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Contact angle Measurements of a Polyphenyl Ether to 190° C On M-50 Steel

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CONTACT ANGLE MEASUREMENTS OF A POLYPHENYL ETHER TO 190° C ON M-50 STEEL

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SUMMARY

Contact angle measurements were performed for a five ring polyphenyl ether isomeric mixture on M-50 steel in a dry nitrogen atmosphere. Two different techniques were used: (1) a tilting plate apparatus and (2) a sessile drop apparatus. Measurements were made for the temperature range 25° to 190° C. Surface tension was measured by a differential maximum bubble pressure technique over the range 23° to 220° C in room air.

The critical surface energy of spreading (γ_C) was determined for the polyphenyl ether by plotting the cosine of the contact angle (θ) versus the surface tension (γ_{LV}). The straight line intercept at $\cos \theta = 1$ is defined as γ_C. γ_C was found to be 30.1 dynes/cm for the tilting plate technique and 31.3 dynes/cm for the sessile drop technique. These results indicate that the polyphenyl ether is inherently autophobic (i.e., it will not spread on its own surface film until its surface tension is less than γ_C). This phenomenon is discussed in light of the wettability and wear problems encountered with this fluid.

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INTRODUCTION

Polyphenyl ethers are among the most thermally and oxidatively stable organic fluids known. Therefore, they have often been considered as possible high temperature lubricants (refs. 1 and 2). However, these fluids have exhibited poor boundary lubricating characteristics in friction and wear tests (refs. 3 to 5), pump loops (ref. 6) and bearing tests (ref. 7). They are particularly poor lubricants under dry inert conditions (refs. 3, 6, 8, and 9).

It has been previously theorized (ref. 3) that, at least some of these problems, may be related to the spreading characteristics of this fluid class on metal surfaces. Therefore, the objective of this study was to determine the wettability properties of a five ring polyphenyl ether (5P-4E) by measuring contact angles as a function of temperature.

Tests were performed from 25° to 190° C in a dry nitrogen atmosphere using a tilting plate and a sessile drop apparatus. Surface tension was measured by the maximum bubble pressure technique from 23° to 220° C in air.

EXPERIMENTAL MATERIALS

Lubricant

The polyphenyl ether used in these studies was an isomeric mixture of five-ring components. This fluid contained no additives. Typical properties of this fluid appear in table I. Its structure is shown in figure 1.

This fluid is the base stock for the lubricant meeting military specification MIL-L-87100 (ref. 10). It will be referred to as 5P-4E. Symbols and abbreviations appear in the appendix.

Contact Angle Specimens

Specimens for contact angle measurements were made of CVM M-50 tool steel, having a ROCKWELL C hardness of 62-64. Specimens were ground and lapped to a surface finish of about 10×10^{-8}m (4μ inch)R_a. This particular material was chosen because it is the most common material for making balls and races of high temperature bearings.

APPARATUS

Surface Tension

A differential maximum bubble pressure apparatus was used to measure surface tension as a function of temperature. It is shown schematically in figure 2. This device and the procedure for its use are completely described in reference 11.

Contact Angle

Two different techniques were used to measure contact angle as a function of temperature (1) a tilting plate apparatus and (2) a sessile drop apparatus.

The tilting plate apparatus is shown schematically in figure 3. It consists of a stainless steel fluid reservoir (~0.5 liter) and a small M-50 steel plate (4.1 x 1.3 x 0.24 cm) which can dip into the liquid in the reservoir at various angles. The plate is attached to a lever arm which is rotated at slow speed by a motor. The reservoir and plate are contained in a chamber for atmosphere control. Contact angles are measured with a goniometer through a side window. The fluid is heated by a variable resistance heater located in the base of the reservoir. Temperature is monitored by a thermometer immersed in the fluid.

A sessile drop apparatus was also used to measure contact angles. This apparatus is shown in figure 4. It consists of a low power microscope for horizontal observation of a fluid drop. A drop is placed on the test specimen which is in turn placed on a heated platen. A light source allows for back illumination of the drop. A cover allows for atmosphere control. Specimen temperature is sensed by a contact thermocouple and maintained by a temperature controller. Contact angles are measured by a goniometer eyepiece.

PROCEDURE

Tilting Plate Apparatus

The fluid reservoir and M-50 steel plate were thoroughly cleaned by scrubbing with a paste of levigated alumina and water, rinsed with tap water and finally distilled water. The plate was then positioned in the chamber. Approximately 0.5 liter of polyphenyl ether was thoroughly degassed by heating to 150° C under a vacuum. The degassed fluid was transferred to the reservoir after the chamber had been purged for 30 minutes with dry nitrogen. A continuous nitrogen purge was maintained during the test. The reservoir heater was set for the proper fluid temperature. After temperature stabilization, the plate was tilted so that the fluid recedes off the plate and a curved meniscus formed. The plate is continuously rotated at slow speed (~1 rpm) until the meniscus becomes straight as it contacts the plate. At this point, the angle of the plate is measured with a goniometer. Then the temperature is increased, allowed to stabilize, and the procedure repeated. Only advancing angles were measured.

Sessile Drop Apparatus

For tests with this apparatus, the M-50 steel plate was cleaned as previously described. It was then placed on the platen and the cover closed. A nitrogen flow is maintained over the specimen. Several drops of degassed polyphenyl ether were placed on the specimen through a port in the top of the cover. This was accomplished by dipping a flamed platinum wire in the degassed lubricant and touching the plate. Drop size varied but typically was in the range of 0.5 to 1.5 ul.

The light source and microscope stage were then adjusted to produce a sharp silouette of the drop. Then a goniometer eyepiece was used to measure the contact angle as illustrated in figure 5.

RESULTS

Surface Tension

Surface tension as a function of temperature for 5P-4E, measured by the maximum bubble pressure technique, appears in figure 6. A maximum value of 46 dynes/cm was obtained at 23° C. The surface tension then decreases linearly with increasing temperature. A temperature coefficient of surface tension ($d\gamma/dT$) of 0.088 dynes/cm C° was obtained.

CONTACT ANGLES

Contact angles for various temperatures for 5P-4E using both test devices appear in table II. Values range from a high contact angle of 50° at 70° and 90° C for the plate apparatus to a low contact value of 5° at 180° C for the sessile drop technique. Values for the plate apparatus are consistently higher than from the sessile drop measurements.

DISCUSSION

When a liquid forms a finite contact angle on a surface ($\theta \neq 0$), we say the liquid is non-spreading. If the contact angle is zero, the liquid wets the surface completely and spreads freely over the surface at a rate depending on viscosity and surface roughness.

At room temperature, the surface-free energies of organic liquids and lubricants are less than 100 ergs/cm^2. Metals have surface-free energies ranging from 500 to 5000 ergs/cm^2. Theoretically, one would then expect all organic liquids to spread freely on any high energy solid. This is because the spreading would result in a large decrease in the free energy of the system.

If one considers low energy solids such as polymers, the situation could, and does, exist where the surface energy (surface tension) of a fluid is greater than that of the surface. For that situation, the fluid would not spread and a drop having a finite contact angle would occur. An analogous situation could occur if low energy contaminant films are present on the high energy solid surface (ref. 12).

Considering the materials in this study, 5P-4E and M-50 steel, one would predict that this fluid type should spread freely on a clean M-50 surface. However, it has been well documented (refs. 3, 6, 8) that this does not always occur. Another class of chemically similar fluids, the C-ethers, have exhibited similar wetting problems (refs. 6 and 13). This non-spreading phenomenon occurred in spite of procedures to remove polar impurities which might have produced oleophobic films.

Many years ago, Hare and Zisman (ref. 14) reported similar non-wetting properties for certain pure organic fluids such as 1-octanol, trichlorodiphenyl and tri-o-cresyl phosphate. It was theorized that these fluids were non-spreading because the molecules adsorbed on the solid surface formed a film whose critical surface energy was less than the surface tension of the fluid itself. Hare and Zisman coined a term "autophobic liquids" to describe this behavior.

Since two of the fluids mentioned by Hare and Zisman were aromatic and thus were chemically somewhat similar to the aromatic polyphenyl ether (5P-4E), it seemed plausible that 5P-4E may also be autophobic.

To check this possibility, two things are needed: surface tension as a function of temperature and the critical surface energy of spreading, γ_C. The surface tension for 5P-4E is easily measured and appears in figure 6 for temperatures from 23° to 220° C.

The critical surface energy of spreading γ_C, of an absorbed monolayer is more difficult to measure. The classical technique to measure γ_C for low energy polymer surfaces is to plot the cosine of the contact angle ($\cos\theta$) for a homologous series of organic liquids as a function of their surface tension (γ_{LV}). Empirically, a rectilinear relation was established. The γ_C was defined by the intercept of the horizontal line $\cos\theta = 1$ with the extrapolated straight line plot of $\cos\theta$ versus γ_{LV}. A typical plot for the wettability of polytetrafluoraethylene (PTFE) by a series of n-alkanes appears in figure 7 (ref. 12). This yields a γ_C for PTFE of approximately 18.5 dynes/cm at 20° C. Essentially, this means that, at 20° C, a n-alkane having a surface tension >18.5 dynes/cm will not spread on a PTFE surface. On the other hand, a n-alkane with a surface tension <18.5 dynes/cm or less will spread spontaneously.

To determine the γ_C of an absorbed surface film, a modification of this technique can be used. If one were to use a series of organic liquids of varying surface tensions, the possibility exists for chemical or physical interaction with the absorbed surface film. This could alter the wetting properties of the surface.

Another way to determine γ_C for the surface film would be to measure contact angle as a function of temperature. As temperature varies, the surface tension varies and an analogous plot of $\cos\theta$ versus γ_{LV} could be plotted for one fluid. One problem using this procedure is that γ_C can also change with temperature. Surface film density will decrease with increasing temperature. However, this effect is not great and γ_C will increase only slightly as temperature rises (ref. 12).

A second consideration is the possibility of lubricant and metal oxidation and lubricant degradation at high temperatures. The contact angle measurements were all performed in a nitrogen atmosphere to preclude any oxidation problems. Surface tension measurements were made in air. This, in part, was done because of experimental difficulties involved in supplying nitrogen to the bubble pressure apparatus. However, it is not felt that an air atmosphere presented any problems for these tests. 5P-4E is oxidatively stable at the highest temperature (220° C) reached in the surface tension measurements. In addition, the bubbles are formed continuously well below the liquid surface. It would take time for oxidation products to diffuse to that depth from the surface.

Therefore, the contact angle data from table II has been plotted in the standard cos θ versus γ_{LV} format. The data for the tilting plate apparatus appears in figure 8 and for the sessile drop apparatus in figure 9. A least squares technique was used to determine the best straight line for each set of data. Extrapolated to cos $\theta = 1$, γ_C was determined to 30.1 dynes/cm for the tilting plate technique and 31.3 dynes/cm for the sessile drop technique. This is good agreement considering that two completely different techniques were used.

These values indicate that the polyphenyl ether will not spread on its own surface film until its surface tension falls below about 30-31 dynes/cm. This surface tension corresponds to a fluid temperature of approximately 190°-200° C.

Therefore, 5P-4E is inherently non-spreading on steel surfaces over most of its practical temperature range. This fact may contribute to some of the wear problems (ref. 8) associated with this fluid. This may partially explain the order of magnitude drop in wear that occurs at temperatures above 200° C, as shown in figure 10 for a dry nitrogen atmosphere. A similar drop in wear occurs above 100° C for dry air but here oxidation effects on the surface and fluid are coming into play. It also seems likely that the C-ethers are also autophobic. Chemically, the C-ethers are very similar to the polyphenyl ethers since they are mixtures of thiophenyl ethers. Thus, the wetting problems associated with this fluid (refs. 6 and 13) may be explained by a similar phenomenon. Preliminary contact angle measurements of C-ethers on steel support this supposition.

It should be noted that additives can alter the chemistry of absorbed surface films and thus their wetting characteristics. Some studies along this line have been reported (ref. 3).

SUMMARY OF RESULTS

A tilting plate and a sessile drop technique were used to determine contact angles of a five-ring polyphenyl ether (5P-4E) on M-50 steel in dry nitrogen. A maximum bubble pressure technique was used to determine surface tension. The major results were:

(1) The critical surface energy of spreading (γ_C) was determined to be 30.1 and 31.3 dynes/cm from the tilting plate and sessile drop techniques, respectively.

(2) It was concluded that 5P-4E is inherently autophobic (i.e., it is unable to spread on its own surface film).

(3) This phenomenon is discussed in light of the wettability and wear problems encountered with this fluid.

APPENDIX - SYMBOLS

γ_c	Critical surface energy of spreading, dynes/cm
γ_{LV}	Liquid surface tension, dynes/cm
5P-4E	Five ring polyphenyl ether
$\frac{d\gamma_{LV}}{dT}$	Temperature rate of change of surface tension, dynes/cm-C°
PTFE	Polytetrafluoroethylene
C-ether	Thiophenyl ether

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TABLE I. - SOME PROPERTIES OF A FIVE-RING POLYPHENYL ETHER

Kinematic viscosity, m^2 sec (cS)	
At 38° C (100° F)	3.6×10^{-4} (360)
At 99° C (210° F)	1.3×10^{-5} (13)
At 350° C (662° F)	7.2×10^{-7} (0.72)
Pour point, °C (°F)	5(40)
Flash point, °C (°F)	288 (550)
Fire point, °C (°F)	350 (662)
Density at 38° C (100° F), kg/m^3 (g/ml)	1.19×10^3 (1.19)
Thermal decomposition (isoteniscope), °C (°F)	443 (830)
Vapor pressure at 343° C (650° F), torr	12
Surface tension at 25° C (77° F), N/cm (dynes/cm)	5×10^{-4} (50)

TABLE II. - CONTACT ANGLES FOR A FIVE RING POLYPHENYL ETHER ON M-50 STEEL AT VARIOUS TEMPERATURES IN A DRY NITROGEN ATMOSPHERE

Temperature, °C	Contact angle, deg	
	Tilting plate apparatus	Sessile drop apparatus
25		30,32,34
50		27,27,29
70	47,50	
75		24,24,27
80	40	
90	50	
100	40,42	22,23,24
110	37,38	
115	41	
120	33,36	
125		19,20,22
130	29,33	
140	31,36	
145	37	
150	29,34	15,16,17
155	34	
160	27,28	
165	31	
170	22,27	
175	24	7,9,11
180	18,20	5,5,11
185	20	
190	22	

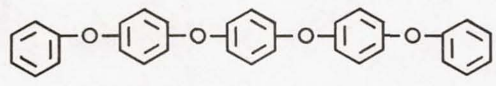

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Figure 1. - Experimental lubricant structure of five ring polypheny ether (5P-4E).

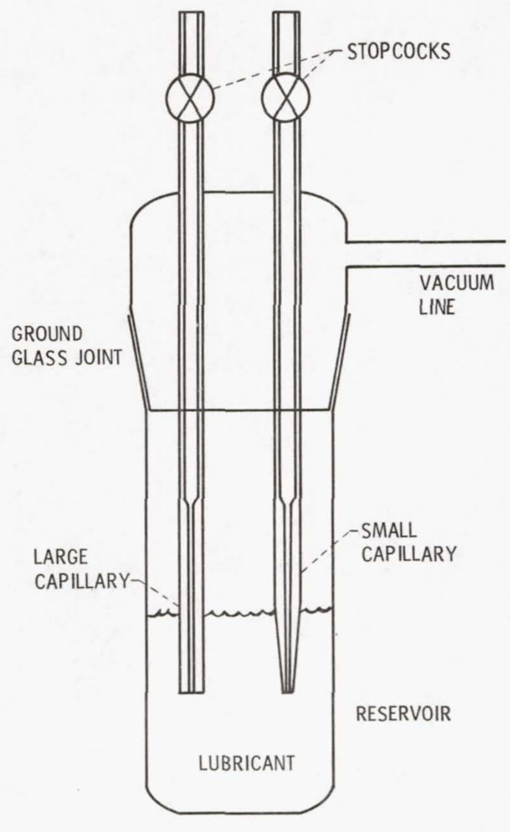

Figure 2. - Bubble pressure apparatus.

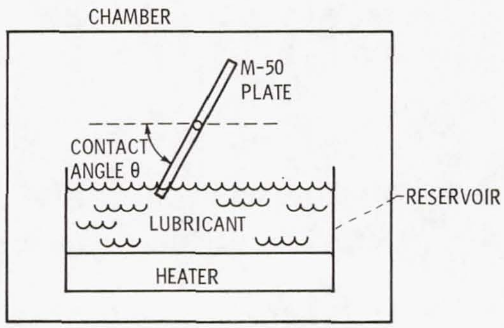

Figure 3. - Schematic diagram of tilting plate contact angle device.

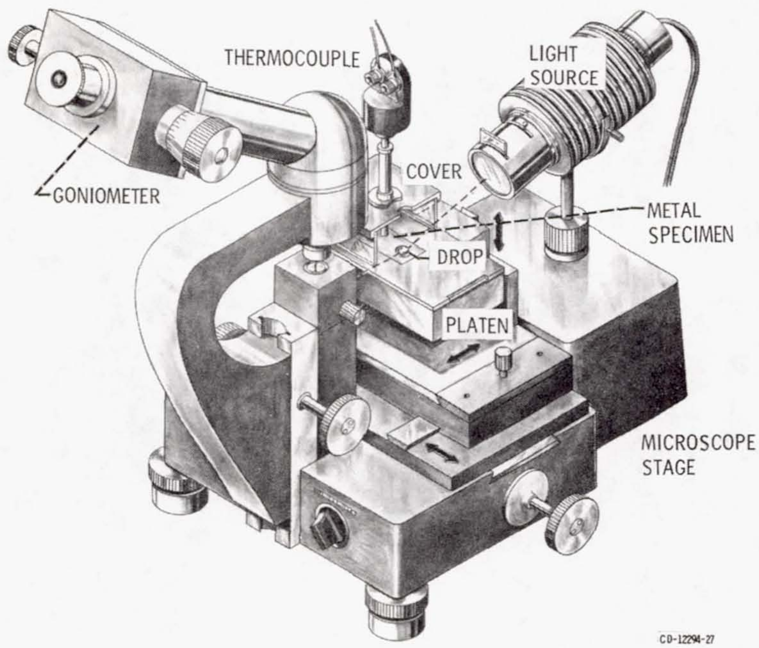

Figure 4. - Sessile drop apparatus.

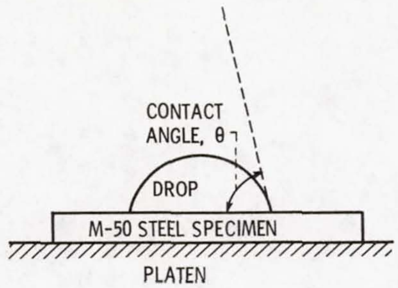

Figure 5. - Representation of contact angle measurement from sessile drop apparatus.

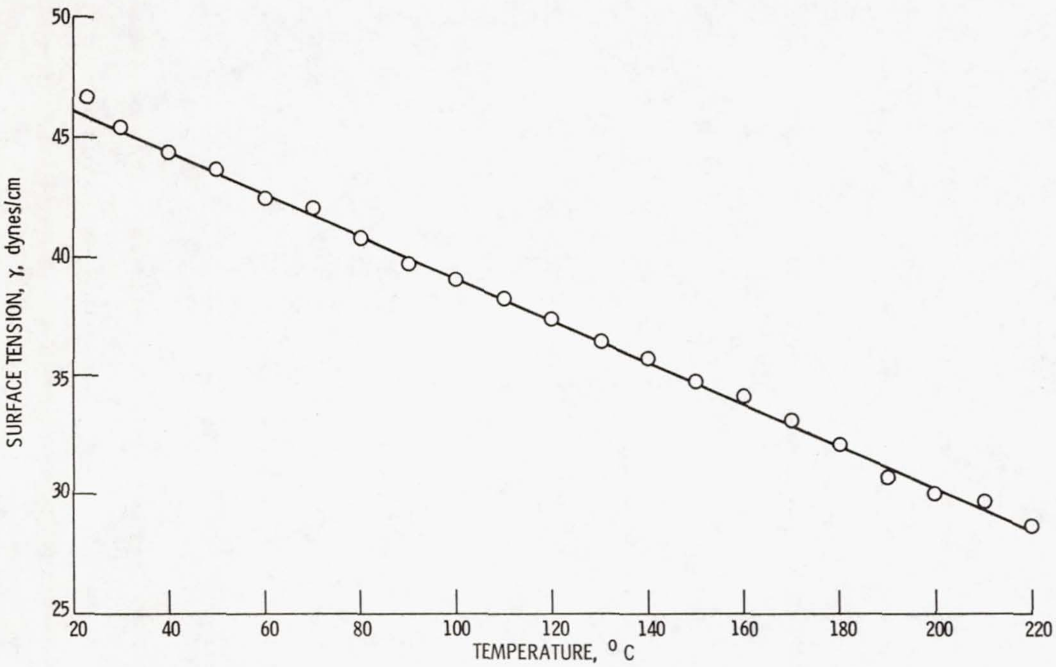

Figure 6. - Surface tension as a function of temperature for a five-ring polyphenyl ether using the maximum bubble pressure technique (ref. 11).

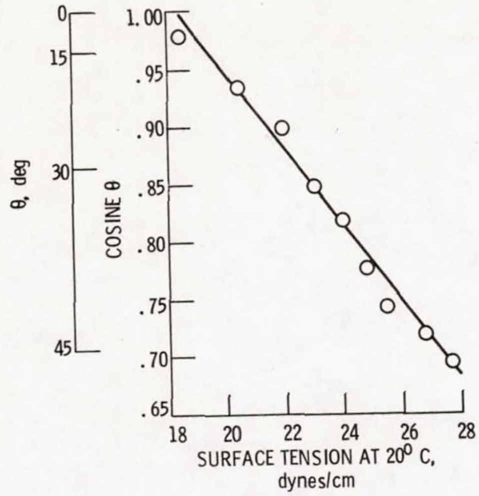

Figure 7. - Wettability of polytetrafluoroethylene by n-alkanes (from ref. 12).

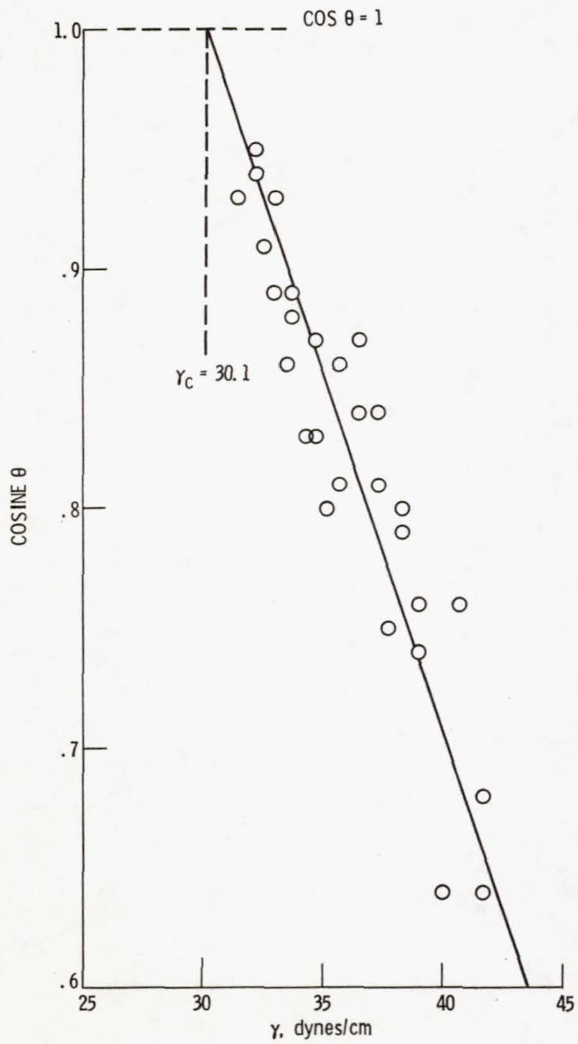

Figure 8. - Cosine of the contact angle of 5P-4E on M-50 steel as a function of surface tension - tilting plate apparatus (dry nitrogen atmosphere).

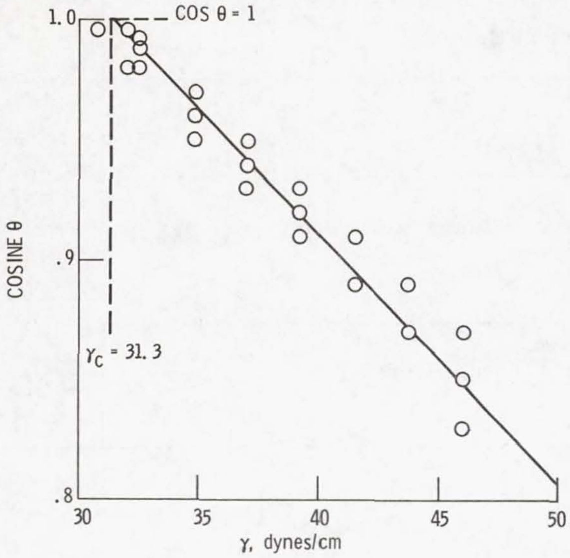

Figure 9. - Cosine of the contact angle of 5P-4E on M-50 steel as a function of surface tension - sessile drop apparatus (dry nitrogen atmosphere).

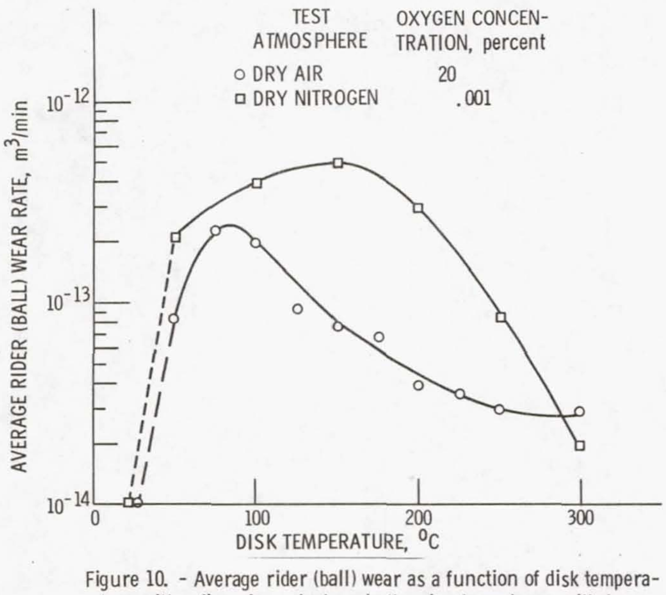

Figure 10. - Average rider (ball) wear as a function of disk temperature with a five-ring polyphenyl ether in atmospheres with two oxygen concentrations. Specimen material, CVM M-50 steel; 1 kilogram; sliding speed, 17 meters per minute (100 rpm); test duration, 25 minutes (from ref. 8).

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15. Supplementary Notes

16. Abstract

Contact angle measurements were performed for a polyphenyl ether on steel in nitrogen. A tilting plate and a sessile drop apparatus were used. Surface tension was measured with a maximum bubble pressure apparatus. Critical surface energies of spreading were found to be 30.1 and 31.3 dynes/cm. It was concluded that the polyphenyl ether is inherently autophobic and will not spread on its own surface film.

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