtained with other materials, in particular $SbSbS_4$ could be compared.

IV. Results and Discussion

Test results and analysis of these results are presented in the following sections.

A. $SbSbS_4$ as a Solid Lubricant

$SbSbS_4$ has been referred to be a solid lubricant. According to the general usage of this term, $SbSbS_4$ in the solid form and not in combination with a fluid or other solid material would be expected to reduce substantially friction and wear. To achieve this function a layer of the solid lubricant must exist at the contact surface between sliding members and a significant proportion of the sliding and shear must take place on or within this layer. The mechanical properties of the solid lubricant layer are such that traction forces are lower than would otherwise exist. As discussed previously, the solid lubricant function may depend on temperature and pressure. (The gaseous environment may also be important, but in the present investigation, it was confined to room air.) To explore the solid lubricant behavior of $SbSbS_4$, tests were conducted at various temperatures and loads. An example of the variation of friction coefficient with sliding distance at room temperature obtained with the 3-pin on disk machine is shown in Fig. 7. In these tests dry powder was spread on the disk surface and the test commenced. As noted earlier, vanes located on the pin holding member continually returned powder to the wear track on the disk after it was pushed away by the pins. The friction coefficient trace in Fig. 7 rises rapidly with large fluctuations to a value of about 0.7. Examination of the pin and disk sliding contact surfaces revealed the presence of a relatively thick compacted film of $SbSbS_4$. Optical micrographs of disk and pin contact surfaces are shown in Fig. 8(a) and 8(b). Close examination of the disk surface revealed some small areas of bare metal in the wear track. It appears that during sliding the film was sometimes attached to the pin and sometimes to the disk. The frictional behavior was controlled by shear between the thick film and the metal surfaces and to some extent by shear within this film. The shear stresses involved are much larger than with MoS_2 which under comparable conditions gave a friction coefficient of 0.05.

Additional tests on dry $SbSbS_4$ were conducted at higher temperatures. Figure 9 shows the variation of friction coefficient with temperature. In this experiment the heater was switched on and the temperature allowed to rise while sliding took place. The friction coefficient remained at a value of approximately 0.8 until a temperature of about 225°C was reached. The friction coefficient then decreased with increasing temperature to a value of about 0.4. The maximum temperature attainable (limited by heater power capacity) was about 250°C. On turning the heater off the coefficient of friction recovered to its original value when a temperature of about 175°C was reached. Sliding was terminated in one test at 250°C. After cooling to room temperature, examination of the specimen surfaces showed that again there were thick patches of solid film in the wear track (Fig. 10). Flakes of the film were stripped from the surface using an extraction replica and examined in the transmission electron microscope. They were determined to be the crystalline phase Sb_2S_3 by means of electron diffraction. Thus the original amorphous compound $SbSbS_4$ underwent a transformation involving the loss of an S atom. During the elevated temperature tests which were carried out in air, oxidation of the steel surface occurred, turning it first to a straw color and then blue when 250°C was reached.

A test was run without $SbSbS_4$ lubrication to investigate the effects of specimen oxidation. The friction coefficient vs temperature results are shown in Fig. 11. The behavior is somewhat similar to that obtained with

$SbSbS_4$. Comparing Fig. 9 and 11 it can be seen that despite the larger fluctuations, the friction coefficient in unlubricated sliding is close to 0.8 until a temperature of about 190°C is reached. The friction coefficient then drops to about 0.6. On turning off the heat at 250°C, the friction coefficient increased slowly with decreasing temperature reaching its initial value of 0.8 at about 60°C. Although oxidation of the steel specimen surfaces may contribute to the results obtained with $SbSbS_4$, it cannot account for a large part of the observed effect.

The test procedures used above (rising and falling temperatures) do not necessarily establish the critical temperatures at which changes in friction coefficient occur. However, the results do indicate that variations in friction coefficient may be dependent on factors other than a change in the lubricating qualities of $SbSbS_4$. Additional experiments, perhaps in an inert atmosphere would be required to separate the effects of oxidation from those due to $SbSbS_4$. With respect to the solid lubricating characteristics of $SbSbS_4$ two observations are important: (1) over the temperature range from 22°C to 225°C the compound exhibits a friction coefficient on steel much higher than with good solid lubricants, (2) $SbSbS_4$ forms a rather strongly adherent film on the surface. The latter property of $SbSbS_4$ may contribute to its good performance as an additive as discussed later in this report.

A different test device (reciprocating linear slider) was used to reach a temperature of 650°C. The friction coefficient vs temperature data for $SbSbS_4$ determined using this tester are shown in Fig. 12. Friction is constant at about 0.24 up to 250°C, then it decreases gradually to 0.14 at a temperature of 450°C. Again it is clear that $SbSbS_4$ becomes a much more effective solid lubricant at high temperatures and may compare favorably in friction coefficient with inorganic lubricant compounds (Fig. 3). This could account for the increased load capacity of greases containing $SbSbS_4$. It should be noted, however, with this test the coefficient of friction values were much lower than were found for the pin-on-disk test. The reason for this difference is not clear at the present time.

In order to evaluate the high pressure lubrication properties of $SbSbS_4$ under conditions that minimize frictional heating effects, the ring compression test was used. Since pressures are at or above the yield strength of steel, this is a very severe lubricant test. However good solid lubricants perform well under such conditions. Data on several lubricants obtained with 1018 steel rings are listed in Table 8. Basically these results show that $SbSbS_4$ did not provide the same measure of solid lubrication as MoS_2 under these conditions. MoS_2 reduced friction from a value of 0.24 obtained without lubricant to 0.035. When RM81 grease was employed, a value of 0.05 was obtained. Blending 5 w/o MoS_2 with the grease gave 0.04. $SbSbS_4$ gave a friction value of 0.19 alone and 0.06 when used with the RM81 grease. These results indicate that $SbSbS_4$ is not a solid lubricant at room temperature in the conventional sense at higher contact pressures. It may be concluded that $SbSbS_4$ (or its reaction products) is an effective lubricant at temperatures from 225°C to 650°C. In this regard it is much better than MoS_2 which oxidizes at 350°C in air and is then no longer effective.

B. Confirming Four-Ball Tests and Pin and V-Block Load Capacity Tests

Four-ball EP tests were conducted on RM81 base grease, RM81+5 w/o $SbSbS_4$ and RM81+5 w/o MoS_2. The data are plotted in Fig. 13 together with the results of King and Asmerom (5). The agreement is very good, thus confirming the outstanding EP behavior of $SbSbS_4$ as an additive in this test.

Pin and V-block EP tests conducted using ASTM method D3233 demonstrated the significant superiority of RM81+5 w/o $SbSbS_4$ over the base grease alone. However, the difference here between RM81+5 w/o $SbSbS_4$ and RM81+5 w/o MoS_2 was not nearly as great. In addition to the relatively soft 1137 steel block (20 HRC) and 3135 steel pin (90 HRB), the standard specimen materials specified in Method D3233, three hardened steel specimen materials and a non-steel, Ti-6Al-4V, were examined. These results are shown in Table 9. When the hardened steel specimens were used, the failure load was nearly doubled for the RM81 base grease, compared to the standard specimens. With RM81+5 w/o MoS_2, a moderate increase was obtained with 4130 steel and 440C steel compared to the standard specimens but there was almost no change for 52100 steel. When RM81+5 w/o $SbSbS_4$ was used, the failure load was about the same for all steel specimens.

It may also be noticed that there was essentially no difference in failure load for RM 81+5 w/o MoS_2 and RM 81+5 w/o $SbSbS_4$ when 4130 steel and 440C steel specimens were used. Large differences were primarily the result of using SAE 52100 steel as found in the four-ball test results.

To understand these results it is necessary to consider in more detail the pin and V-block test itself. The failure load, as described earlier, is determined by specimen pin fracture, fracture of the locking pin, or by extreme wear. Mechanical properties of the specimens and other metallurgical factors as well as lubricant properties will almost certainly play a role in determining failure load. A good example of the importance of "other" metallurgical factors is demonstrated by the almost complete ineffectiveness of the lubricants in question with Ti-6Al-4V. With specimens of the latter material, failure occurred during run-in at 1330 N (300 lb). The higher failure loads of RM 81 base grease when tested with 52100, 4130 and 440C steel compared to the 1137/3135 steel combination appear to be a result of the higher strength of the former steels. The friction coefficient and load traces for tests employing the 1137/3135 specimen combination lubricated with RM 81 are shown in Fig. 14a. Run-in is not shown; only the portion where the load was automatically advanced to failure is shown. The friction coefficient remains constant with increasing load until it rises abruptly at a load of $\sim$2700 N (600 lb) and the test is terminated, in this case, by fracture of the specimen pin. Figures 14b, c and d show corresponding friction coefficient, temperature, and load traces for specimens of 52100, 440C, and 4130 steels, respectively. Only the run-in portion of the test during which failure occurred is shown for Ti-6Al-4V in Fig. 14e. A marked rise in the friction coefficient occurs at 2700-3100 N (600-700 lb) for the steels, 52100, 4130 and 440C but actual failure of the specimen pin (or locking pin) did not take place until a much higher load was attained. In fact, the friction coefficient is seen to recover to a lower value, after its initial rise, before increasing to failure. Although direct analytical information was not obtained to explain this behavior, it is hypothesized that chemical reactions with the lubricant or perhaps oxidation led to the intermediate reduction of friction force. Chemical reaction is certainly favored by the rising temperature which accompanies frictional heating. Variations in friction such as those shown in Fig. 14b-d are well known to occur with steel under non-lubricant sliding conditions in air (27).

Load, temperature, and friction coefficient traces similar to those for RM 81 are shown for RM 81+5 w/o MoS_2 and RM 81+5 w/o $SbSbS_4$ in Figures 15 and 16, respectively. These examples are representative; other tests did not necessarily repeat in detail the small variations shown but the general behavior was quite similar. In common with RM 81, the mixture RM 81+5 w/o MoS_2 shows a rise in the coefficient of friction at 2700-3100 N (600-700 lb). That rise did not, however, lead to the failure of the pin for the standard 1137/3135 steels, as occurred with the base grease alone. In fact, recovery occurred and the ultimate failure load for 1137/3135 steel was about the same as for 52100 steel. With RM 81+5 w/o $SbSbS_4$ (Fig. 16) an initial decrease in coefficient of friction occurred and a rise was not observed until a load in the range 5800-6700 N (1300-1500 lb) was reached. In summary, these results indicate that with steel specimen materials, there is an increase in friction coefficient at 2700-3100 N (600-700 lb) for the RM 81 base grease. Addition of 5 w/o MoS_2 reduces the size of this increase while 5 w/o $SbSbS_4$ eliminates or perhaps delays it until a load in the range 5800-6700 N (1300-1500 lb) is reached.

A common feature of both MoS_2 and $SbSbS_4$ is the presence of sulfur. Because of the well known effectiveness of sulfur as an EP agent, 0.43w/o elemental sulfur powder was blended with RM 81 base grease and subjected to the pin and V-block test. The load and friction force traces for one test are shown in Fig. 17. The behavior is similar to that of RM 81+5 w/o $SbSbS_4$.

C. Comparison of $SbSbS_4$ with Other S-containing and Solid Lubricant Additives

Additional pin and V-block tests were conducted on the RM 81 base grease with several solid lubricant additives and three proprietary soluable sulfur-containing organic additives. These were compared with elemental sulfur. The solid lubricants (PbO, HBO_3 and PbO plus graphite) were chosen because they are excellent high temperature solid lubricants. It was hypothesized that the $SbSbS_4$ might behave in a similar manner. The organic sulfur and elemental sulfur additives were included to evaluate the role of sulfur reactivity. The additives examined together with their measured maximum pass loads in the pin and V-block test are listed in Table 10. Separate tests were carried out at 445 N (100 lb) load increments starting with 445 N (100 lb) until a load was reached at which failure occurred before an arbitrarily chosen period of 30 minutes was attained. The maximum load at which the 30 min. test could be completed was designated the maximum pass load for the lubricant. None of the solid additives listed in Table 10 except $SbSbS_4$ sustained a load of 1780 N (400 lb) without failure. With a soluble sulfur containing additive, Anglomal, and when 1% elemental sulfur was dissolved in RM 81, a maximum pass load of 1780 N (400 lb) was obtained. Also, 0.2% dissolved sulfur in RM 81+5 w/o MoS_2 raised the maximum pass load from 1330 N (300 lb) to 1780 N (400 lb).

These results strongly suggest that the sulfur effect is more significant than the possible high temperature solid lubricant effect. To investigate further the significance of sulfur on the behavior of $SbSbS_4$, pin and V-block 30 minute wear tests were carried out on white paraffinic mineral oil containing S and $SbSbS_4$. The white mineral oil was used to avoid the possible effects of soaps or impurities in the grease. The lubricants studied are listed in Table 7. Two of the lubricants were prepared by first mixing 5 w/o $SbSbS_4$ dry powder in mineral oil and then filtering out the solid residue. In one case the mixture was heated to 120°C for 30 min. before cooling to room temperature and filtering, and in the other case the mixture was stirred at room temperature for 16 hrs. before filtering. The filtering process itself required several hours. X-ray fluorescence analysis of the filtrates indicated the presence of 0.16 w/o S in the heated and 0.08 w/o S in the unheated filtrate but only a trace concentration (<0.001%) of antimony was detected in both cases. The $SbSbS_4$ powder itself was reported (28) to contain less than 0.1 w/o uncombined sulfur. These results indicate that some sulfur is given up to mineral oil by the $SbSbS_4$ compound. The pin and V-block test results given in Fig. 18 show that the filtered blends exhibit a wear behavior that is similar to mineral oil having the same concentration of elemental sulfur.

These results clearly demonstrate that sulfur interaction with the steel surface plays an extremely important role in the EP and antiwear behavior of $SbSbS_4$.

D. Anti-wear Behavior of $SbSbS_4$ As An Additive

The superior EP performance of $SbSbS_4$ as an additive to RM 81 base grease has already been described. King and Asmerom (5) have employed four-ball wear tests (ASTM D2266 and D2596) to demonstrate that the wear rate characteristic of RM 81+5 w/o $SbSbS_4$ is equal to or better than either RM 81+5 w/o MoS_2 or RM 81 alone. The test conditions specified by ASTM D2266 and D2596 are relatively severe with respect to load and speed, and consequently, also as regards temperature. The question arises as to what the behavior of $SbSbS_4$-containing greases would be under less severe conditions, particularly where the temperature might not much exceed room temperature (22°C) and the physical rather than chemical-reactive properties might be stressed. To answer this question a series of block on ring tests was conducted at a load of 267 N (60 lb) and sliding speed of 5.5 cm/s. The results of tests on three different lubricants, RM 81 base grease, RM 81+5 w/o $SbSbS_4$ and RM 81+0.43 w/o S, are shown in Fig. 19. The concentration of elemental sulfur listed was chosen to equal the quantity of sulfur that would be available from 5w/o $SbSbS_4$ if the latter compound was converted to Sb_2S_3. The steady state wear rate obtained with RM 81 was 7×10^{-9} mm³/mm and is substantially higher than the value 1.8×10^{-10} mm³/mm obtained with RM 81+5 w/o $SbSbS_4$. It may be noted that a relatively high run-in wear rate was obtained with RM 81+5 w/o $SbSbS_4$ and that a sliding distance in excess of 1000 m was required to enter the steady state regime. The calculated steady state wear coefficient* for RM 81+5 w/o $SBSbS_4$ is $K = 5 \times 10^{-9}$. This value is indicative of mild wear and demonstrates the good anti-wear characteristic of $SbSbS_4$ under these conditions.

$$*K = \frac{\text{volume loss} \cdot \text{hardness}}{\text{load} \cdot \text{sliding distance}}$$

Similar tests conducted on RM 81+0.43 w/o S gave essentially the same wear rate as those for RM 81+5 w/o $SbSbS_4$. This result seems to further substantiate the sulfur contribution in the case of $SbSbS_4$. Additional tests will be required to better establish the comparative behavior of elemental sulfur and $SbSbS_4$.

E. Analysis of Debris and Surface Films

The observation of thick films on surfaces lubricated with dry $SbSbS_4$ powder has already been discussed. These films were easily revealed by optical microscopy. Specimens lubricated with mineral oil and grease, both with and without additives, were not covered with such thick films. Depending on test conditions and the lubricant used, solid films could sometimes be seen with the optical microscope. In some cases the entire wear surface appeared to be covered by a film, while in other cases only part or none of the surface was covered by a visible film. It is thought that the explanation for these apparently disparate observations lies in the fact that all surfaces were covered by films but that the thickness varied. Only when the films were sufficiently thick were they observed. Since the existance of a solid film and the nature of that film are probably the most important factors determining boundary lubrication characteristics, a study was initiated to characterize films that were present under test conditions employed in this investigation.

Two approaches were taken to study the films. Both employed transmission electron microscopy. In one method wear debris particles from used lubricants were examined. It was assumed that either some portion of the original film resided on those particles or that the entire particle was in fact film that had been rubbed off the surface. In the second method, fragments of the film were stripped off the surface by means of a replica technique. The debris particles and film fragments were examined in an analytical electron microscope (AEM). Crystal structure information was obtained by means of electron diffraction and information on composition for elements with atomic numbers equal to or greater than 11 (Na) was obtained by means of an x-ray energy dispersive spectrometer system (EDS).

Debris particles from two pin and V-block tests have been examined. In the first case, RM 81+0.2 w/o S was used as a lubricant and the test was conducted at a load of 1330 N (300 lb) for a period of 30 min. A considerable quantity of debris was accumulated in the grease that remained on the specimens at the end of the test. Relatively large metal particles were visible optically. An abundance of very small particles was also present. A number of these small particles, often in clusters, were examined on carbon support films in the TEM. Electron diffraction indicated that the particles had a crystal structure appropriate to the spinel form of iron oxide, Fe_3O_4. Energy dispersive x-ray analysis indicated the presence of Fe; a sulfur peak also was observed. There were no diffraction lines to indicate that sulfur was combined with iron to form a sulfide. It is not known to what extent sulfur may be incorporated in the Fe_3O_4 structure.

In the second case, debris particles were studied that had been generated in a test employing mineral oil to which $SbSbS_4$ powder had been added and subsequently filtered. A 30 minute wear test was conducted at a load of 2220 N (500 lb) with this lubricant. Debris particles from the used oil were similar to those from the test employing RM 81+0.2 w/o S to the extent that some large metal particles were present together with a large quantity of very small particles. Electron diffraction analysis of the small particles, however, indicated that they were very nearly identical in structure to a variety of pyrrhotite, Fe_{1-x} (5C) and not Fe_3O_4. Pyrrhotites are iron-deficient iron sulfides exhibiting a variety of different super-structures based on the hexagonal NiAs subcell.

Film fragments removed from two block wear scars after conducting ring and block tests were examined. Both blocks were tested under approximately the same conditions, 267 N (60 lb) load and sliding distance of ~5000m. In one test RM 81+5 w/o $SbSbS_4$ was used as a lubricant and in the other test RM 81+0.43 w/o S was employed. It may be recalled that 0.43 w/o S corresponds to the amount of sulfur that would be available if 5 w/o $SbSbS_4$ was converted entirely to Sb_2S_3. Film fragments from the test employing RM 81+5w/o $SbSbS_4$ were of two types. One type of fragment was essentially structureless in appearance, Fig. 20(a). According to electron diffraction it was amorphous. EDS analysis indicated that it was composed of Sb and S. Thus, it is hypothesized that the film was derived directly from the amorphous $SbSbS_4$ powder as a result of the powder particles being rubbed over the surface during sliding. The second type of film also shown in Fig. 20(a) appeared to be composed of very small crystallites about 10 nm in size. Bright field and dark field micrographs of a different polycrystalline fragment are shown in Fig. 20(b) and (c). The crystal structure was determined by electron diffraction to be consistent with pyrrhotite $Fe_{1-x}S$ (5c). As further support of this identification, EDS indicated the presence of both Fe and S at about the same concentration. A similar analysis of film fragments from the block lubricated with RM81+0.43 w/o S, (Fig. 21) revealed only polycrystalline films which were very similar in appearance to polycrystalline films found with RM81+5 w/o $SbSbS_4$. Electron diffraction, however, indicated a crystal structure consistent with pyrite, FeS_2. By means of EDS it was determined that the concentration of S was considerably higher than Fe.

The results described above concerning the nature of debris particles and surface films are preliminary. Additional specimens need to be examined both from duplicate tests and conducted under different conditions to confirm the present observations and establish more fully the relationship between lubricant composition, test conditions, and film characteristics. However, analysis of the present results suggests the following. Iron oxide may form when a sulfur containing lubricant is employed under conditions when oxygen has ready access to the contact surface and frictional heating results in an elevated temperature. Under conditions where oxygen was not so readily available or lower loads and temperatures existed, sulfides are present when sulfur bearing additives are used. Perhaps the most significant result, however, is that with $SbSbS_4$ the iron sulfide, pyrrhotite, was identified as the principle constituent of the surface film.

V. Conclusions

1) When used as a dry powder $SbSbS_4$ yields a coefficient of friction of 0.5-0.8 at temperatures below about 225°C in air.

2) At temperatures above approximately 225°C, $SbSbS_4$ exhibits a friction coefficient in the range 0.2-0.4, and therefore has characteristics of a high temperature solid lubricant.

3) When rubbed dry, $SbSbS_4$ forms a thick adherent and durable film on contacting steel surfaces at temperatures from 20°C to 250°C.

4) When employed as an additive in a lithium soap based grease, $SbSbS_4$ was found to exhibit outstanding extreme pressure performance with steel specimens according to pin and V-block and 4-ball tests. These results confirm those of other investigators.

5) $SbSbS_4$ as an additive in lithium soap grease was not an effective EP lubricant against Ti-6Al-4V.

6) The extreme pressure behavior of $SbSbS_4$ was similar to other known sulfur releasing additives.

7) The boundary friction and wear characteristics of $SbSbS_4$ when employed as an additive in mineral oil and grease (lithium soap) appear to be associated with the release of sulfur. Iron sulfide films were identified on steel surfaces. A solid film of amorphous $SbSbS_4$ was also formed on the surface.

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FIGURE CAPTIONS

1. Concentration effect on weld point for $SbSbS_4$ and MoS_2 in lithium grease. Data from King and Asmerom (5).

2. Schematic representation of four-ball extreme pressure test behavior.

3. Friction coefficients for a variety of solid materials vs temperature (13).

4. Load carrying capacity vs chemical reactivity for EP agents (15).

5. Schematic drawing of three-pin on disk wear test machine.

6. Photograph of reciprocating high temperature friction and wear test machine.

7. Friction coefficient vs sliding distance for dry $SbSbS_4$ powder using three pin on disk tests (242 N load, 10 cm/s sliding speed, 52100 steel pins, 0-2 tool steel disk),

8. Optical photograph of film generated on disk (0-2 tool steel) and on pin (52100 steel ball) (b) surfaces after sliding with $SbSbS_4$ powder at room temperature.

9. Friction coefficient variation with temperature for dry $SBSbS_4$ powder using three-pin on disk test (52100 steel pins, 0-2 too steel disk).

10. Optical micrograph of wear track on disk surface showing adherent film after sliding at 250°C (52100 steel pins, 0-2 tool steel disk).

11. Coefficient of friction variation with temperature for unlubricated sliding using three-pin on disk test (52100 steel pins, 0-2 tool steel disk).

12. Coefficient of friction vs temperature using reciprocating sliding test rig (M-1 tool steel specimens).

13. Four ball EP test data compared to results from King and Asmerom (5) (52100 steel balls).

14. Pin and V-block EP test results on RM81 base grease using different specimen materials. Test procedure was similar to that described in ASTM D3233 Method A. Simultaneous record of load, coefficient of friction and block temperature shown. (a) 1137 steel V-blocks and 3135 steel pin, (b) 52100 steel, (c) 440C stainless steel, (d) 4130 steel, (e) Ti-6Al-4V.

15. Same conditions as Fig. 14(a) with RM81+5 w/o MoS_2.

16. Same conditions as Fig. 14(a) with RM81+5 w/o $SbSbS_4$.

17. Same conditions as Fig. 14(a) with RM81+0.43 w/o S.

18. Pin and V-block 30 min. wear test results on mineral oil blends (1137 steel V-blocks and 3135 steel pin).

19. Block and Ring wear test results on RM81, RM81+5 w/o $SbSbS_4$ and RM81+0.43 w/o S (52100 steel specimens).

20. Transmission electron micrograph of film fragments stripped from block wear scar after block and ring tests (52100 steel specimens). Test lubricant was RM81+5 w/o $SbSbS_4$. (a) Amorphous $SbSbS_4$ film and crystalline pyrrhotite film fragments are present, (b) crystalline pyrrhotite film at higher magnification, (c) dark field image of (b) to indicate size of individual grains.

21. Transmission electron micrograph of film fragment stripped from block (52100 steel) wear scar lubricated with RM81+0.43 w/o S. Polycrystalline film was determined to be FeS_2.

TABLE 1

Seizure and Weld Load Results for Base Grease and Additives (5)

	Lithium Grease (RM 81)	RM 81+ 5% MoS_2	RM 81+ 1%$SbSbS_4$	RM81+ 5%$SbSbS_4$
Seizure Load (kg)	40	50	50	100
Weld load (kg)	160	250	400	750

TABLE 2

Gansheimer's Results on Solid Additives in Oil (6)

Material	O.K. Load (kg)
$Zn_2P_2O_7$	260
$Ca(OH)_2$	200-220
MoS_2	200-220
Graphite	200-220
ZnS	160
Base Oil	100

TABLE 3

Load Wear Index & Weld Loads for Oxides as Additives (9)

Oxides*	Load Wear Index (kg)	Weld Load (kg)
B_2O_3	74	> 800
CaO	72	500
Bi_2O_3	59	500
Sb_2O_3	58	> 800
CdO	54	630
BaO	53	315
PbO	51	200
CuO	45	252
ZnO	42	200
SnO_2	35	200
NiO	34	252
Fe_2O_3	29	200
MgO	19	160
SiO_2	15	160
Al_2O_3	14	160

*In all cases the oxide concentration was 15 wt.%.

TABLE 4

Solid Lubricant Types

Organic	Soaps, Fats, Waxes
Polymers	Teflon, Polyethylene, Methacrylates
Metals	Indium, Tin, Lead, Silver
Inorganics	AX, AX_2, Oxides, Sulfides, Chlorides
Glasses	B_2O_3, PbO-SiO_2, PO_4

TABLE 5

Friction Coefficients of Some Sulfides (29)

Solid Material	Friction Coefficient
MoS_2	0.047
WS_2	0.08
TiS_2	0.20
CuS_2	0.21
PbS_2	0.15

TABLE 6

Calibration Data for Ring Compression Tests (25)

Measured Decrease of Internal Diameter (%)	Friction Coefficient
+60	0.57
50	0.40
40	0.28
30	0.18
20	0.12
10	0.08
+ 5	0.06
0	0.055
- 5	0.040
-10	0.042
-20	0.025
-30	0.02
-40	0

TABLE 7

List of Lubricants Employed in Study

Dry Powders

$SbSbS_4$
MoS_2

Grease Blends

RM 81
RM 81+5 w/o $SbSbS_4$
RM 81+5 w/o MoS_2
RM 81+0.2 w/o S
RM 81+0.43 w/o S
RM 81+1.0 w/o S
RM 81+5 w/o S
RM 81+5 w/o PbO
RM 81+5 w/o HBO_3
RM 81+5 w/o $SbSbS_4$
RM 81+5 w/o Anglamol*
RM 81+5 w/o A60048*
RM 81+5 w/o 60294*
RM 81+PbO + Graphite
RM 81+0.2 w/o S + 5 w/o MoS_2
RM 81+0.2 w/o S + 5 w/o Sb_2S_3

Paraffinic Mineral Oil Blends

Min Oil
Min Oil +5 w/o $SbSbS_4$ 16 hr. filtered → 0.08 w/o S, trace Sb (< 0.001 w/o)
Min Oil +5 w/o $SbSbS_4$ -30 min at 120°C filtered → 0.16 w/o S, trace Sb (< 0.001 w/o)
Min Oil +0.1 w/o S
Min Oil +0.2 w/o S

*Additives provided by Lubrizol Corp. See footnote, p. 1.

TABLE 8

Friction Coefficients of Various Lubricants
Determined by Ring Compression Test

Lubricant	Friction Coefficient	Surface Damage
None	0.24	Some welds at outer edge. Polished inner radius
RM 81 Grease	0.050	Original grinding marks on inner radius. Polished on outer radius
MoS_2 powder	0.035	Highly polished surface, film of MoS_2
$SbSbS_4$ powder	0.19	Roughened surface, no evidence of film
RM 81 grease + MoS_2 (5%)	0.040	Original grinding marks, polished at outer edge
RM 81 grease + $SbSbS_4$ (5%)	0.060	Rough surface

TABLE 9

Pin and V-Block E.P. Test Results
According to ASTM D3233 Method A

Test Specimens	RM 81	RM 81 + 5% MoS_2	RM 81 + 5%$SbSbS_4$	RM 81 + 0.43% S
52100	5500 N 1250 lb	7000 N 1575 lb	8000 N 1800 lb	-
4130	5300 N 1200 lb	9000 N 2025 lb	8700 N 1950 lb	-
440C	6100 N 1375 lb	2900 N 2000 lb	9100 N 2050 lb	-
Ti-6Al-4V	*	*	*	-
3135 PM/ 1137 V-blocks	2300 N 525 lb	6900 N 1550 lb	8700 N 1950 lb	8000 N 1800 lb

*Seized during run-in at 1300 N (300 lb)

TABLE 10

Pin and V-Block 30 Min. Constant Load E.P. Test Results on Various Additive Compounds

Lubricant	Max Pass Load
RM 81	890 N (200 lb)
RM 81+5 w/o MoS_2	1330 N (300 lb)
RM 81+5 w/o $SbSbS_4$	1780 N (400 lb)
RM 81+5 w/o PbO	890 N (200 lb)
RM 81+5 w/o HBO_3	1330 N (300 lb)
RM 81+5 w/o Sb_2S_3	< 1330 N (300 lb)
RM 81+PbO+Graphite+	< 1330 N (300 lb)
RM 81+5% Anglamol 33*	1780 N (400 lb)
RM 81+5 w/o Anglamol 6004A*+	< 1780 N (400 lb)
RM 81+5 w/o OS#60294*+	< 1780 N (400 lb)
RM 81+0.2% S	1330 N (300 lb)
RM 81+0.2%S+5 w/o MoS_2	1780 N (400 lb)
RM 81+0.2%S+5 w/o Sb_2S_3	1330 N (300 lb)
RM 81+1.0%S	1780 N (400 lb)

*Provided by Lubrizol Corp. Angamol 33 and OS#60294 are sulfur-containing additives. Anglamol 6004A is a sulfur-phosphorous additive. See footnote, p. 1.
+Failure occurred at the indicated load; tests not carried out at smaller loads.

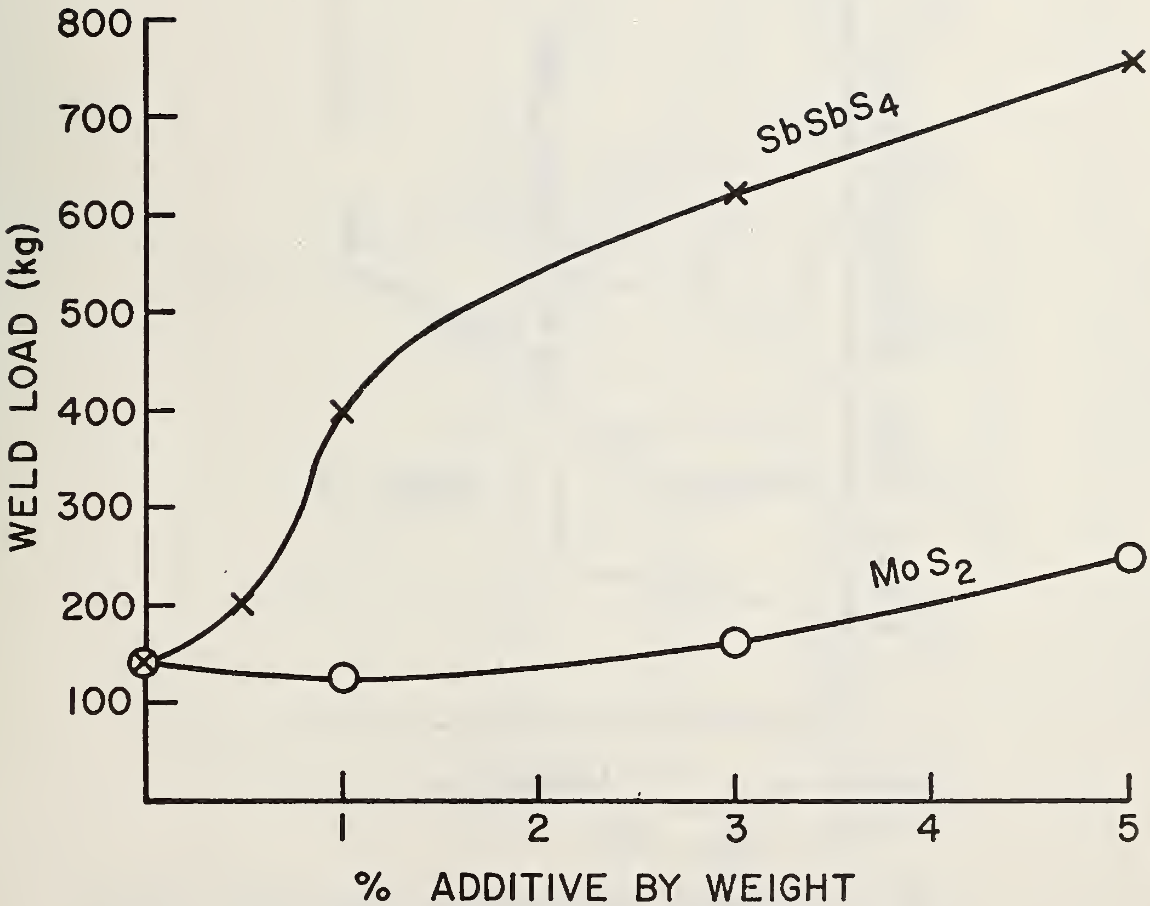


Fig. 1 Concentration effect on weld point for $SbSbS_4$ and MoS_2 in lithium grease. Data from King and Asmerom (5).

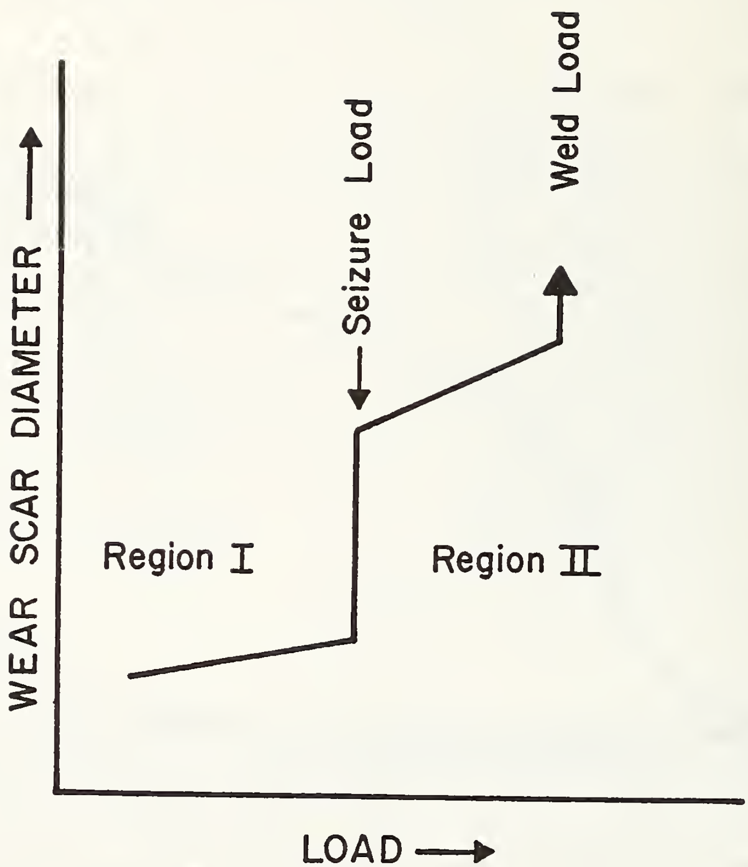


Fig. 2 Schematic representation of four-ball extreme pressure test behavior.

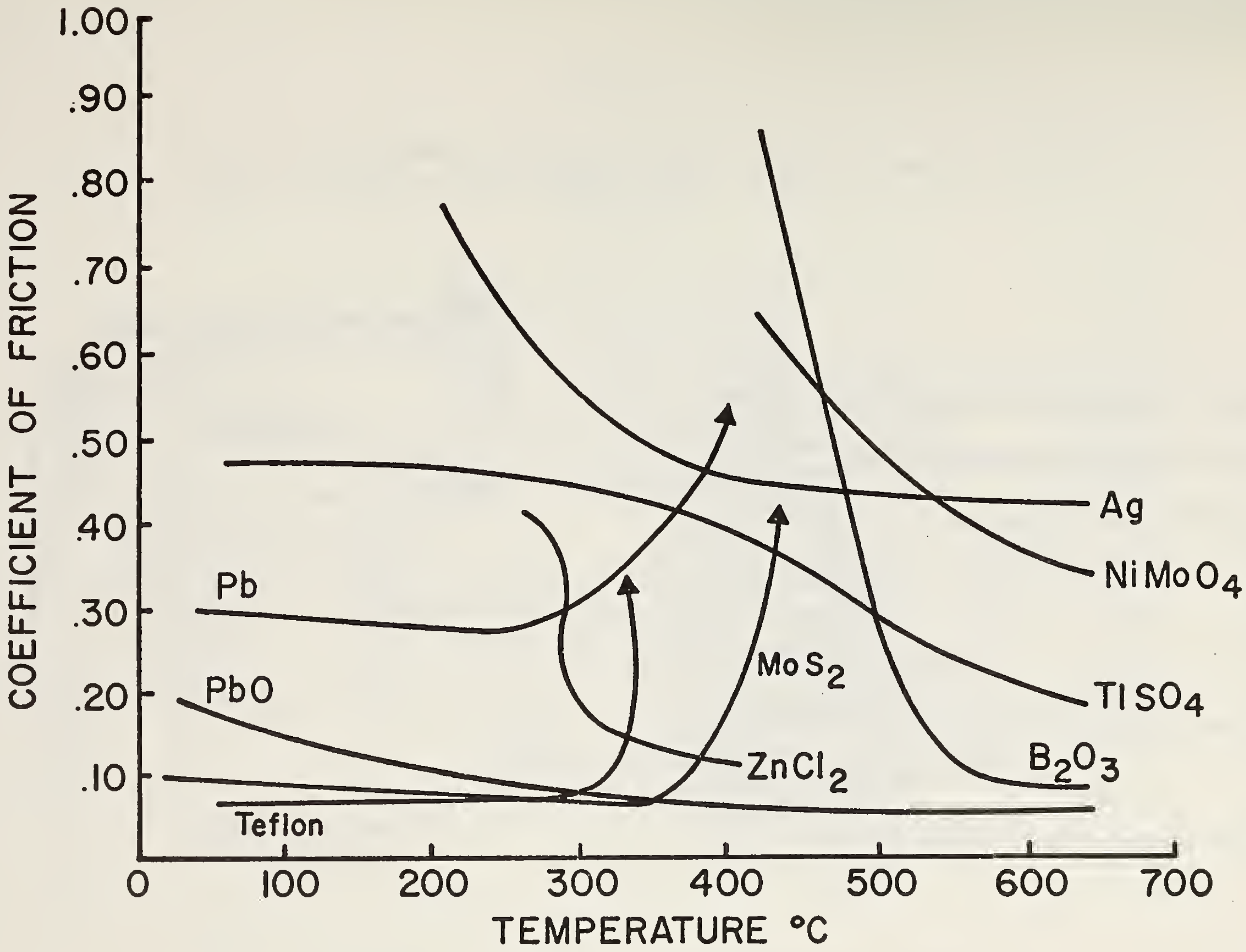
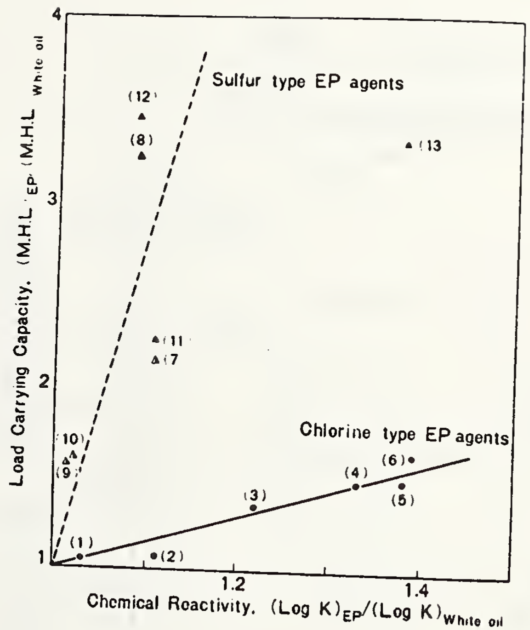


Fig. 3 Friction coefficients for a variety of solid materials vs temperature (12).



(1)	Monochlorobenzene	1.0%
(2)	Pentachlorodiphenyl	1.0%
(3)	Methylpentachloro Stearate	0.5%
(4)	Chlorinated paraffin	1.0%
(5)	Hexachloroethane	1.0%
(6)	Methyltrichloro stearate	1.0%
(7)	Dibenzyldisulfide	0.5%
(8)	Elementary Sulfur	0.5%
(9)	Didodecyldisulfide	0.5%
(10)	Diphenyldisulfide	0.5%
(11)	Binary system of Dibenzyldisulfide (0.5%) and Pentachlorodiphenyl (1.0%)	
(12)	Binary system of Elementary Sulfur (0.5%) and Pentachlorodiphenyl (1.0%)	
(13)	Binary system of Elementary Sulfur (0.5%) and Hexachloroethane (1.0%)	

Fig. 4 Load carrying capacity vs chemical reactivity for EP agents (15).

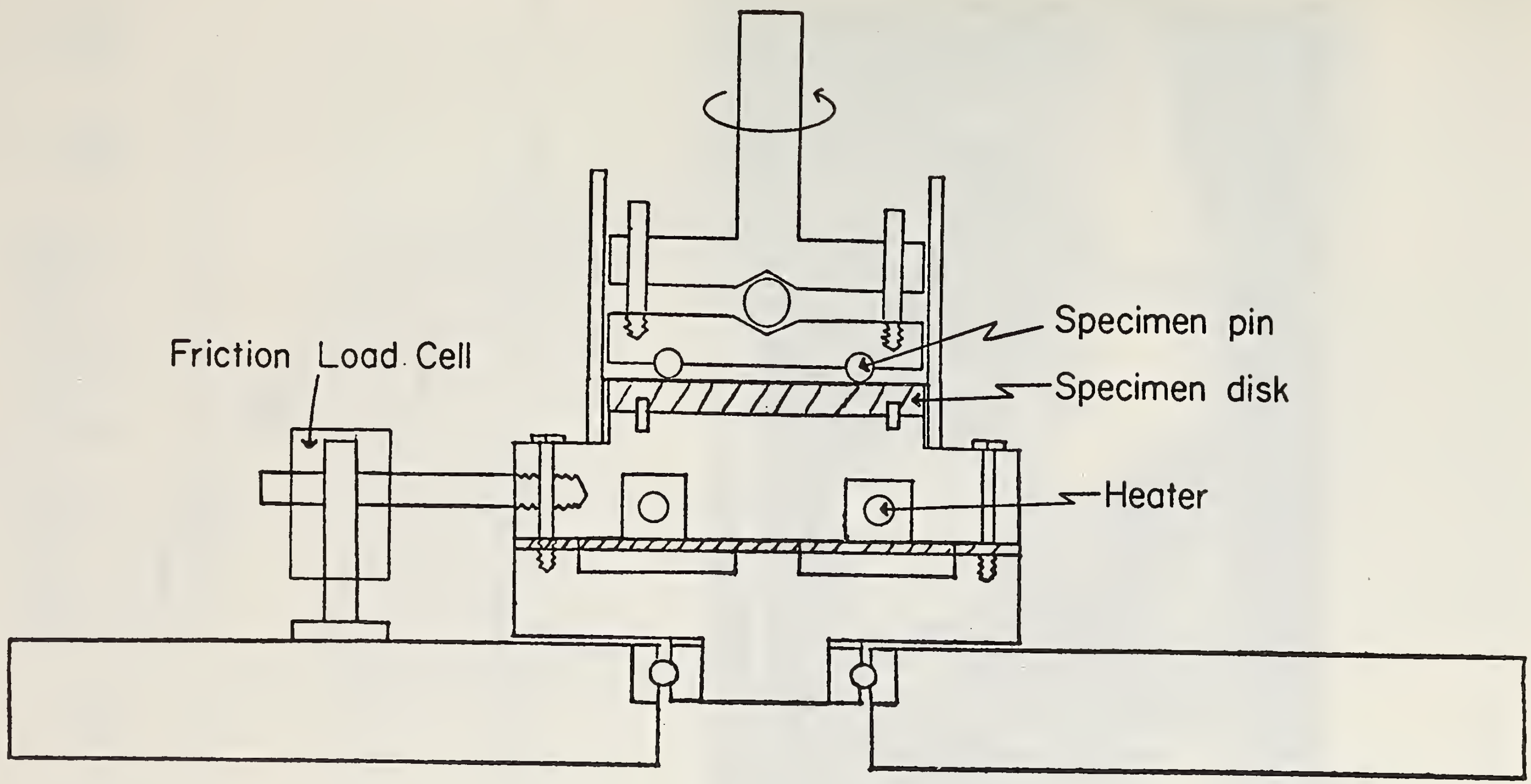


Fig. 5 Schematic drawing of three-pin on disk wear test machine.

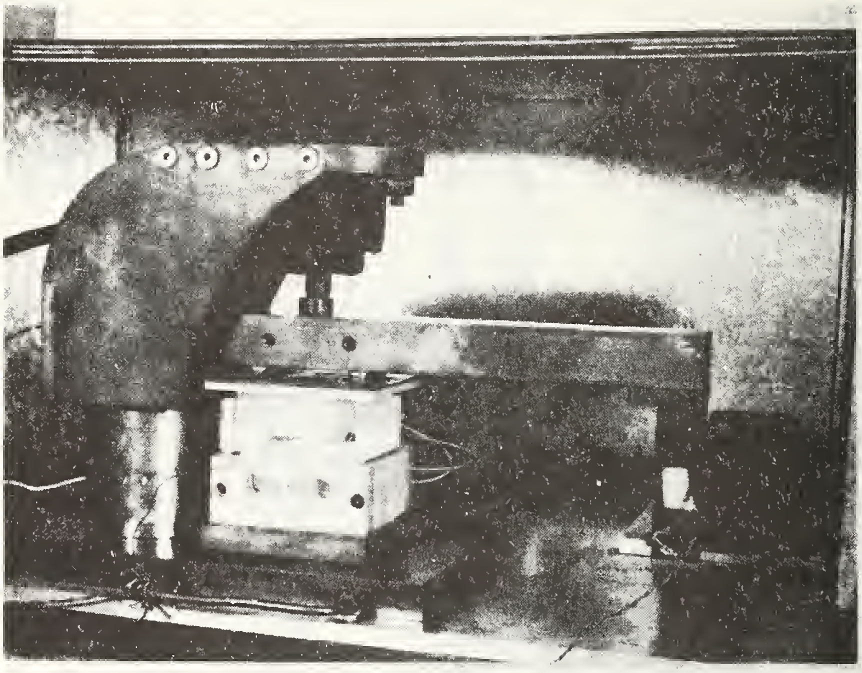


Fig. 6 Photograph of reciprocating high temperature friction and wear test machine.

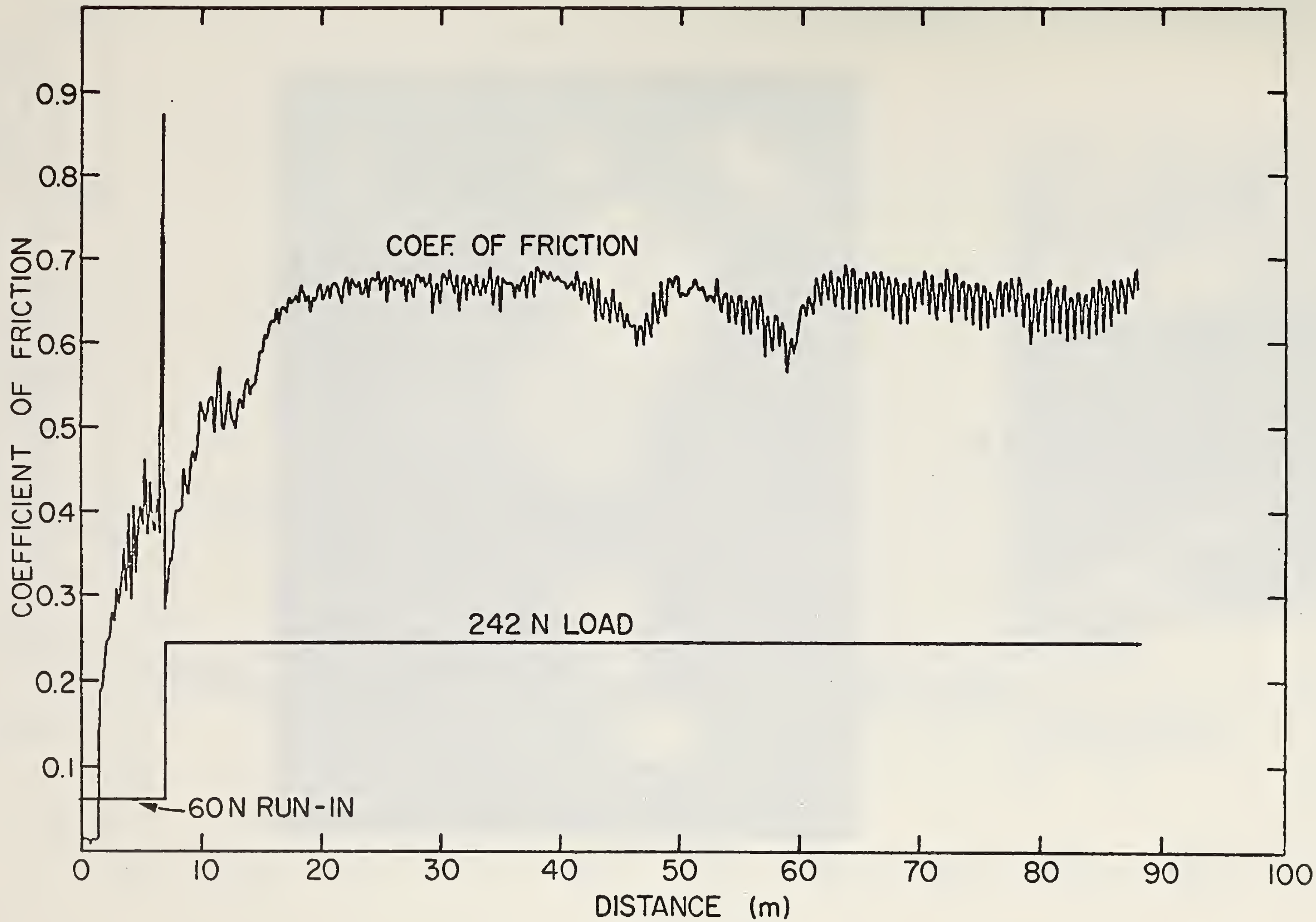
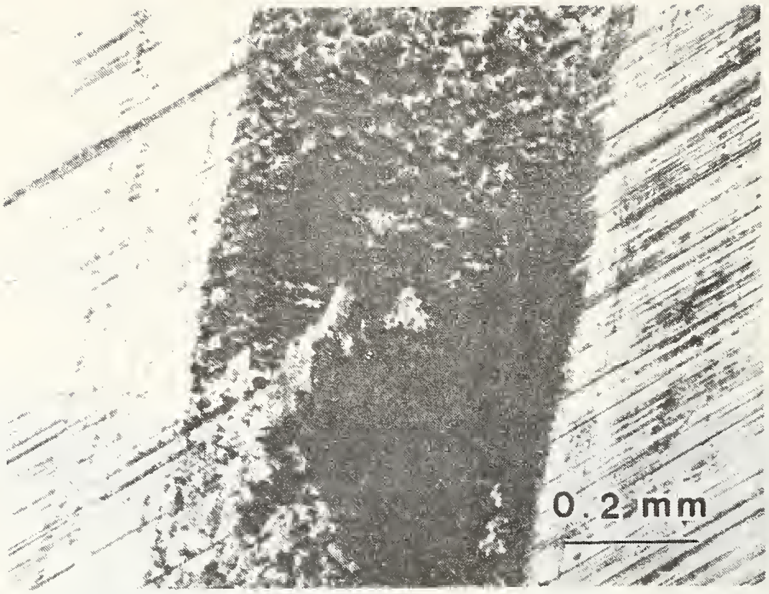


Fig. 7 Friction coefficient vs sliding distance for dry $SbSbS_4$ powder using three-pin on disk tests. (242 N load, 10 cm/s sliding speed, 52100 steel pins, 0-2 tool steel disk).



a

b

Fig. 8 Optical photograph of film generated on disk (0-2 tool steel) and on pin (52100 steel ball) (b) surfaces after sliding with $SbSbS_4$ powder at room temperature.

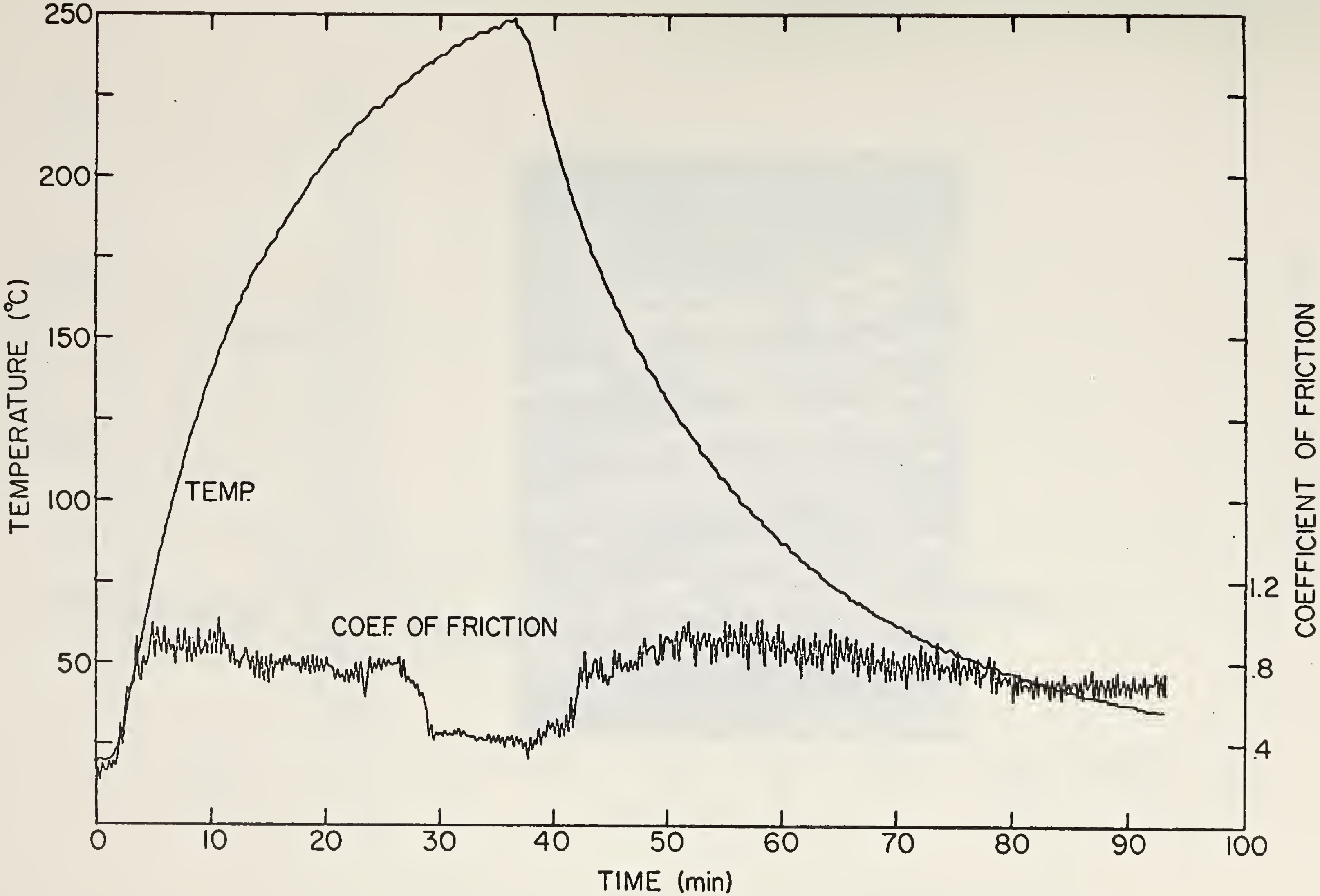


Fig. 9 Friction coefficient variation with temperature for dry $SbSbS_4$ powder using three-pin on disk test (52100 steel pins, 0-2 tool steel disk).

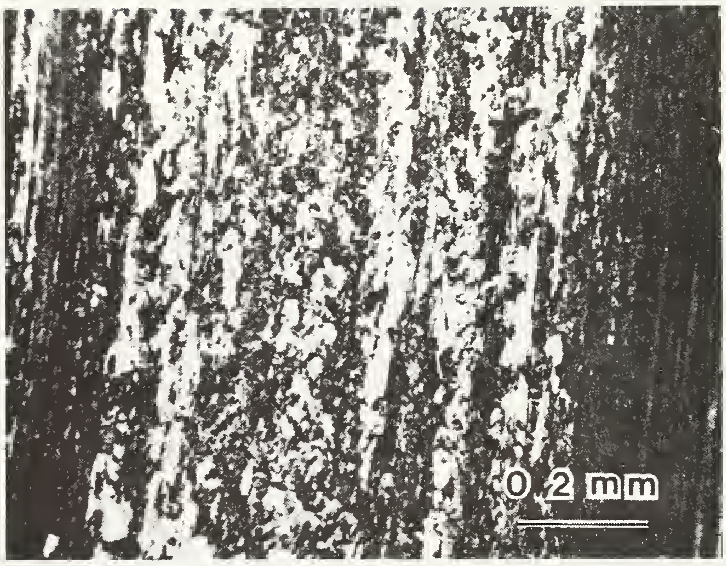


Fig. 10 Optical micrograph of wear track on disk surface showing adherent film after sliding at 250°C (52100 steel pins, 0-2 tool steel disk).

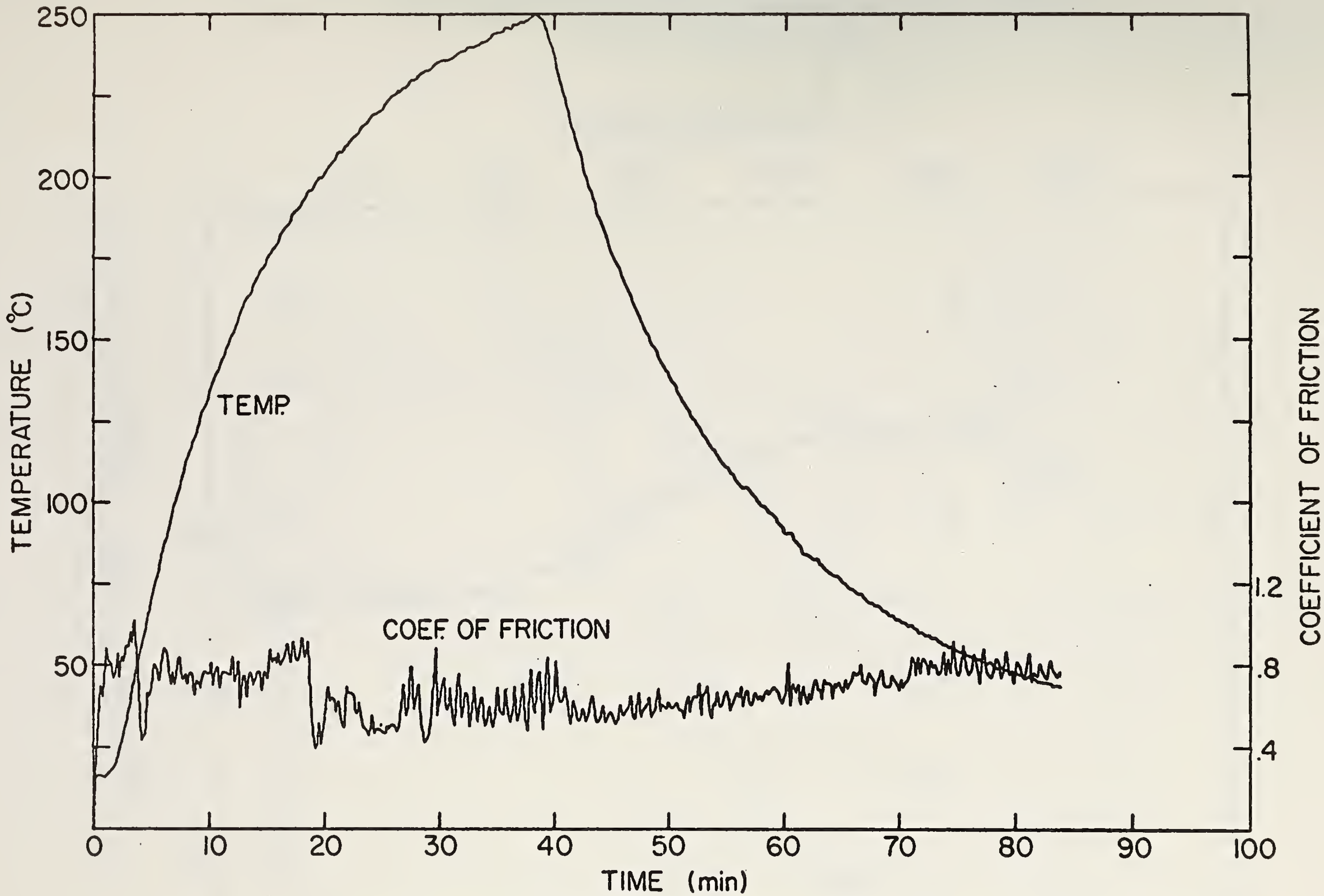


Fig. 11 Coefficient of friction variation with temperature for unlubricated sliding using three-pin on disk test (52100 steel pins, 0-2 tool steel disk).

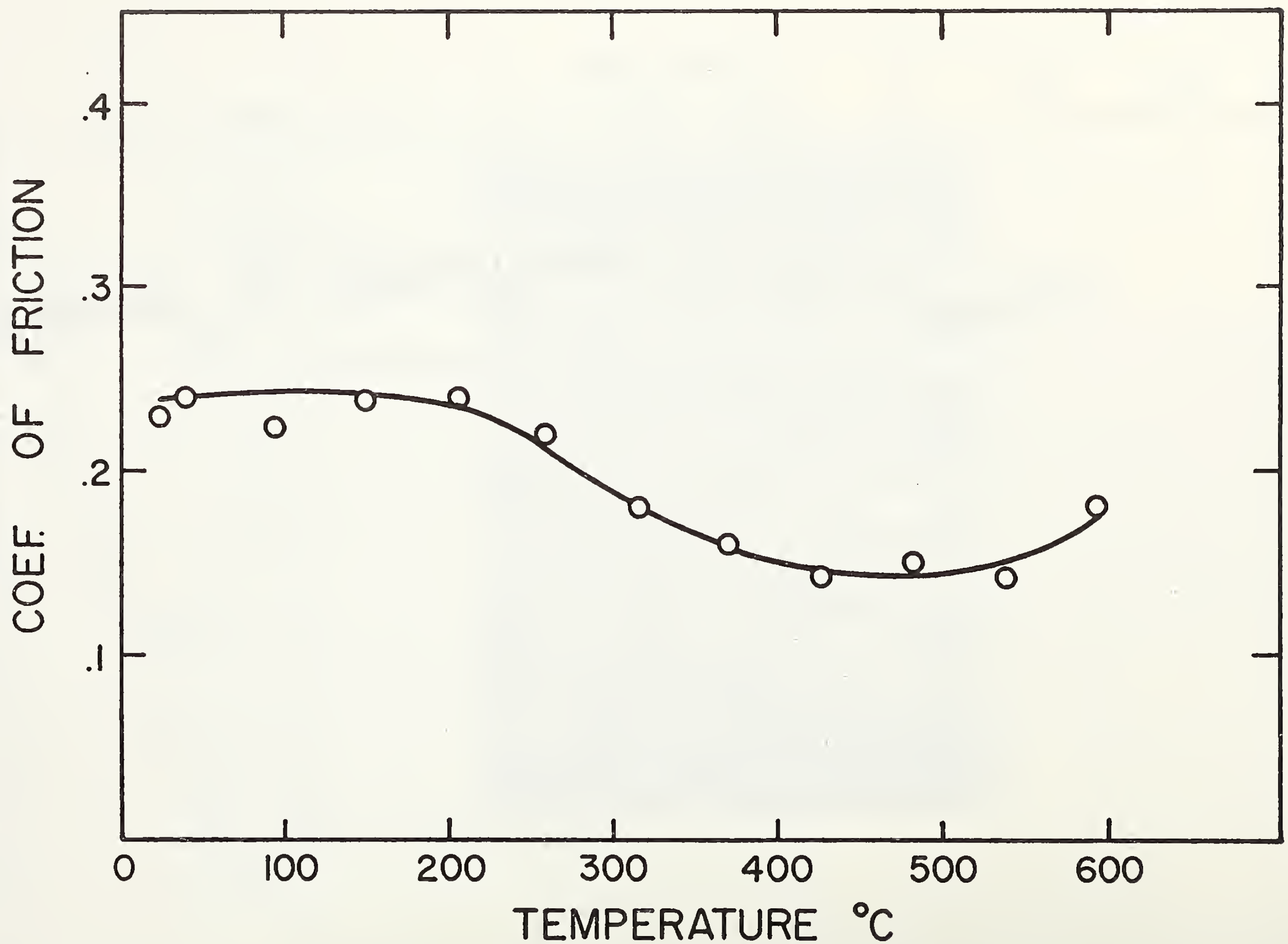


Fig. 12 Coefficient of friction vs temperature using reciprocating sliding test rig. (M-1 tool steel specimens).

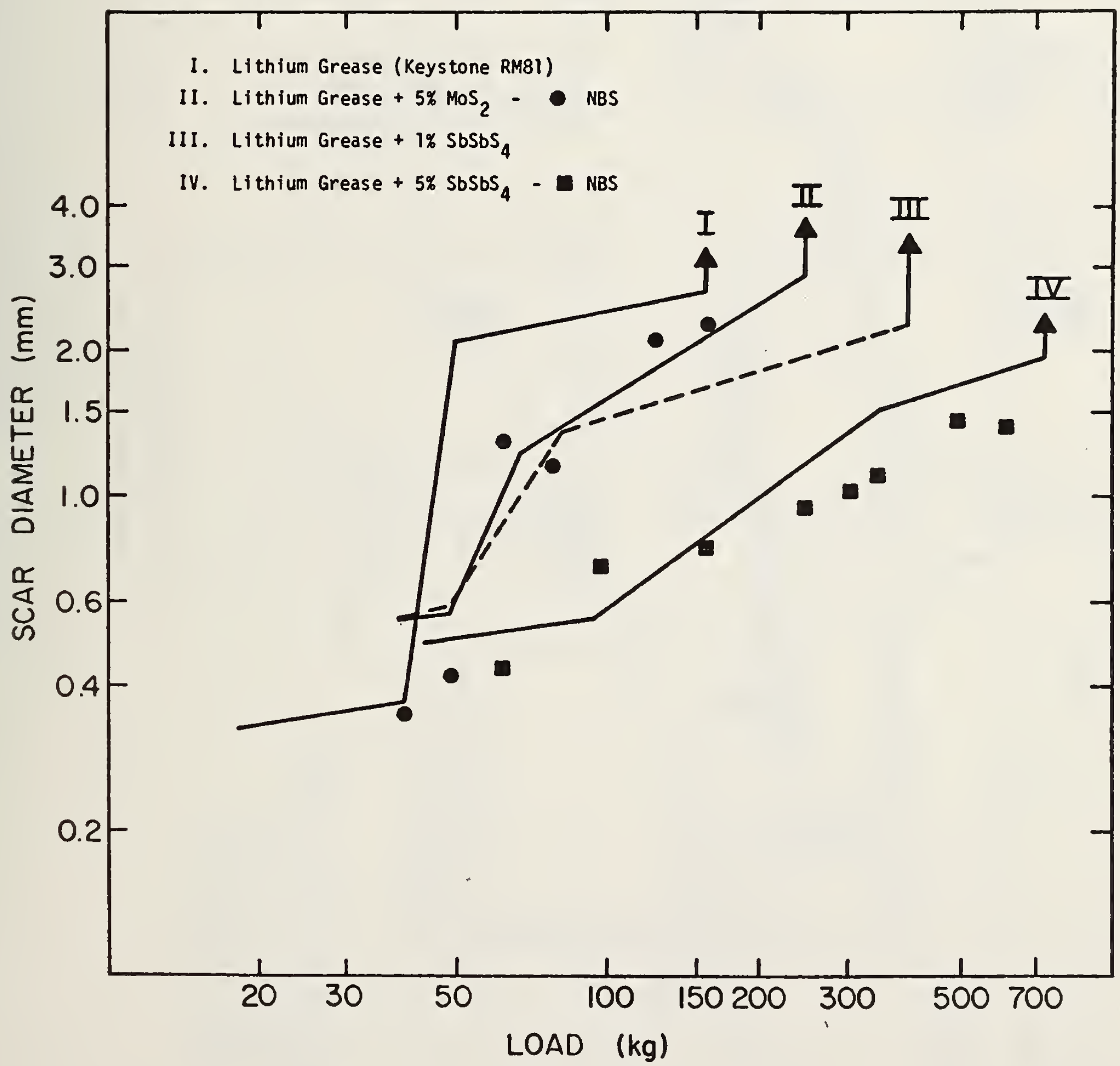


Fig. 13 Four ball EP test data compared to results from King and Asmerom (5). (52100 steel balls).

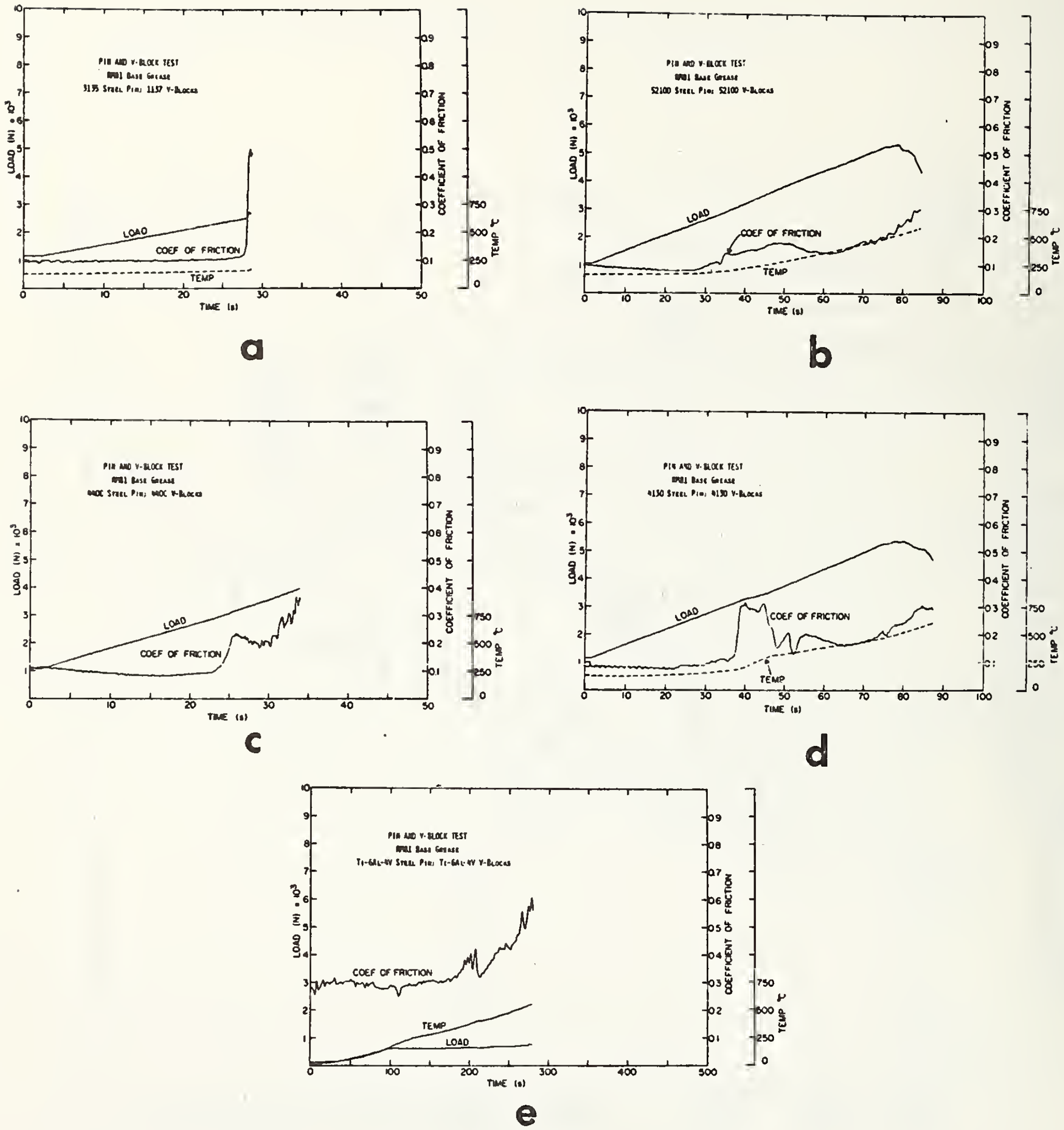


Fig. 14 Pin and V-block EP test results on RM81 base grease using different specimen materials. Test procedure was similar to that described in ASTM D3233 Method A. Simultaneous record of load, coefficient of friction and block temperature shown. (a) 1137 steel V-blocks and 3135 steel pin, (b) 52100 steel, (3) 440C stainless steel, (d) 4130 steel, (e) Ti-6Al-4V.

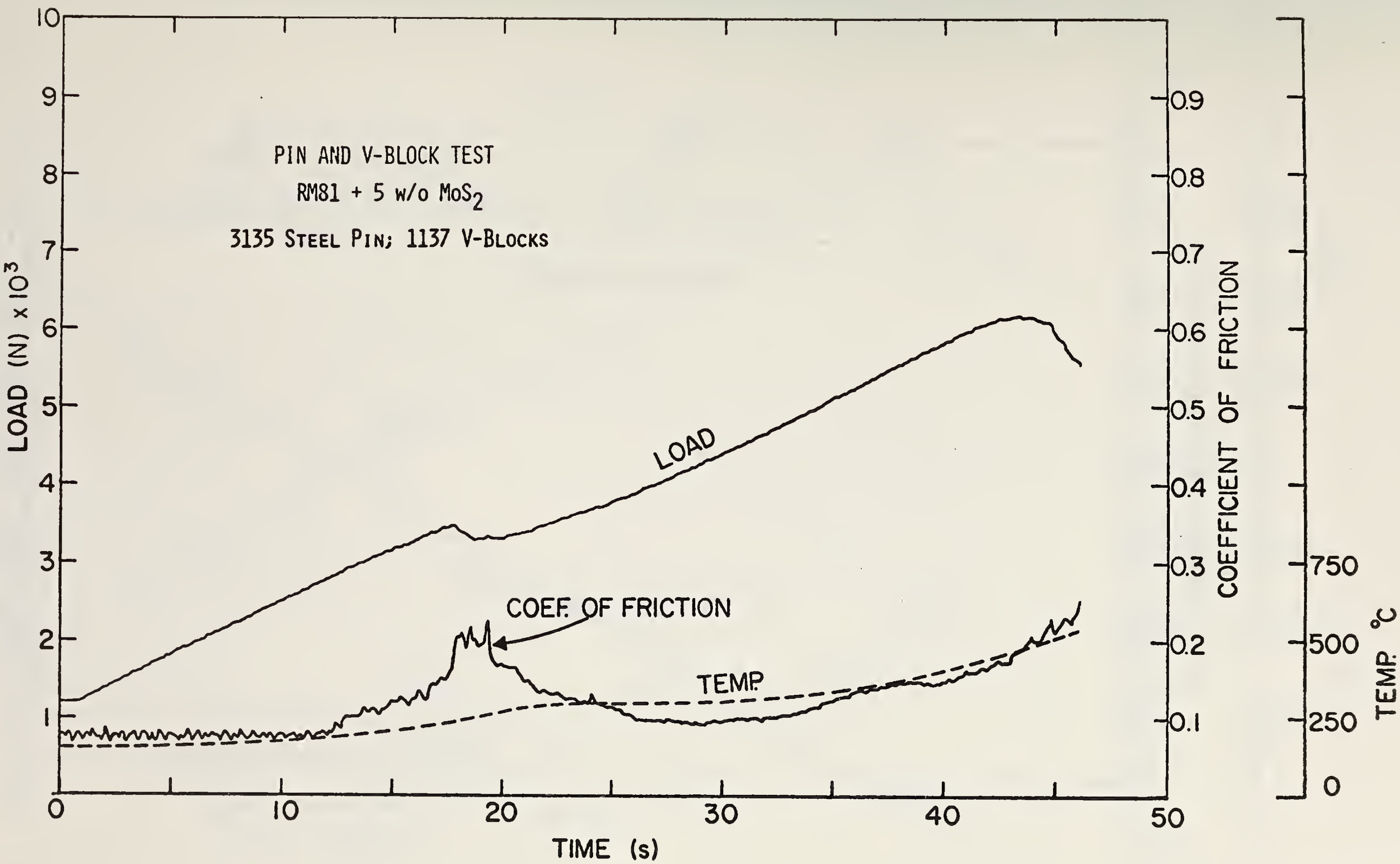


Fig. 15 Same conditions as Fig. 14(a) with RM81+5 w/o MoS_2.

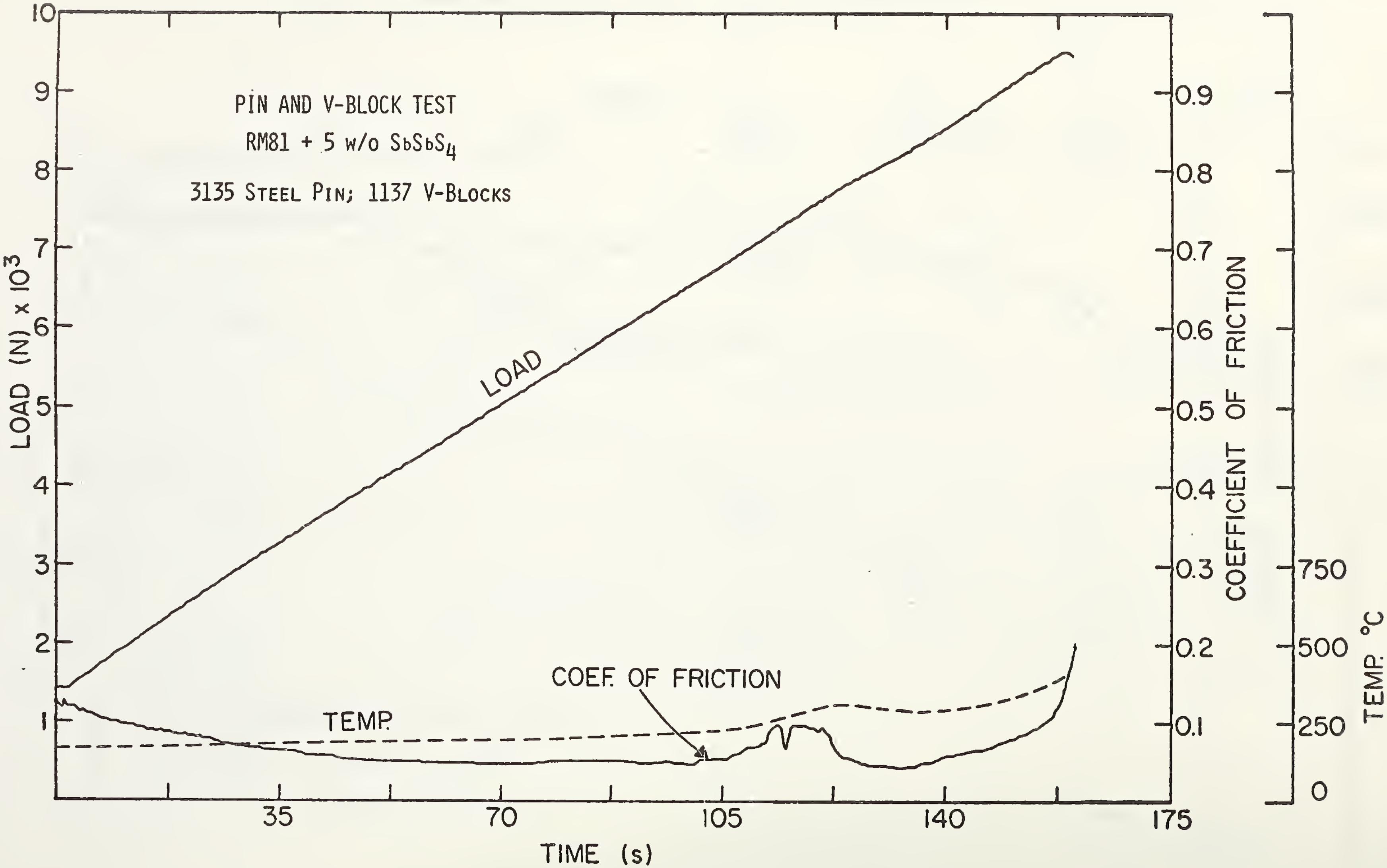


Fig. 16 Same conditions as Fig. 14(a) with RM81+5 w/o $SbSbS_4$.

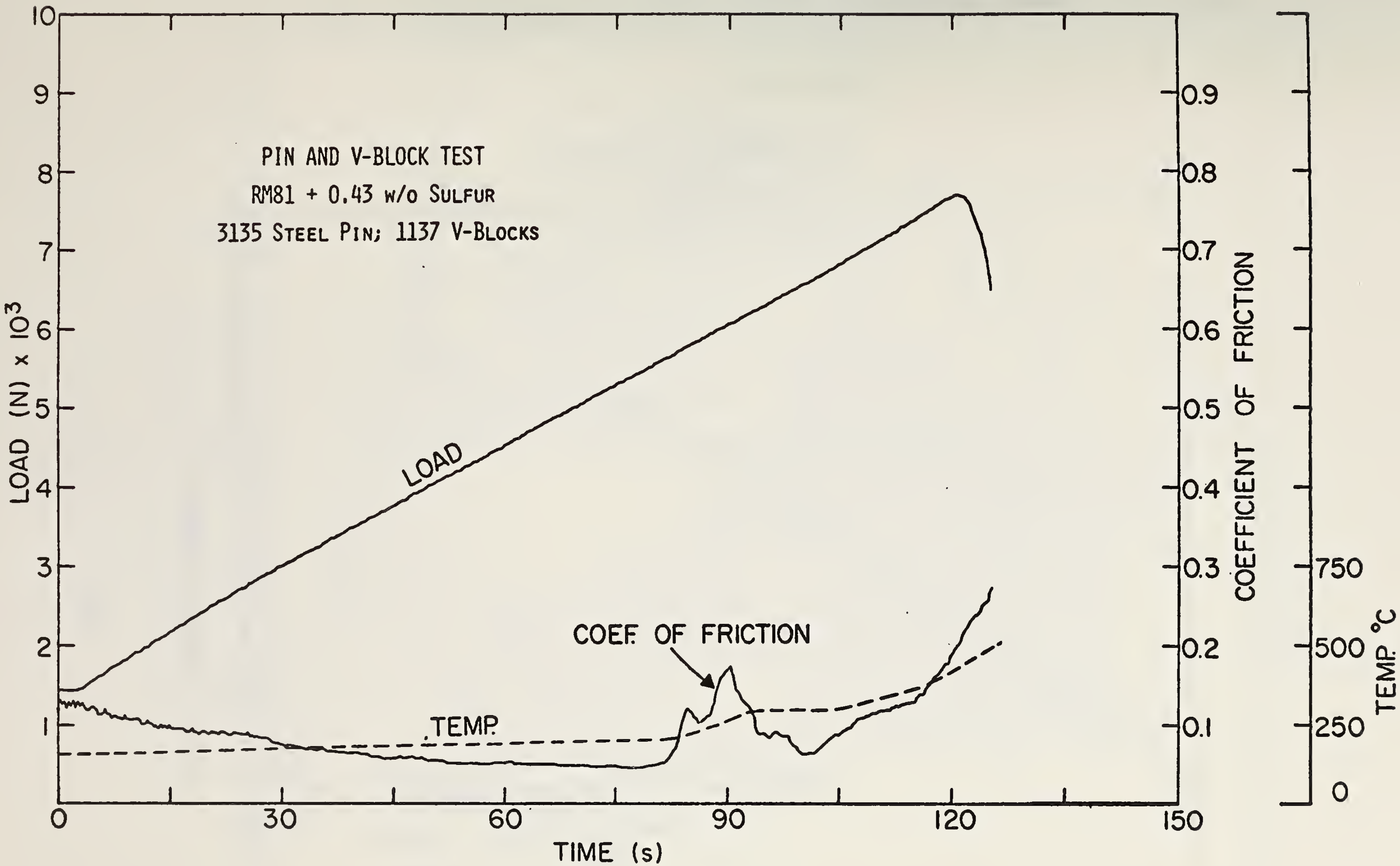


Fig. 17 Same conditions as Fig. 14(a) with RM81+0.43 w/o S.

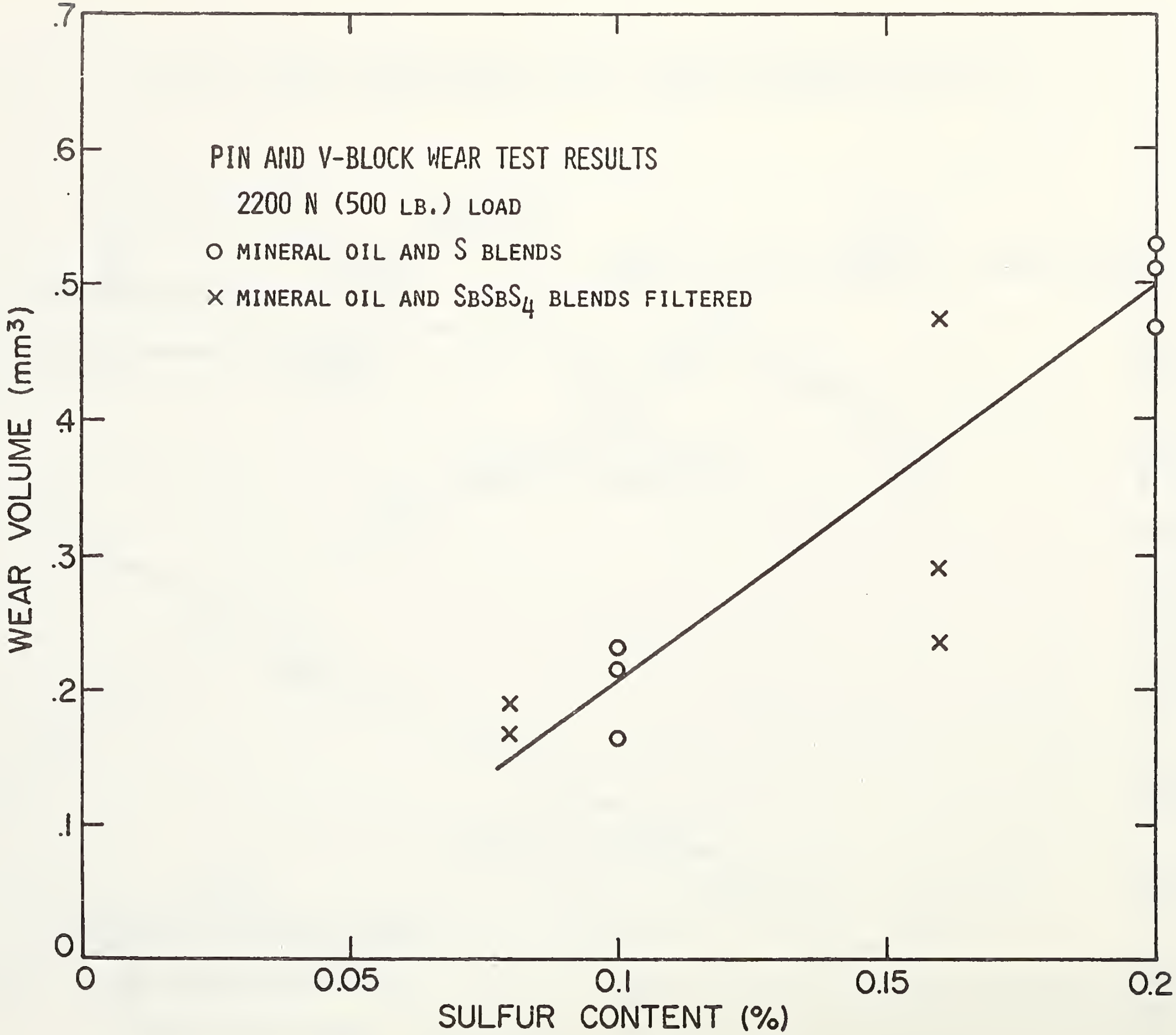
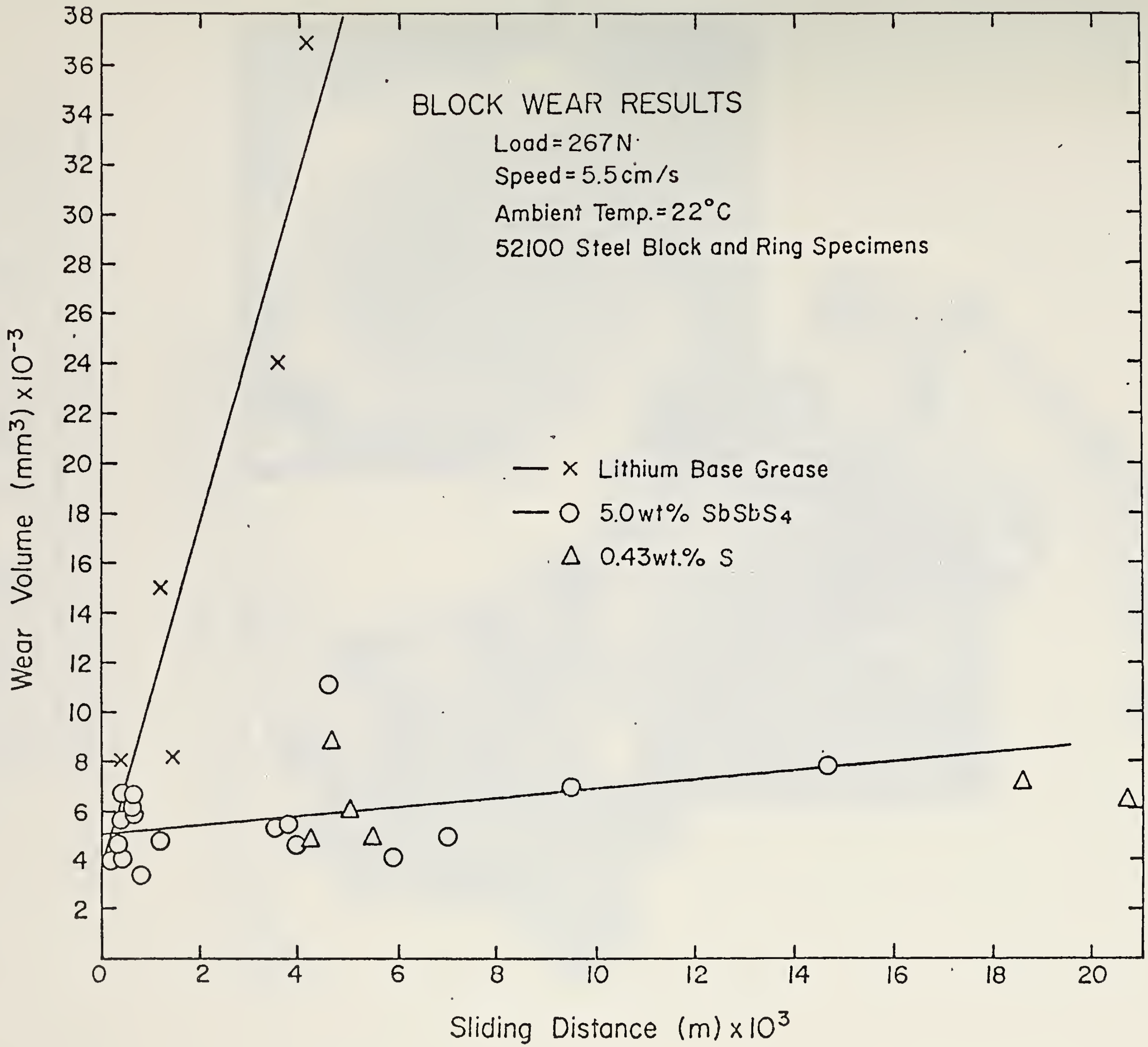


Fig. 18 Pin and V-block 30 min. wear test results on mineral oil blends (1137 steel V-blocks and 3135 steel pin).


BLOCK WEAR RESULTS
Load = 267 N
Speed = 5.5 cm/s
Ambient Temp. = 22°C
52100 Steel Block and Ring Specimens
Lithium Base Grease
5.0 wt% SbSbS4
0.43 wt.% S
Wear Volume (mm3) x 10-3
Sliding Distance (m) x 103

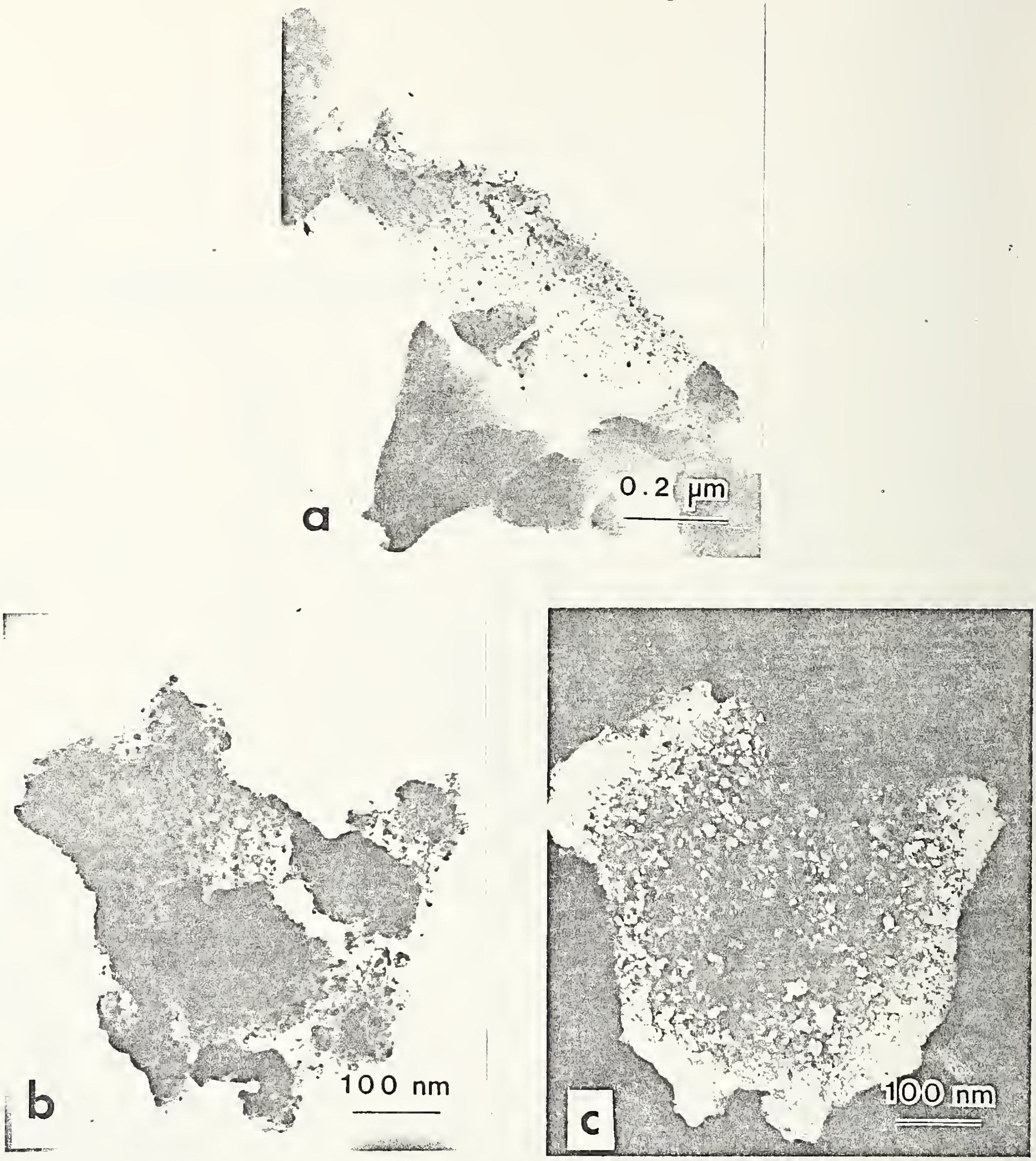


Fig. 20 Transmission electron micrograph of film fragments stripped from block wear scar after block and ring tests (52100 steel specimens). Test lubricant was RM81+5 w/o $SbSbS_4$. (a) Amorphous $SbSbS_4$ film and crystalline pyrrhotite film fragments are present. (b) Crystalline pyrrhotite film at high magnification. (c) Dark field image of (b) to indicate size of individual grains.

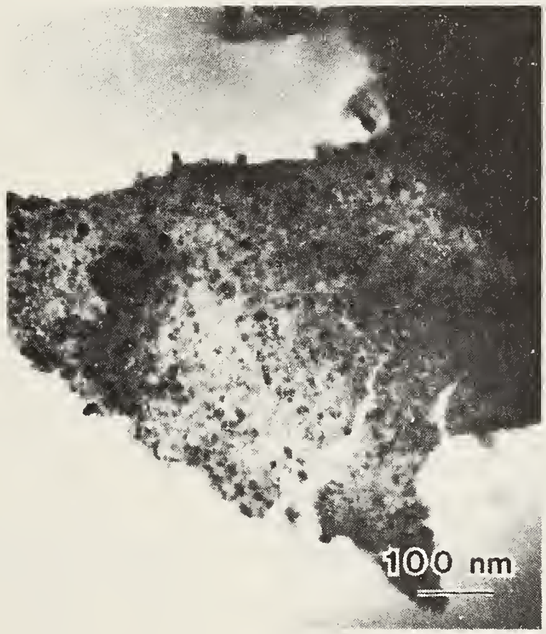


Fig. 21 Transmission electron micrograph of film fragment stripped from block (52100 steel) wear scar lubricated with RM81+0.43 w/o S. Polycrystalline film was determined to be FeS_2.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Studies have been carried out to determine certain basic properties of the complex metal sulfide, $SbSbS_4$, that pertain to its use as a solid lubricant and lubricant additive material. Past research had demonstrated that this material exhibited superior extreme pressure (EP) performance, antiwear properties, and high temperature stability. The present research has verified the performance under EP conditions as an additive to a base grease. However the performance of $SbSbS_4$ as a solid lubricant (in

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5. AUTHOR(S)

L. K. Ives, M. B. Peterson, J. S. Harris, P. A. Boyer, A. W. Ruff

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Studies have been carried out to determine certain basic properties of the complex metal sulfide, $SbSbS_4$, that pertain to its use as a solid lubricant and lubricant additive material. Past research had demonstrated that this material exhibited superior extreme pressure (EP) performance, antiwear properties, and high temperature stability. The present research has verified the performance under EP conditions as an additive to a base grease. However the performance of $SbSbS_4$ as a solid lubricant (in the form of a powder) was not found to be effective at temperatures below about 225° C. It was noted though that when used as a dry powder lubricant, the compound did produce a thick adherent film on steel surfaces in sliding contact. Six different types of wear and friction tests were carried out under various conditions of load, sliding speed, contact geometry, temperature, and time, in order to fully explore the potential of $SbSbS_4$ as a lubricant on several different metals. In a number of cases, its performance was compared with MoS_2 and with other sulfur containing additives in lubricants. Electron microscopy studies on film material removed from the sliding contact surfaces have shown that the interaction of sulfur released from $SbSbS_4$ with the steel surface, presumably at locally elevated temperatures, is a principal mechanism. However, the physical characteristics of the $SbSbS_4$ film in the contact zone probably also have a significant role in its overall performance.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Antimony thioantimonate; electron microscopy; lubricant additive; solid lubricant; wear; wear debris.

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