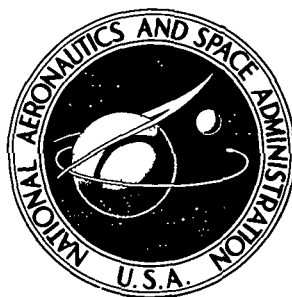


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FRICITION, WEAR, AND THERMAL STABILITY  
STUDIES OF SOME ORGANOTIN  
AND ORGANOSILICON COMPOUNDS

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# FRICTION, WEAR, AND THERMAL STABILITY STUDIES OF SOME ORGANOTIN AND ORGANOSILICON COMPOUNDS

by William R. Jones, Jr.

Lewis Research Center

## SUMMARY

Thermal decomposition temperatures were determined for a number of organotin and organosilicon compounds. A ball-on-disk sliding friction apparatus was used to determine the friction and wear characteristics of two representative compounds, (1) 3-tri-n-butylstannyl (diphenyl) and (2) 3-tri-n-butylsilyl (diphenyl). Results were compared to those previously obtained with a polyphenyl ether and a C-ether. Friction and wear test conditions included a 1-kilogram load, a 17-meter-per-minute (100-rpm) sliding speed, 25<sup>o</sup> to 225<sup>o</sup> C disk temperatures, a dry-air (<100 ppm water) atmosphere, and a 25-minute test duration. In general, the 3-tri-n-butylstannyl (diphenyl) and the 3-tri-n-butylsilyl (diphenyl) compounds yielded friction and wear results either lower than or similar to those obtained with a polyphenyl ether and a C-ether.

The maximum thermal decomposition temperatures obtained in the silicon and tin series were 358<sup>o</sup> C with 3-tri-n-octylsilyl (diphenyl) and 297<sup>o</sup> C with 4-triphenylstannyl (diphenyl). Increasing the steric hindrance around the silicon or tin atoms increased the thermal stability. Future work with these compounds will emphasize their possible use as antiwear additives rather than base fluids, because of preparation difficulties, high cost, and lower than expected thermal decomposition temperatures.

## INTRODUCTION

Higher flight speeds and higher output engines of advanced aircraft are creating needs for improved or new high-temperature liquid lubricants (ref. 1). Several classes of synthetic fluids have been proposed as potential lubricants for high-temperature applications. These classes include polyphenyl ethers (refs. 2 to 6), C-ethers (refs. 7 to 10), polyethers (refs. 11 to 13), and synthetic hydrocarbons (refs. 12 to 14). Another class of compounds which has elicited considerable interest as possible high-temperature

lubricants or lubricant additives is the organometallics. This group includes siloxanes, ferrocenes, silanes, and stannanes (refs. 15 to 19).

Tetraalkylsilanes have been studied as base stocks for high-temperature lubricant formulations (ref. 17). Thermal decomposition temperatures as high as 350° C were reported. Some of these fluids exhibited good viscosity properties up to 316° C (i. e., they have a wide liquid range). They also exhibited good lubricating ability to 200° C in four ball tests. The major difficulty encountered with these fluids was their poor stability in oxidation and corrosion tests at 260° C.

A number of organotin compounds have been synthesized for use as lubricant additives to improve the oxidation stability (ref. 18) or the antiwear behavior (ref. 19) of base stocks. Recently, Zimmer and coworkers (refs. 20 to 23) have prepared a variety of sterically hindered Group IVA organometallic compounds. These compounds are characterized by decreased reactivity because of the bulky groups shielding the central atom.

The objectives of this investigation were (1) to determine the thermal decomposition temperatures (by isotenscope) for a number of organotin and organosilicon compounds, (2) to determine the friction and wear characteristics of a selected organotin and organosilicon compound, and (3) to compare these results to those obtained with a polyphenyl ether and a C-ether.

Experimental conditions with the ball-on-disk sliding friction apparatus included a 1-kilogram load (initial Hertz stress,  $10^9$  N/m<sup>2</sup>), a 17-meter-per-minute (100-rpm) sliding speed, 25° to 225° C disk temperatures, a dry-air (<100 ppm water) atmosphere, and a 25-minute test duration. All organotin and organosilicon compounds were synthesized at the University of Cincinnati, Cincinnati, Ohio, under NASA grant NGL 36-004-056.

## EXPERIMENTAL LUBRICANTS

The general chemical structures of the organotin and organosilicon compounds are shown in figure 1. The two compounds selected for the friction and wear tests, a 3-tri-n-butylstannyl (diphenyl) and 3-tri-n-butylsilyl (diphenyl), are illustrated by figures 1(b) and (d), respectively, where R is the n-butyl alkyl group.

The two reference fluids used in these studies were a five-ring polyphenyl ether and a C-ether. The polyphenyl ether is an isomeric mixture of five-ring components and contains no additives. The C-ether is a blend of three- and four-ring components which are structurally related to the polyphenyl ethers. This is a base fluid which con-

tains only an antifoam additive. Some typical properties of these four fluids are listed in table I.

## APPARATUS

### Ball-on-Disk Apparatus

The ball-on-disk sliding friction apparatus is shown in figure 2. The test specimens were contained inside a stainless-steel chamber. The atmosphere was controlled with respect to moisture content.

A stationary 0.476-centimeter-radius ball was placed in sliding contact with a rotating 6.3-centimeter-diameter disk. A sliding speed of 17 meters per minute (100 rpm) was maintained. A normal load of 1 kilogram (initial Hertz stress,  $10^9 \text{ N/m}^2$ ) was applied with a deadweight. Balls and disks were made of CVM M-50 steel having a Rockwell C hardness of 62 to 64.

The disk was partially submerged in a polyimide cup containing the test lubricant and was heated by induction. Bulk lubricant temperature was measured with a thermocouple. Disk temperature was monitored with an infrared pyrometer. Frictional force was measured with a strain gage and was recorded on a strip-chart recorder.

### Thermal Decomposition Apparatus (Tensimeter)

The tensimeter (an automated isoteniscope) apparatus shown in figure 3 consists of two units: the sample oven with its associated temperature programmer and the electronics module containing the recorder. The basic operation of the tensimeter consists of heating a liquid sample and of plotting the isothermal rate of increase of vapor pressure (due to thermal decomposition) at a number of temperatures.

The sample assembly appears in figure 4. The sample cell is a glass bulb having a 5-cubic-centimeter volume, with a stem extending through the oven wall to a valve and pressure transducer mounted outside the oven.

### Atmosphere Monitoring and Control

Dry air (<100 ppm water) was the only atmosphere used in this investigation. It was obtained by drying and filtering service air. The moisture content was monitored by a moisture analyzer with an accuracy of  $\pm 10$  parts per million.

## PROCEDURE

### Friction and Wear Tests

Disks were ground and lapped to a root-mean-square surface finish of approximately  $10 \times 10^{-8}$  to  $20 \times 10^{-8}$  meter (4 to 8  $\mu$ in.). The root-mean-square surface finish of the balls was about  $2.5 \times 10^{-8}$  meter (1  $\mu$ in.). Specimens were scrubbed with a paste of levigated alumina and water, rinsed with tap water and distilled water, and then placed in a desiccator.

The organotin and organosilicon compounds were tested in the as-received condition. The specimens were mounted, and 20 cubic centimeters of lubricant were placed in the lubricant cup. The test chamber ( $3.7 \times 10^3$  cm<sup>3</sup> volume) was purged with dry air (<100 ppm water) for 10 minutes at a flow rate in excess of  $50 \times 10^3$  cubic centimeters per hour. The disk was heated by induction to the test temperature while rotating, and the ball was then loaded against the disk. The test atmosphere flow rate was reduced to  $35 \times 10^3$  cubic centimeters per hour, and a  $6.9 \times 10^{-3}$ -newton-per-square-meter (1-psig) pressure was maintained in the chamber. The lubricant was heated only by heat transfer from the rotating disk. The bulk lubricant temperature was essentially the same as the disk. The bulk lubricant temperature was essentially the same as the disk temperature for the entire temperature range.

Frictional force and bulk lubricant temperature were continuously recorded. Disk temperature was continuously monitored. Experiments were terminated after 25 minutes, and the rider (ball) wear scar was recorded.

### Thermal Decomposition Tests

A 3- to 4-cubic-centimeter sample of test fluid is placed in the sample cell. The cell is attached to the cell assembly, and the fluid is degassed and refluxed under vacuum. The cell assembly is then placed in the oven. The sample is heated to an initial temperature about  $50^{\circ}$  C ( $122^{\circ}$  F) below the suspected decomposition temperature. After a 5-minute stabilization period, the increase in vapor pressure, if any, is recorded as a vertical bar during a fixed time interval. The programmer raises the sample temperature by a preset amount, usually  $5^{\circ}$  C, and the previous process is repeated. A typical plot appears in figure 5.

This is essentially a plot of the logarithm of the isothermal rate of vapor pressure increase as a function of reciprocal absolute temperature. A straight line is drawn which connects the tops of the recorded bars at the higher temperatures. The intersection with the temperature reference axis is the thermal decomposition temperature

$T_D$ . This temperature axis corresponds to a pressure rise of 50 torr per hour, which is the definition of the  $T_D$ . The activation energy for decomposition  $E'$  may be calculated from the slope of the straight line.

## RESULTS AND DISCUSSION

### Thermal Decomposition Results

Table II lists the thermal decomposition results for both the organotin and organo-silicon series of compounds. Both meta- and paralinked compounds have been included, and their general chemical structures are illustrated in figure 1.

Emphasis was placed on the metalinked compounds for two reasons. First, from theoretical considerations, the metalinked compounds should be more thermally stable than their para-analogs. Thermal decomposition usually proceeds by means of free radicals. If the potential free radical cannot be stabilized by resonance, it will be more difficult to form than one which is stabilized. This stabilization is not possible with metalinkages. Second, metalinkages produce a more asymmetrical molecule, which should reduce the melting points and thus produce a greater liquid range.

A minimum quantity of 3 to 5 cubic centimeters of fluid is required for each thermal decomposition test. If a compound was a solid at room temperature or was available only in small quantities, a mixing procedure had to be utilized. The compound was mixed with a four-ring polyphenyl ether to produce a concentration of 20 to 50 percent by volume. The polyphenyl ether had a thermal decomposition temperature ( $T_D$ ) of about  $450^\circ\text{C}$ . Therefore, any decomposition taking place below this temperature must be attributed to the tin or silicon compound. However, there is a dilution effect which causes a small error (approx 7 percent) in the  $T_D$  measurement. The amount of the error was determined by checking the  $T_D$  of a standard fluid mixed with the polyphenyl ether. The fluids tested as mixtures are noted in table II and their corrected  $T_D$  values are given. In general, the reproducibility of  $T_D$  values for pure compounds is better than  $\pm 5^\circ\text{C}$ . However, the  $T_D$  values for the mixtures may vary by  $\pm 10^\circ\text{C}$ .

The substituents in table II are listed in order of increasing steric hindrance. As can be seen, the thermal stability generally increases with increasing steric hindrance (i. e., increasing size of the substituent groups). This is somewhat surprising, since steric crowding usually causes a decrease in thermal stability (ref. 24). A possible explanation could be that if vibrational energies are evenly distributed over the entire molecule, a higher energy (i. e., higher temperature) would be required to rupture the same bond in a larger molecule than in a smaller one.

It is apparent that the steric factor does not influence the  $T_D$  in a linear fashion. Much greater changes in  $T_D$  occur in the latter part of the series (n-hexyl to neopentyl)

than in the initial part (methyl to n-hexyl). An example from the literature may serve to illustrate this nonlinear effect on reaction rates. Dostrovsky and Hughes (refs. 25 to 29) have shown that the rate of basic ethanolysis of alkyl bromides decreases enormously with the increasing bulk of groups attached to the carbon atom under attack. The reaction is

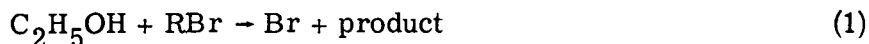


Table III shows the relative reaction rates as the size of the R group increases. Again the greatest effect occurs with the bulky neopentyl group.

A second interesting observation from table II is that the paracompounds do not appear to be less stable than their meta-analogs. Within experimental error their thermal stabilities appear to be essentially the same. Apparently resonance stabilization of decomposition products is not an important factor with the compounds studied in this investigation.

The highest thermal stability attained in the tin series was  $297^\circ\text{C}$  with the para-phenyl derivative. In the silicon series, the meta-n-octyl derivative yielded the highest  $T_D$  ( $358^\circ\text{C}$ ). One disubstituted compound (3,3'-bis(tri-n-propyl-tin)biphenyl) was synthesized and found to be less thermally stable ( $T_D = 214^\circ\text{C}$ ) than the monosubstituted derivative ( $T_D = 236^\circ\text{C}$ ).

## Friction and Wear Results

The meta-n-butyl derivatives were chosen as the representative compounds from each series for the friction and wear tests. The n-butyl derivatives were selected because of their ease of preparation and the fact that they were both viscous liquids at room temperature.

Figure 6 contains the friction and wear results for these two fluids. The temperature range studied was  $25^\circ$  to  $225^\circ\text{C}$ . The upper temperature limit was dictated by fluid volatility. As can be seen, the tin derivative yields slightly lower wear than the silicon analog at low temperatures ( $25^\circ$  to  $75^\circ\text{C}$ ) but greater wear at the higher temperatures ( $75^\circ$  to  $225^\circ\text{C}$ ). The increase in wear rate at the high temperatures for both fluids may in part be due to loss of lubricant by evaporation.

The coefficient of friction for the tin derivative is essentially constant over the entire temperature range. The silicon analog exhibited a linearly increasing friction coefficient.

A comparison of the tin and silicon results with those obtained previously with two high-temperature aromatic lubricants, a C-ether (ref. 9) and a five-ring polyphenyl



ether (5P-4E) (ref. 10), appears in figure 7. As can be seen, both the tin and silicon compounds yielded lower wear than the 5P-4E over practically the entire overlapping temperature range. From 25<sup>o</sup> to 75<sup>o</sup> C the tin and silicon compounds exhibit wear rates similar to those obtained with a C-ether. From 75<sup>o</sup> to 225<sup>o</sup> C, the tin compound yielded wear similar to that for the C-ether, and the silicon compound yielded wear lower than that for the C-ether. Figure 8 summarizes the wear results for the four fluids at four disk temperatures.

The coefficient of friction as a function of temperature for all four fluids appears in figure 7. In general, all fluids exhibited similar friction coefficients from 25<sup>o</sup> to 150<sup>o</sup> C. From 150<sup>o</sup> to 225<sup>o</sup> C, the lowest friction was observed with the tin compound and the highest with 5P-4E.

It must be emphasized that this study is only a preliminary investigation of the friction and wear characteristics of the tin and silicon compounds. Because of the difficulty in preparation, high cost, and lower than expected thermal decomposition temperatures of these compounds, future work will emphasize their possible use as anti-wear additives rather than as base fluids.

## SUMMARY OF RESULTS

Thermal decomposition temperatures were determined for a number of organotin and organosilicon compounds. A ball-on-disk sliding friction apparatus was used to determine the friction and wear characteristics of two representative compounds, (1) 3-tri-n-butylstannyl (diphenyl) and (2) 3-tri-n-butylsilyl (diphenyl). Conditions included a dry-air atmosphere (<100 ppm water), a 1-kilogram load, a 17-meter-per-minute sliding speed, and disk temperatures of 25<sup>o</sup> to 225<sup>o</sup> C. Test specimens were made of CVM M-50 steel. The major results were as follows:

1. In general, the 3-tri-n-butylstannyl (diphenyl) and the 3-tri-n-butylsilyl (diphenyl) compounds yielded friction and wear results either lower than or similar to those obtained with a polyphenyl ether and a C-ether.
2. The maximum thermal decomposition temperatures obtained in the silicon and tin series were 358<sup>o</sup> and 297<sup>o</sup> C, respectively.
3. Increasing the steric hindrance (i. e., increasing the size of the substituent groups) around the silicon or tin atoms increased the thermal stability in both series.
4. Future work with these compounds will emphasize their possible use as anti-

wear additives rather than base fluids because of preparation difficulties, high cost; and lower than expected thermal decomposition temperatures.

Lewis Research Center,  
National Aeronautics and Space Administration,  
Cleveland, Ohio, December 4, 1972,  
501-24.

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TABLE I. - TYPICAL PROPERTIES OF EXPERIMENTAL FLUIDS

Test fluid	38° C	99° C	Density g/cm <sup>3</sup>	Thermal decomposition temperature, T <sub>D</sub> , °C (a)
	Kinematic viscosity, m <sup>2</sup> /sec (cS)			
3-Tri- <u>n</u> -butylstannyl (diphenyl)	9.98×10 <sup>-6</sup> (9.98)	2.4×10 <sup>-6</sup> (2.4)	----	236
3-Tri- <u>n</u> -butylsilyl (diphenyl)	22.9×10 <sup>-6</sup> (22.9)	3.6×10 <sup>-6</sup> (3.6)	----	295
C-ether	25×10 <sup>-6</sup> (25)	4.1×10 <sup>-6</sup> (4.1)	1.18	390
Five-ring polyphenyl ether	360×10 <sup>-6</sup> (360)	13×10 <sup>-6</sup> (13)	1.19	443

<sup>a</sup>Maximum T<sub>D</sub> obtained with 3-tri-n-octyl silyl (diphenyl), 358° C; maximum T<sub>D</sub> obtained with 4-triphenyl stannyl (diphenyl), 297° C.

TABLE II. - THERMAL DECOMPOSITION TEMPERATURES (FROM ISOTENISCOPE) FOR VARIOUS ORGANOTIN AND ORGANOSILICON COMPOUNDS

Type of compound	Substituent <sup>a</sup>								
	Methyl	Ethyl	<u>n</u> -propyl	<u>n</u> -butyl	<u>n</u> -hexyl	<u>n</u> -octyl	2-Ethyl hexyl	Phenyl	Neopentyl
	Thermal decomposition temperature (from isoteniscope), T <sub>D</sub> , °C								
Meta-trialkylstannyl	b <sub>230</sub>	---	b, c <sub>236</sub>	236	b <sub>236</sub>	---	b <sub>260</sub>	---	b <sub>283</sub>
Para-trialkylstannyl	---	---	b <sub>240</sub>	b <sub>240</sub>	---	---	---	b <sub>297</sub>	---
Meta-trialkylsilyl	278	b <sub>296</sub>	276	295	b <sub>300</sub>	358	---	---	---
Para-trialkylsilyl	b <sub>311</sub>	---	---	b <sub>320</sub>	---	---	---	---	---

<sup>a</sup>Substituents given in order of increasing steric hindrance.

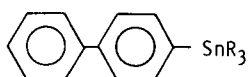
<sup>b</sup>Value corrected for dilution effects (compound was mixed with a four-ring polyphenyl ether to produce a 20 to 50 vol. % concentration).

<sup>c</sup>Value for 3, 3' disubstituted derivative was 214° C.

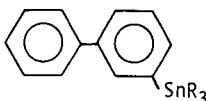
TABLE III. - RELATIVE REACTION RATES  
 FOR BASIC ETHANOLYSIS OF ALKYL  
 BROMIDES (R-Br) AS FUNCTION OF  
 SIZE OF ALKYL GROUP (R)

[Data from refs. 25 to 29.]

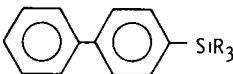
Alkyl group	Reaction rate relative to that of methyl group
Methyl	1.0
Ethyl	$5.7 \times 10^{-2}$
n-propyl	$1.6 \times 10^{-2}$
Isobutyl	$1.7 \times 10^{-3}$
Neopentyl	$2.4 \times 10^{-7}$



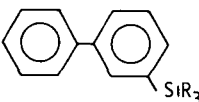
(a) Para-tin.



(b) Meta-tin.



(c) Para-silicon.



(d) Meta-silicon.

Figure 1. - General chemical structures of organotin and organosilicon compounds. Alkyl group is represented by R.

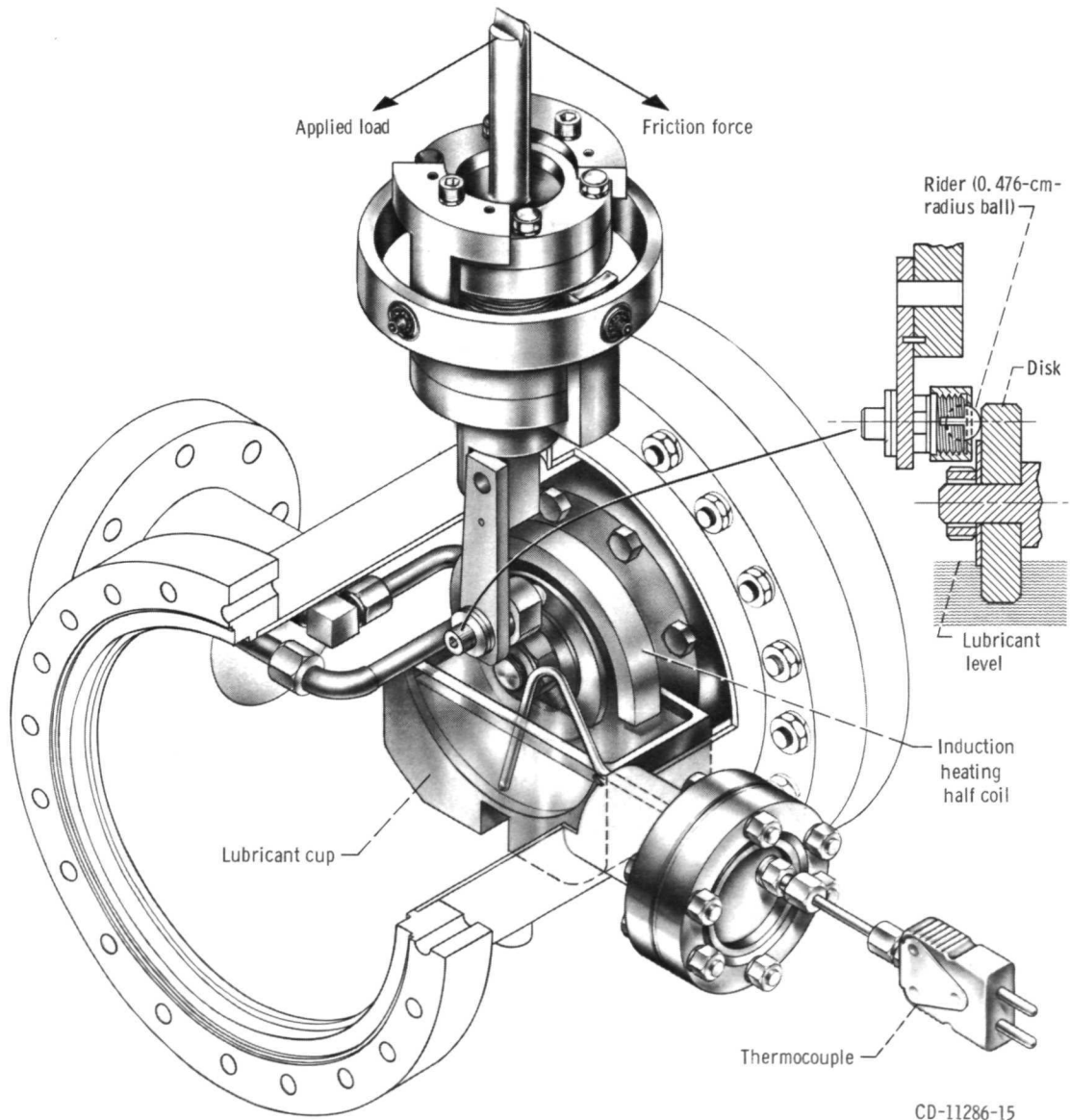


Figure 2. - Friction and wear apparatus.

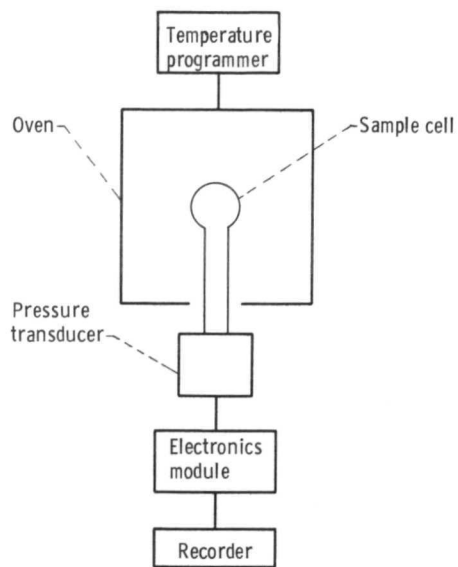


Figure 3. - Recording tensimeter.

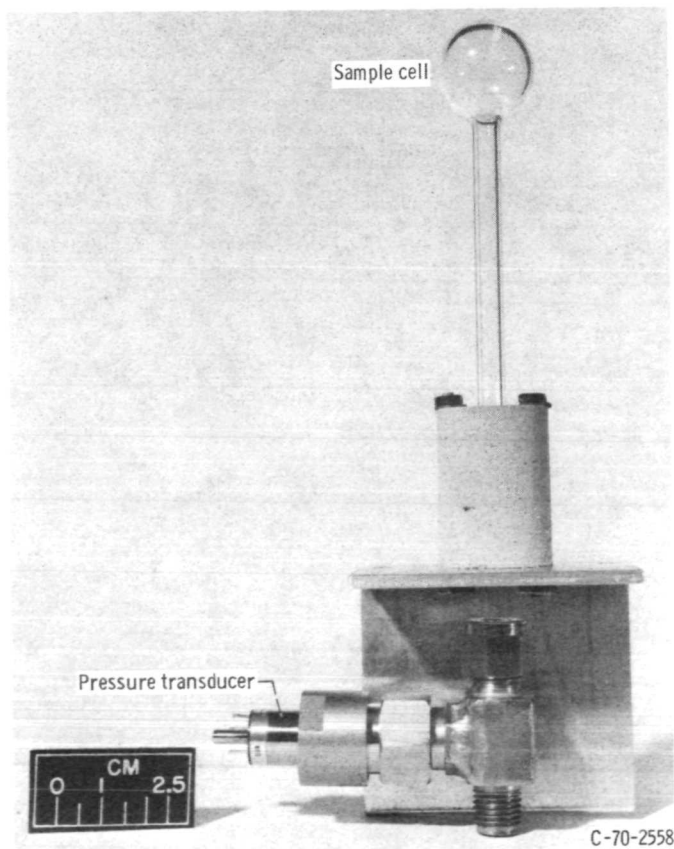


Figure 4. - Sample cell assembly.



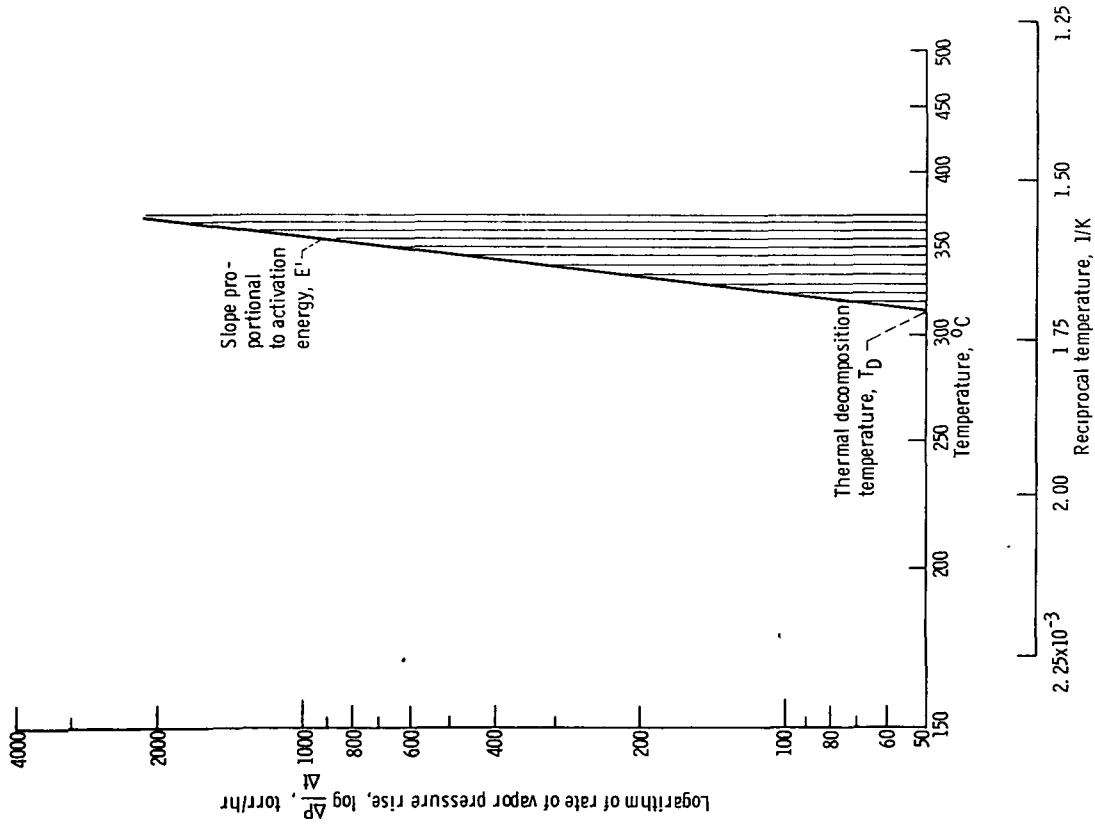


Figure 5. - Typical thermal decomposition curve, logarithm of rate of vapor pressure rise as function of reciprocal of absolute temperature. Heating interval,  $5^{\circ}\text{C}$  ( $9^{\circ}\text{F}$ )

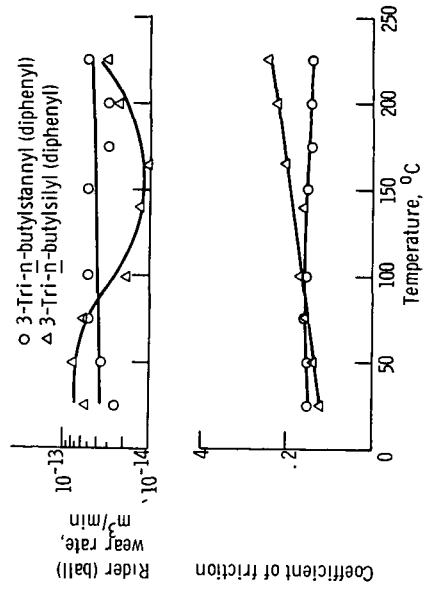


Figure 6. - Coefficient of friction and rider (ball) wear rate for 3-tri-n-butylstannyl (diphenyl) and 3-tri-n-butylsilyl (diphenyl) as function of disk temperature. Load, 1 kilogram, sliding speed, 17 meters per minute (100 rpm); test duration, 25 minutes; M-50 steel specimens; dry-air atmosphere.

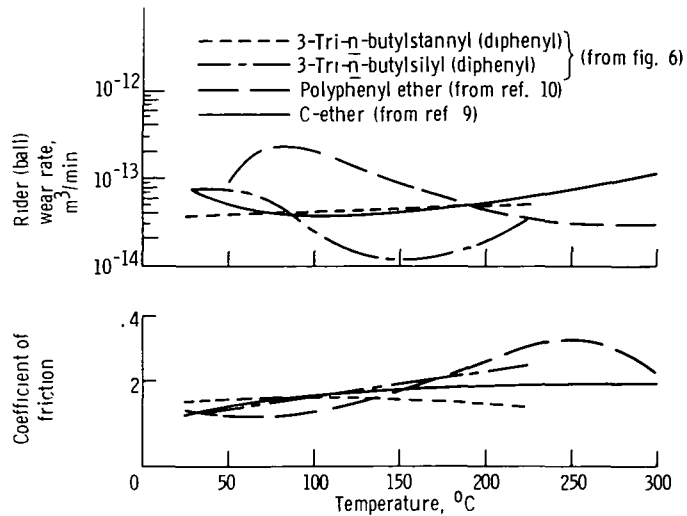


Figure 7. - Coefficient of friction and rider (ball) wear rate for 3-tri-n-butylstannyl (diphenyl), 3-tri-n-butylsilyl (diphenyl), a polyphenyl ether, and a C-ether Load, 1 kilogram; sliding speed, 17 meters per minute (100 rpm); test duration, 25 minutes; M-50 steel specimens, dry-air atmosphere

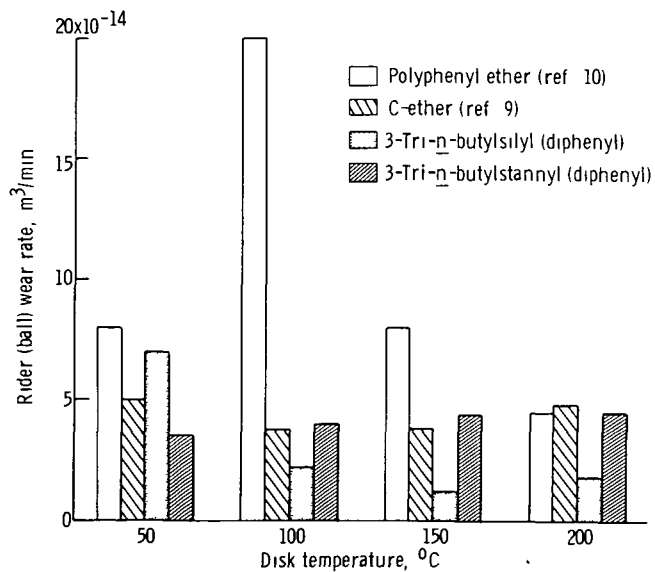


Figure 8. - Rider (ball) wear rates for four fluids at four disk temperatures in dry air Load, 1 kilogram; sliding speed, 17 meters per minute (100 rpm); test duration, 25 minutes; M-50 steel specimens



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—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

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