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BOUNDARY LUBRICATION OF FORMULATED C-ETHERS IN AIR TO 300° C

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ABSTRACT

Friction and wear measurements were made in dry and moist air on CVM M-50 steel lubricated with six C-ether formulations containing phosphorus ester and organic acid additives. Results were compared to those obtained with a formulated Type II ester and the C-ether base fluid. A ball-on-disk sliding friction apparatus was used. Experimental conditions were a 1-kilogram load, 17 meter-per-minute (100 rpm) surface speed, and a 25° to 300° C disk temperature range. The C-ether base fluid and the C-ether formulations yielded lower wear than the ester under most test conditions. The C-ether formulations exhibited higher friction coefficients than the ester from 150° to 300° C and similar or lower values from 25° to 150° C.

E-6682

INTRODUCTION

Advanced aircraft and re-entry vehicles will place increased thermal stresses on hydraulic fluids and lubricants. Maximum fluid temperatures in excess of 316 C have been estimated for future applications (1, 2). At these elevated temperatures, fluids must operate without appreciable degradation and must also provide effective lubrication for bearing and hydraulic system components.

Presently available fluids such as the super-refined mineral oils (3), hindered esters (4, 5), fluorinated polyethers (6) and polyphenyl ethers (3, 7) have one or more deficiencies which limit their use at high temperatures. These deficiencies include poor oxidation stability, poor boundary lubricating characteristics and corrosivity. In addition, because of the optimization of the high temperature properties, some of these fluids exhibit poor low temperature fluidity (high pour point).

The C-ethers, which are structurally related to the polyphenyl ethers, are a promising class of fluids for possible high temperature applications (8). They have excellent thermal stability (thermal decomposition temperature of 390 C measured by isoteniscope), good oxidation stability to 260 C and adequate pour points (-29 C). They also exhibit low vapor pressure, high surface tension and excellent shear stability. The main deficiencies of the C-ethers have been their poor boundary lubricating ability and poor wetting characteristics (3, 9). Heat transfer (cooling) problems have also been encountered with this fluid class (1) and are probably a result of its poor wetting properties.

The objectives of this investigation were (1) to determine the boundary lubricating characteristics of six C-ether formulations (containing organic acid and phosphorus ester additives) in dry (<100 ppm H_2O) and moist air (relative humidity 50 percent at 25 C) and temperatures from 25 to 300 C, and (2) to compare these results to those obtained with a fully formulated Type II ester (MIL-L-23699) and the unformulated C-ether base fluid.

Experimental conditions include a 1-kilogram load (initial Hertz stress, 1×10^9 N/m^2), a 17-meter-per-minute surface speed, (100 rpm), and a test duration of 25 minutes. Test specimens were made of consumable electrode vacuum melted (CVM) M-50 steel.

APPARATUS AND PROCEDURE

The ball-on-disk sliding friction apparatus is shown in Fig. 1. 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 was maintained. A normal load of 1 kilogram (initial Hertz stress, $1x10^9$ N/m^2) was applied with a deadweight. Balls and disks were made of CVM M-50 tool steel. Disk and ball hardness was Rockwell C 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.

Disks were ground and lapped to a surface finish of $10x10^{-8}$ to $20x10^{-8}$ meter (4 to 8 μin.) and balls to $2.5x10^{-8}$ meter (1 μin.) rms. Specimens were scrubbed with a paste of levigated alumina and water, rinsed with tap water and distilled water, then placed in a desiccator.

All lubricants tested under dry conditions were degassed at approximately 150 C at 2 torr for 1 hour. Measurements using the Karl Fischer technique indicate that this degassing procedure reduces dissolved water content in C-ethers to less than 20 ppm.

The specimens were assembled and 70 cubic centimeters of lubricant were placed in the lubricant cup. The test chamber ($3.7x10^3$ cm^3 volume) was purged with the test atmosphere for 10 minutes at a flow rate in excess of $50x10^3$ cubic centimeters per hour. The disk was heated by induction to the test temperature while rotating (100 rpm). The ball was then loaded against the disk. Test atmosphere flow rate was reduced to $35x10^3$ cubic centimeters per hour, and a $6.9x10^{-3}$-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 temperature at disk temperatures to 100 C. At disk temperatures of 200 and 300 C, the bulk oil temperatures stabilized at approximately 150 and 200 C, respectively.

Frictional force and bulk lubricant temperature were continuously recorded. Disk temperature was continuously monitored. Experiments were terminated after 25 minutes and the ball wear scar diameter was recorded (from which wear volume was calculated). All tests were performed in triplicate and an average value taken for plotting.

TEST ATMOSPHERES

The two atmospheres used in this study were (1) moist air at a relative humidity (RH) of 50±5 percent at 25 C, and (2) dry air (<100 ppm H_2O). The relative humidity was monitored by a direct reading hygrometer accurate to ±1.5 percent. The low water concentrations were monitored by a moisture analyzer with an accuracy of ±10 ppm.

Dry air was obtained by drying and filtering service air. Moist air was obtained by bubbling the dry gas through a water reservoir. The relative humidity of the moist air was controlled manually to 50±5 percent at 25 C.

EXPERIMENTAL LUBRICANTS

The experimental fluids used in these experiments were a formulated Type II ester, a C-ether base fluid, and three C-ether formulated fluids. Some typical properties of the test fluids appear in Table I. Table II contains the additive contents of the test fluids.

FORMULATED TYPE II ESTER

A fully formulated Type II ester was chosen as a reference fluid for these experiments. This lubricant is commercially available and meets General Electric D50TF1, Pratt and Whitney PWA 521B, and MIL-L-23699 lubricant specifications.

C-ETHER BASE FLUID

The C-ether base fluid used in this study was originally reported in Reference 8. This fluid is a blend of three-ring and four-ring components which are structurally similar to the polyphenyl ethers. This base fluid contains an antifoam additive.

C-ETHER FORMULATIONS

Phosphorus Ester Additives

Formulation I. - The first C-ether formulation studied was the base fluid plus 0.10 WT percent bis (2-chloropropyl)-2-propene phosphonate. This additive should improve the boundary lubricating characteristics of the base fluid.

Formulation II. - The second C-ether formulation studied was the base fluid plus 0.10 WT percent di-isopropyl hydrogen phosphite. This is another additive to improve boundary friction and wear. This

formulation has been previously studied in Reference 1. It performed satisfactorily in short-term (3-hr) bearing tests at a bearing temperature of 316 C in air and nitrogen. However, it required higher oil flow rates to stabilize the bearing temperature than did ester and synthetic paraffinic hydrocarbon lubricants.

Formulation III. - The third C-ether formulation studied is identical to Formulation II except that 0.05 WT percent trichloroacetic acid has been added to improve fluid wettability. This particular formulation has also been studied previously (Ref. 10). This fluid provided marginally adequate boundary lubrication in small scale bearing screening tests at 316 C for 100 hours in nitrogen.

Organic Acid Additives

Formulation IV. - Formulation IV was the base fluid plus <0.10 weight percent of a boundary additive (oxalic acid potassium salt)(potassium tetra oxalate)

Formulation V. - Formulation V was the base fluid plus 0.10 weight percent of a boundary additive (perfluoroglutaric acid).

Formulation VI. - Formulation VI was the base fluid plus 0.08 weight percent of a boundary additive (phenylphosphinic acid).

RESULTS
Wear

Formulated Type II ester. - This fluid was chosen as a reference fluid because it appeared to be a typical example of the polyol ester group of MIL-L-23699 lubricants. Wear results for this fluid appear in Fig. 2. No significant differences in wear were observed between the dry and moist air results. Therefore, a single wear-temperature curve appears in Fig. 2.

The wear rate is essentially constant at 1.4×10^{-13} cubic meters per minute over the entire temperature range. Two typical wear scars obtained with this ester at disk temperatures of 50 and 150 C in dry air appear in Figs. 3(a) and (b). Metallic wear debris can be seen in the contact exit. This debris is shown enlarged in Figs. 3(c) and (d). The level of wear and the appearance of the wear scar indicates only marginally adequate lubrication was obtained with this ester.

C-ether base fluid. - Wear results for this base fluid appear in Fig. 4. At 25 C in dry air the wear rate was about 7×10^{-14} cubic meters per minute. The wear rate decreased to a minimum of approximately 4×10^{-14} cubic meters per minute at 100 C and then gradually increased to 10^{-13} cubic meters per minute at 300 C. In moist air a similar wear-temperature curve is observed but with lower wear rates over the entire temperature range. The effect of moisture in reducing wear was more pronounced at the lower temperatures.

A comparison between the friction and wear results for the Type II ester and the C-ether base fluid appears in Fig. 5. In both dry and moist air the C-ether base fluid yielded lower wear than the Type II ester over the entire temperature range. The maximum difference in wear occurred at about 100 C. At 100 C the ester exhibited a wear rate approximately seven times greater in moist air and four times greater in dry air than the wear rate observed for the C-ether base fluid.

C-ether formulations (phosphorus ester additives). - Wear results for C-ether formulations, I, II and III appear in Fig. 6. No significant differences in wear were observed between the dry and moist air results for formulations I and II. Therefore, only a single wear-temperature curve appears in Figs. 6(a) and (b). Formulation III, however, yielded lower wear rates in moist air than in dry air from 100 to 300 C.

A comparison of the wear results for these three formulations and the base fluid appears in Fig. 7. The dry air results of 7(a) indicate essentially no difference in wear rate for the three formulations and the base fluid from 25 to 100 C. From 100 to 300 C Formulations I, II, and III yielded lower wear rates than the base fluid.

In moist air (Fig. 7(b)), these three formulations again yielded lower wear rates above approximately 150 C. However, from 25 to 150 C the wear rate of the C-ether base fluid was lower than the wear rates of the three formulations. The increasing effectiveness of the additives with increasing temperature is most likely related to their greater reactivity at the higher temperatures.

C-ether formulations (organic acid additives).- Wear results for C-ether formulations IV, V and VI, containing organic acid additives, appear in Fig. 8. The wear rate for the Type II ester also appears in Fig. 8.

Moisture in the test atmosphere did not greatly affect the wear results for Formulations IV and VI. However, Formulation V yielded lower wear below and higher wear above 185 C when tested in moist as compared to dry air.

As is evident in Fig. 8, formulations IV and V yielded lower wear than the ester over essentially the entire temperature range. Formulation VI yielded lower wear than the ester from 25 to 150 C and about the same wear from 150 to 300 C.

Comparisons between the wear rates for the three formulations and the C-ether base fluid appear in Fig. 9. In both dry (Fig. 9(a)) and moist air (Fig. 9(b)) Formulations IV and VI yielded higher wear than the base fluid over almost the entire temperature range. Formulation V exhibited a somewhat more complex behavior yielding lower wear than the base fluid under most conditions but higher wear under others.

Coefficient of Friction

Figure 5 contains a comparison between the friction coefficients for the Type II ester and the C-ether base fluid. Figure 6 shows the friction-temperature curves for Formulations I, II, and III. The friction-temperature curves for Formulations IV, V, and VI appear in Fig. 8. As shown in these figures, all C-ether formulations and the C-ether base fluid exhibited slightly higher friction coefficients than the Type II ester from 150 to 300 C and either similar or lower values from 25 to 150 C. In general, above 200 C, the six C-ether formulations yielded slightly lower friction coefficients than the C-ether base fluid.

DISCUSSION

Basically, the conditions of these experiments were so designed that the results should reflect antiwear rather than "EP" characteristics of the formulations. However, since the difference between these two regimes may be due to the temperature level existing in the contact, no doubt some "EP" activity may occur at the higher disk temperatures.

One of the common approaches to rationalize the performance of additives has been to measure their chemical reactivity toward iron or steel. Barcroft (11) and more recently Sakurai, et al (12, 13) have used the hot wire technique for such correlations. A generalized curve of wear as a function of chemical reactivity (from Rowe (14)) is shown in Fig. 10. It can be seen that an optimum reactivity exists for minimum wear for a particular set of conditions. It should also be noted that this optimum value can shift if the severity of the test conditions are altered. For a particular additive system a similar curve should result if wear were plotted as a function of temperature or additive concentration.

Unfortunately, no independent measurements have been made of the reactivities of the additives used in this study. It is interesting to note that most of the formulations exhibited the generalized wear-temperature behavior as shown in Fig. 10. The fact that the C-ether

base fluid yields a similar curve would indicate that the lubricant molecule contains a reactive component. Two formulations (IV and VI) yielded higher wear than the unformulated base fluid. The formulation exhibiting the best overall wear performance was formulation V which contained perfluoroglutaric acid. Formulation III (di-isopropyl hydrogen phosphite and trichloroacetic acid) also gave good overall results.

Di-isopropyl hydrogen phosphite has been reported (15) to give very good antiwear activity in ester base fluids. It has also been reported that phosphites are better antiwear additives than phosphates (16) and that acid phosphites are more reactive than neutral phosphorus compounds (17).

The electron inductive effects of the halogens on the α carbons in perfluoroglutaric acid and trichloroacetic acid (with a pK_a of 0.08) approaches the strength of the inorganic acids. Nevertheless, neither of these additives appeared to be unduly corrosive in these experiments.

Effect of Moisture on Additive Performance

It has been reported (18) that dissolved water may be deleterious with some additives by preventing proper adherence of the additive reaction products. Others have reported (19) that dissolved water is beneficial in promoting boundary film formation. In general there were no great moisture effects for most of the formulations. Only the formulations containing the two strong carboxylic acids yielded different behavior in moist as compared to dry air. Formulation III containing trichloroacetic acid yielded lower wear in moist air above 150 C.

Moisture appeared to be beneficial below 185°C and detrimental above for formulation V (perfluoroglutaric acid). The C-ether base fluid exhibited slightly lower wear rates in moist air. This follows the general lubricating behavior of aromatics as reported by Appeldoorn and Tao (20). Similar behavior was also observed by the author with polyphenyl ethers (7).

In conclusion it has been shown that the C-ethers are susceptible to additive treatment. However, it must be stated that the test conditions of this study are only a part of the spectrum of conditions that a lubricant or hydraulic fluid would be subjected to in service. Different results may be obtained under higher speeds, higher loads and different metallurgies.

SUMMARY OF RESULTS

The major results were the following:

1.   The six C-ether formulations and the C-ether base fluid yielded lower wear than the Type II ester under most test conditions.

2.   In dry air all C-ether formulations (except IV and VI) yielded either similar or lower wear than the C-ether base fluid over the entire temperature range.

3.   In moist air all formulations (except VI, V, and VI) yielded lower wear than the C-ether base fluid from 150 to 300 C but higher wear from 25 to 150 C.

4.   Formulations IV and V yielded higher wear than the C-ether base fluid under all conditions. While formulation V exhibited lower wear than the base fluid under most conditions but higher wear under others.

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TABLE I

TYPICAL PROPERTIES OF THE EXPERIMENTAL FLUIDS

Properties[a]	C-ether base fluid	Type II ester
Kinematic viscosity, m^2/sec (cS)		
at 38°C	2.5×10^{-5} (25)	2.8×10^{-5} (28)
at 99°C	4.1×10^{-6} (4.1)	5.3×10^{-6} (5.3)
at 300°C	6.9×10^{-7} (0.69)	[b]6.8×10^{-7} (0.68)
Pour point, °C	-29	-60
Flash point, °C	239	280
Fire point, °C	285	---
Density at 38°C, g/cm^3	1.19	[c]0.990
Thermal decomposition (isoteniscope), °C[d]	390	316
Vapor pressure at 371°C, torr	140	---
Surface tension at 23°C, N/cm (dynes/cm)[d]	44.8×10^{-4} (44.8)	---

[a]Manufacturer's data except where noted

[b]Extrapolated

[c]Specific gravity (15.6° C/15.6°C)

[d]Measured by author

TABLE II

ADDITIVE CONTENTS OF TEST FLUIDS

Formulated Type II Ester	Antifoam, anticorrosion, aromatic amine antioxidant, combined antioxidant and load carrying agent
C-Ether Base Fluid	Antifoam (dimethyl silicone)
C-Ether Formulation I	Antifoam, bis (2-chloropropyl)-2-propene phosphonate (0.10 wt percent)
C-Ether Formulation II	Antifoam, di-isopropyl hydrogen phosphite (0.10 wt percent)
C-Ether Formulation III	Antifoam, di-isopropyl hydrogen phosphite (0.10 wt percent) trichloroacetic acid (0.05 wt percent)
C-Ether Formulation IV	Antifoam, oxalic acid potassium salt (<0.10 wt percent) (potassium tetraoxalate)
C-Ether Formulation V	Antifoam, perfluoroglutaric acid (0.10 wt percent)
C-Ether Formulation VI	Antifoam, phenylphosphinic acid (0.08 wt percent)
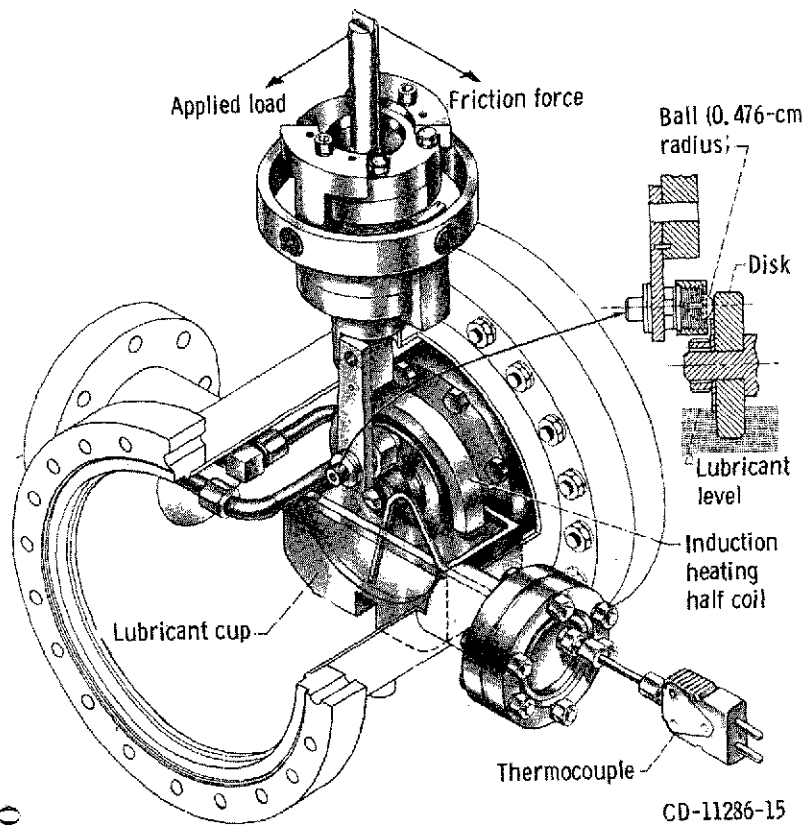
Figure 1. - Friction and wear apparatus.

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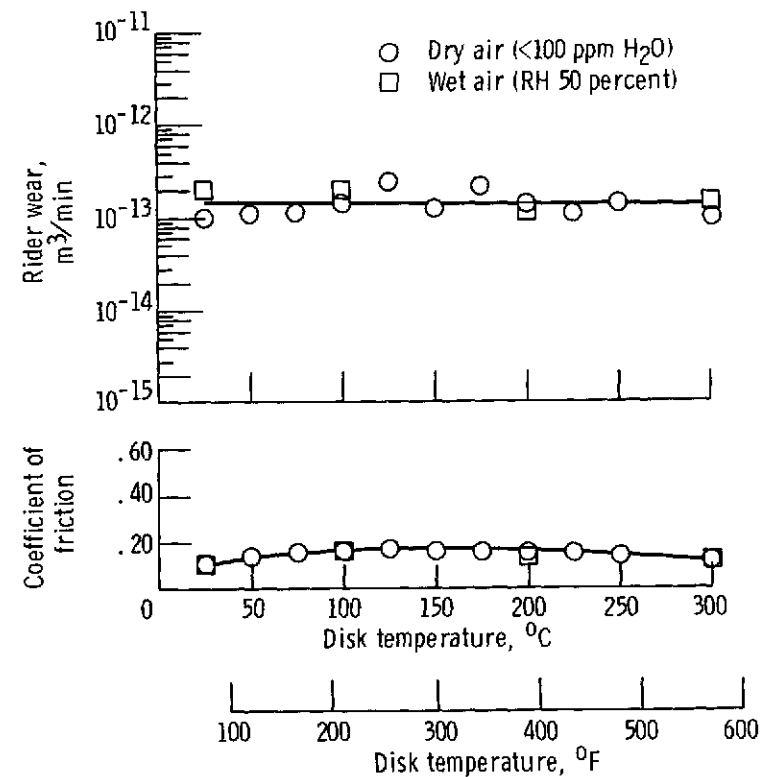
Figure 2. - Coefficient of friction and rider wear as a function of disk temperature for a fully formulated type II ester. Test conditions: 1-kilogram load, 17-meter-per-minute sliding speed, 100-rpm disk speed, dry air (<100 ppm H_2O) and wet air (RH 50 percent), and 25-minute test duration.
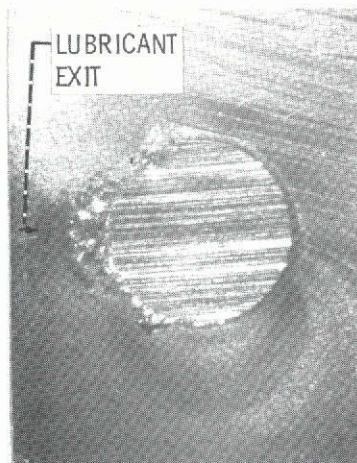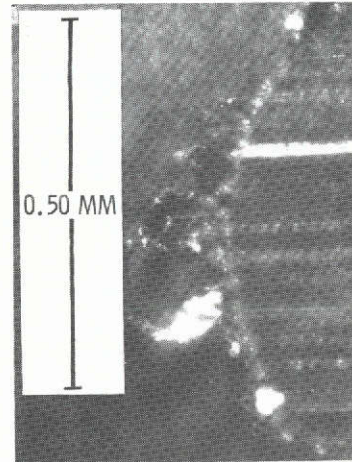
(a) 50° C (122° F).
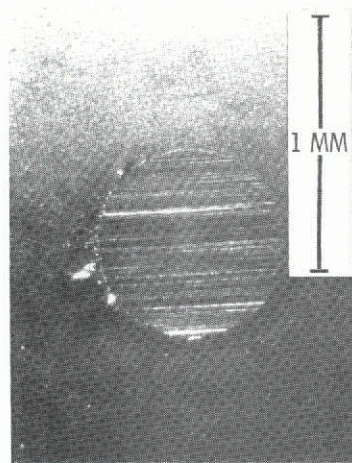
(b) 150° C (302° F).
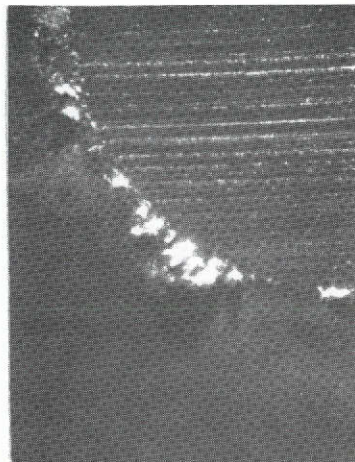
(c) ENLARGED PORTION OF (a).

(d) ENLARGED PORTION ON 9 OF (b).

Figure 3. - Typical rider wear scars for a formulated Type II ester. Test conditions: 1-kilogram load, 17-meter-per-minute sliding speed, dry air (<100 ppm H_2O), M-50 steel test specimens, and 25-minute test duration.
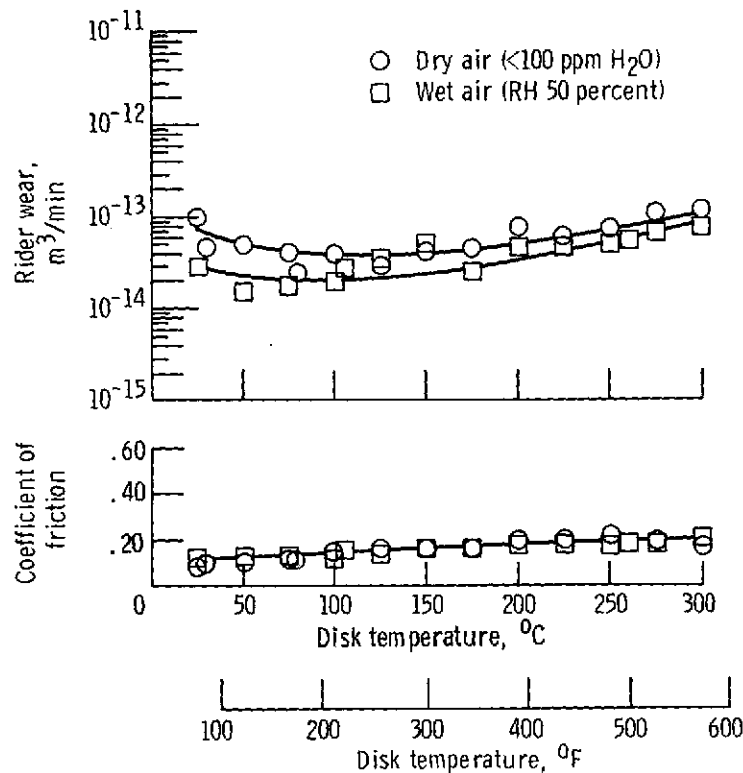
Figure 4. - Coefficient of friction and rider wear as a
function of temperature for a C-ether base fluid.
Test conditions: 1-kilogram load, 17-meter-per-
minute sliding speed, 100-rpm disk speed, dry air
(<100 ppm H_2O) and wet air (RH 50 percent), and
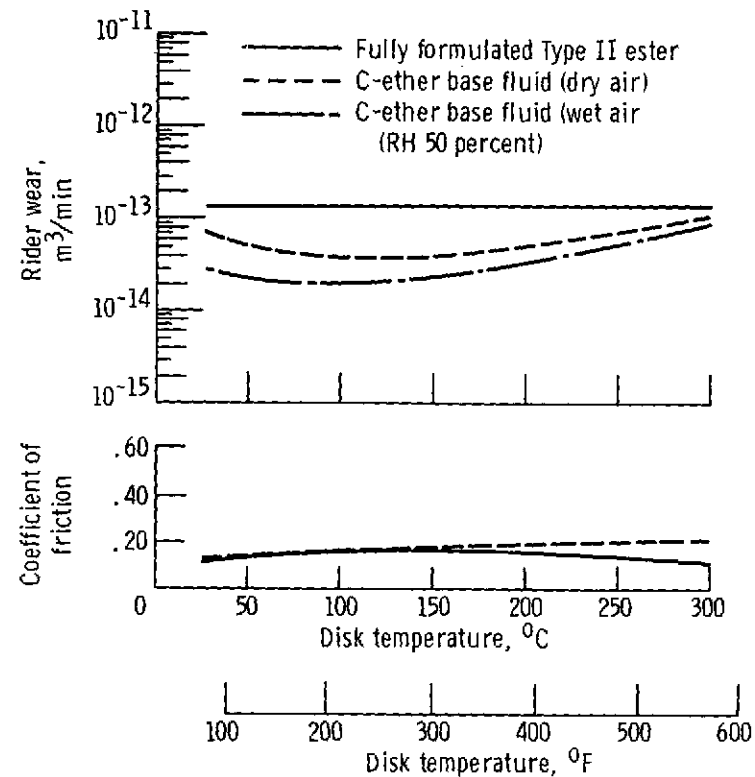25-minute test duration.

Figure 5. - Comparison of friction and wear results for
a formulated Type II ester and a C-ether base fluid
from 25^0 to 300^0 C (77^0 to 572^0 F). Test conditions:
1-kilogram load, 17-meter-per-minute sliding speed,
100-rpm disk speed, dry air (<100 ppm H_2O) and wet
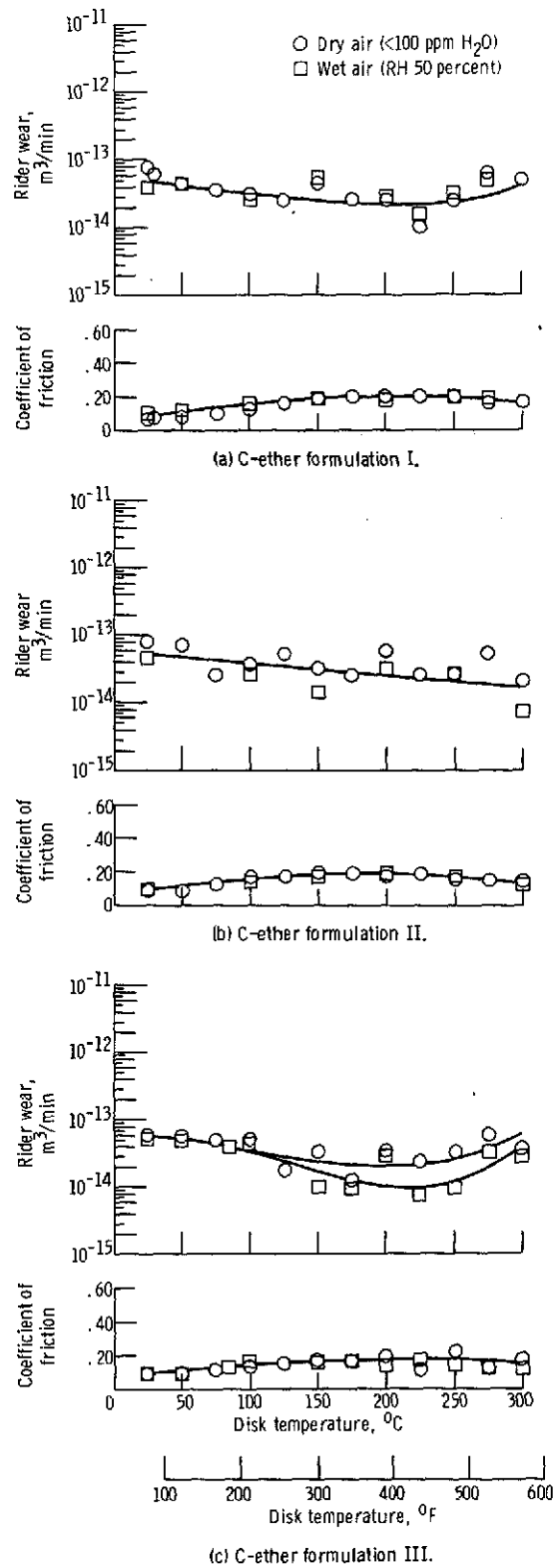air (RH 50 percent), and 25-minute test duration.

O Dry air (<100 ppm H_2O)
□ Wet air (RH 50 percent)

Rider wear, m^3/min

Coefficient of friction

(a) C-ether formulation I.

Rider wear, m^3/min

Coefficient of friction

(b) C-ether formulation II.

Rider wear, m^3/min

Coefficient of friction

Disk temperature, ^oC

Disk temperature, ^oF

(c) C-ether formulation III.

Figure 6. - Coefficient of friction and rider wear as a function of temperature for three C-ether formulations. Test conditions: 1-kilogram load, 17-meter-per-minute sliding speed, 100-rpm disk speed, dry air (<100 ppm H_2O) and wet air (RH 50 percent), and 25-minute test duration.
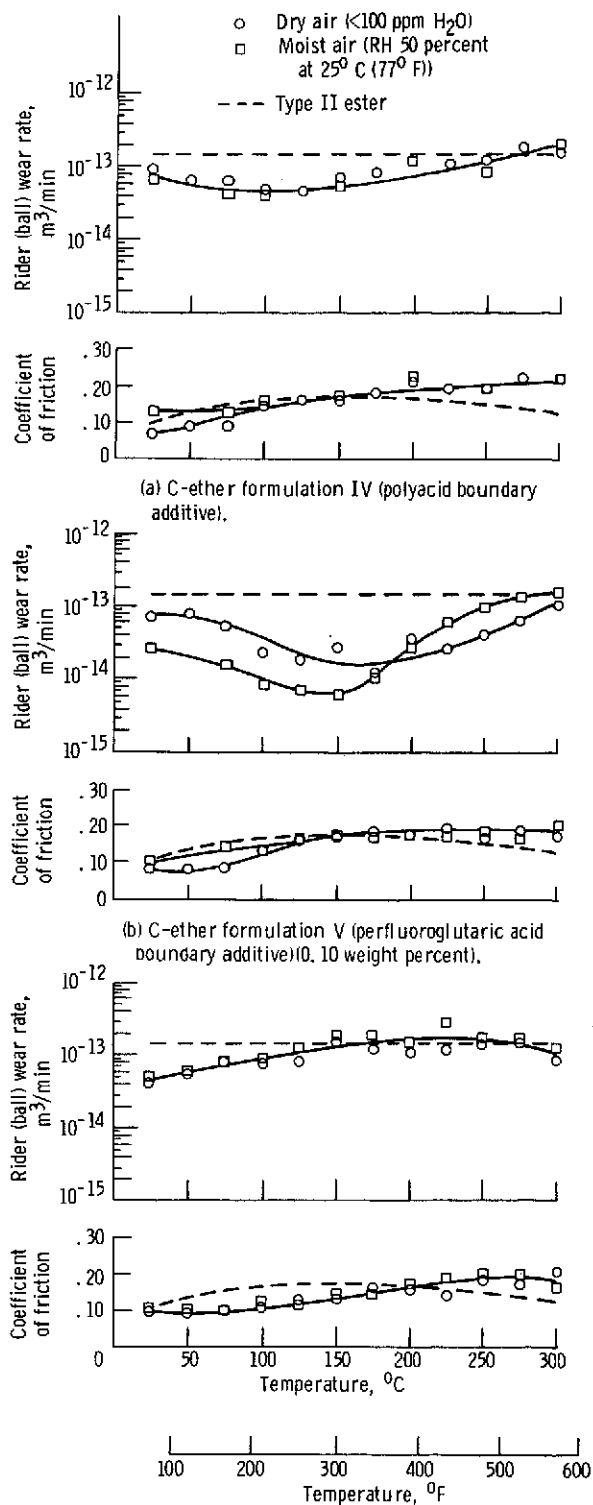
(a) Dry air (<100 ppm H_2O).

(b) Wet air (RH 50 percent).
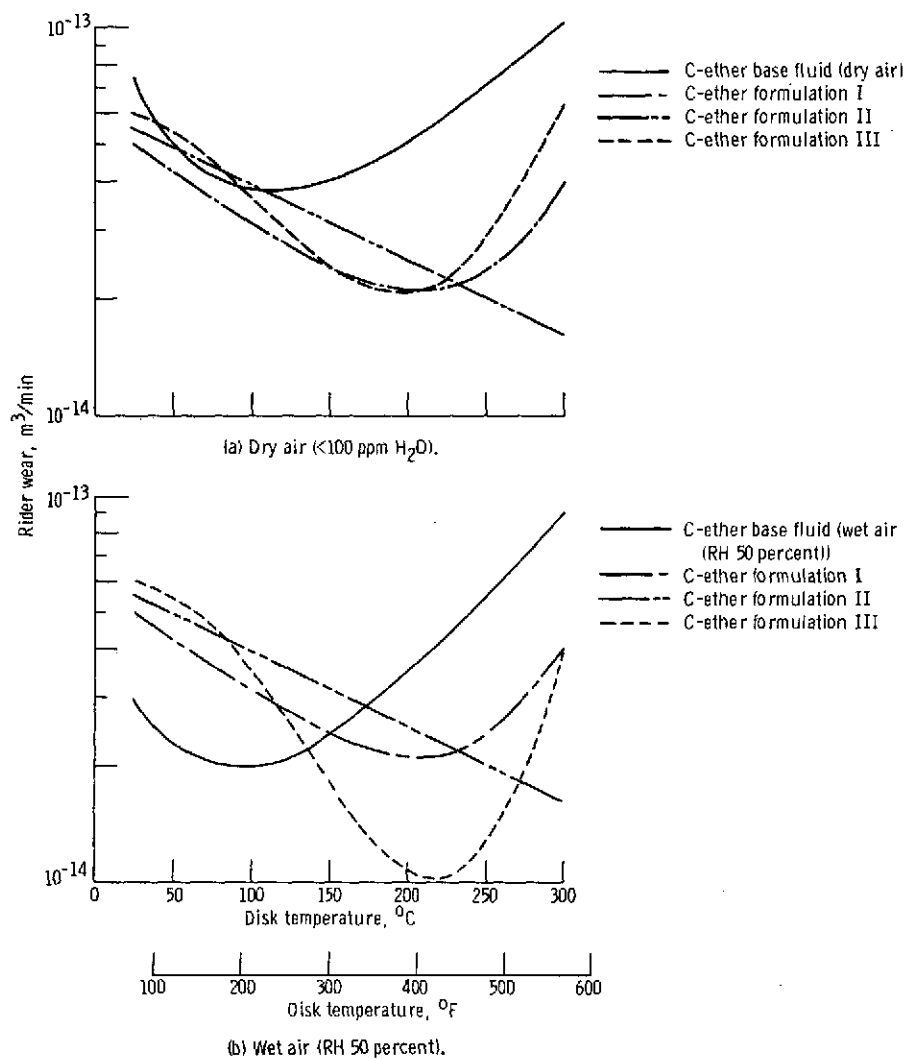
Figure 7. - Rider wear as a function of temperature for a C-ether base fluid and three C-ether formulations.

Figure 8. - Coefficient of friction and rider (ball) wear rate as a function of temperature for three C-ether formulations. Test conditions: M-50 steel specimens; 1-kilogram load; 17-meter-per-minute (100-rpm) sliding speed; dry (100 ppm H_2O) and moist (RH 50 percent at 25° C (77° F) air; 25-minute test duration.

(a) In dry (<100 ppm H_2O) air.

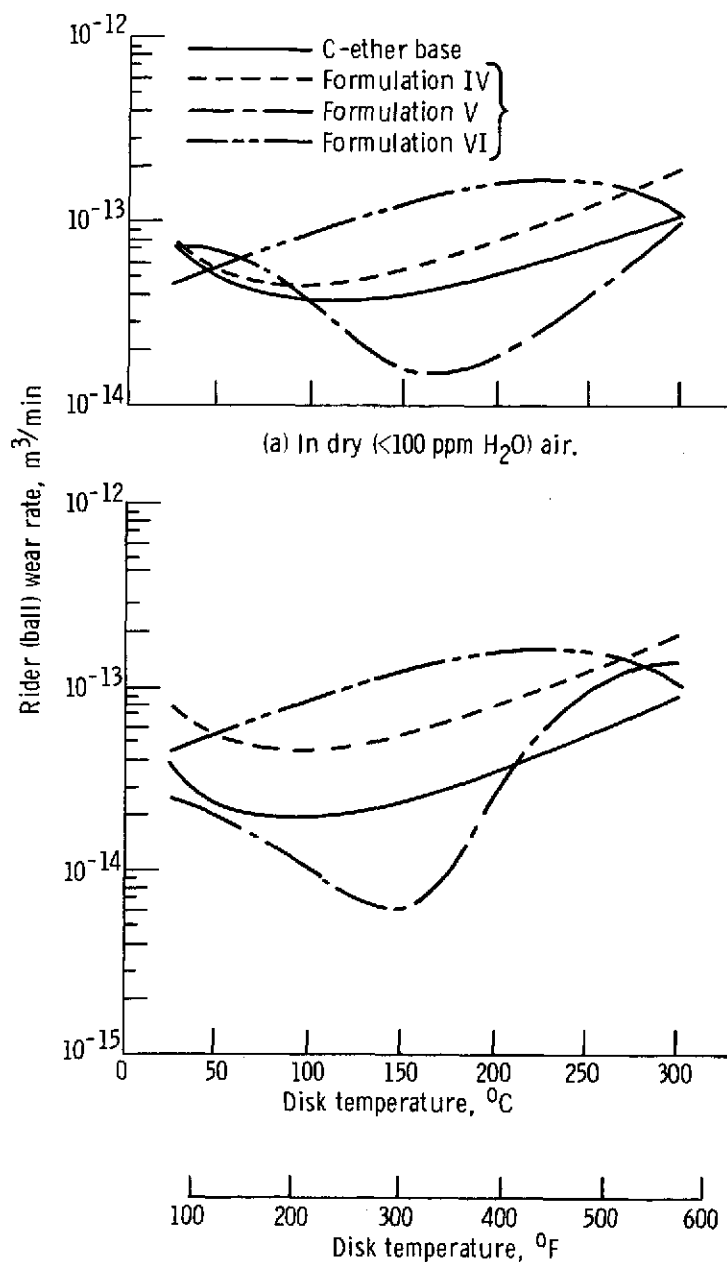(b) In moist (RH 50 percent at 25^0 C (77^0 F)) air.

Figure 9. - Rider (ball) wear rate as a function of temperature for a C-ether base fluid and three C-ether formulations. Test conditions: M-50 steel specimens; 1-kilogram load; 17-meter-per-minute (100-rpm) surface speed; 25-minute test duration.
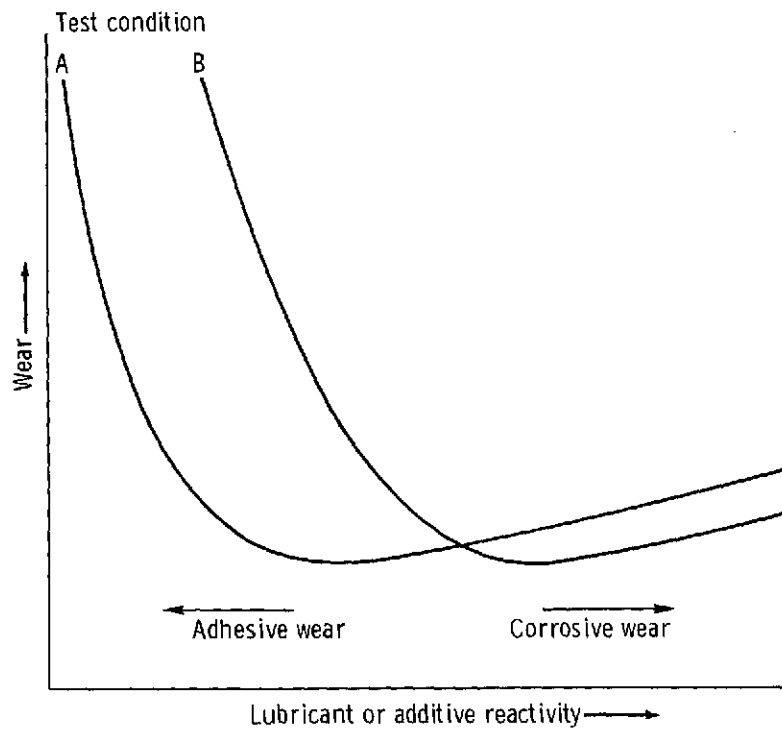
Figure 10. - Schematic illustrating relationship between wear, reactivity, and severity of test conditions (ref. 14). Severity of test condition B is greater than that of test condition A.