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Summary

Steady-state wear and friction measurements were made under boundary lubrication conditions in a pin-on-disk sliding friction and wear apparatus at disk temperatures of 20°, 150°, and 260° C with five C-ether-formulated fluids (modified polyphenyl ether containing phosphorous ester, organic acid, and other additives). Results were compared with those obtained under similar conditions for a fully formulated MIL-L-27502 candidate ester lubricant and the C-ether base stock as reference oils. Test components were annealed, pure-iron riders sliding against rotating consumable-vacuum-melted (CVM) M-50 tool steel disks in a dry-air (<100 ppm H_2O) atmosphere. Other test conditions were a load of 1 kilogram, a disk speed of 50 rpm (7.1- to 9.1-m/min sliding contact velocities), and test times to 130 minutes.

Based on steady-state wear rates and coefficients of friction, three of the C-ether formulations gave better boundary lubrication than the C-ether base fluid and the reference formulated MIL-L-27502 candidate ester. This was true under most test conditions, but most significantly it occurred for three of these formulated C-ether fluids at the highest disk temperature of 260° C.

The other two C-ether formulations yielded higher wear rates and friction coefficients than the C-ether base fluid for most of the temperature range. These are the only examples where C-ethers were found not to be susceptible to additive treatment. Only one C-ether test fluid showed consistently higher steady-state wear rates than the formulated ester fluid, but it had the same or slightly lower friction coefficients over the entire temperature range.

A qualitative method was devised for comparing friction behavior where friction traces obtained during steady-state testing were judged to be either smooth (wide or narrow band) or erratic (spiked or wandering). All the test fluids were classified under one of these four trace variations. No correlation was found between these criteria and quantitative coefficient of friction values, but the trace type seemed to be temperature related. It varied from smooth (wide band) operation at 20° C for all fluids to an erratic (both spiked and wandering) behavior at 260° C for all five formulated C-ether fluids. The reference ester fluid gave a smooth friction trace over the entire temperature range.

Introduction

Efforts in recent years to develop new and improved turbine engine lubricants have been primarily under the sponsorship of Department of Defense organizations. These efforts were aimed at advanced engine developments and anticipated trends toward increased operating temperatures that place greater thermal demands on the lubricants.

The Air Force is seeking a MIL-L-27502 target specification lubricant with an operating temperature capability to 240° C (464° F) for a Mach 3+ engine. Also, it is projected that a 260° C (500° F) capability lubricant will be a necessity for a Mach 4+ engine (ref. 1). Use of heavy coolers of the fuel-air and fuel-lubricant types could preclude the need for higher temperature lubricants. However, the added weight of the coolers limits the aircraft's ability to perform. By employing lubricating fluids with higher temperature oxidative and thermal stabilities, greater advantage can be taken of the improved thrust-weight ratios of new engines.

Experience already exists with at least one high-temperature lubricant of a five-ring polyphenyl ether-base fluid (bis [phenoxyphenoxy] benzene) in an operational military gas turbine flight engine (ref. 2). This fluid meets military specification MIL-L-87100. Although it has excellent high-temperature stability, it also has a very high pour point of about 5° C (41° F) and poor boundary lubricating characteristics. A trichloroethylene diluent is required with this fluid to reduce the pour point and make it operational. The need for good boundary lubricating ability is a well-established requirement for turbine engine bearing lubricants for use in high-speed, high-temperature aircraft.

The lubricant capability breach between current polyol ester fluids and the five-ring polyphenyl ether needs to be filled. It was decided some time ago (ref. 1) that advanced lubricant development might best be approached in two phases. The first phase concentrated on optimizing the polyol ester chemical class of oils to meet or exceed the MIL-L-27502 specification. A newly formulated hindered polyol ester based on polypentaerythritol and developed under the Air Force Materials Laboratory sponsorship (refs. 3 and 4) has a potentially useful maximum bulk oxidative temperature of about 240° C (464° F). This ester is currently undergoing further testing by the U.S. Air Force for possible qualification as a MIL-L-27502 candidate. The second and more long-range phase has been to seek out and develop lubricants capable of meeting the ultimate in high-temperature requirements. One such development has been with C-ether fluids, or the modified polyphenyl ethers, that we are concerned with in this study.

The C-ethers have been under study and development for about 15 years. They were first reported in reference 5 by Monsanto Research, their originator. The second of two NASA contractual studies on C-ethers, completed recently, involved the synthesis and evaluation of C-ether formulations for use as turbojet aircraft engine lubricant fluids useful to 260° C (500° F). These studies are reported in references 6 and 7. Extensive bench screening and tests of large-scale (80-mm bore diameter) bearings at high speed and an oil-in temperature of 260° C were used to evaluate a number of additive packages in the C-ether base oil. Results did indicate that the poor boundary lubricating characteristics of this fluid could be improved by using the proper additive package. However, the screening tests (which included macro- and thin-film oxidation-corrosion tests, friction and wear tests on a rub-block rig, and slow and fast four-ball tests) were not very reliable in selecting the proper candidates for 100-hour bearing endurance tests. Thus the need exists for more simulative and reproducible lubricant screening tests, especially in the boundary lubrication regime.

Progress was made toward establishing more reproducible and reliable testing procedures in the boundary lubrication regime in a recent study of steady-state wear and friction using a pin-on-disk machine (ref. 8). Ester base and C-ether base fluids were studied at room temperature (20° C) in a sliding friction and wear apparatus where steady-state wear rates, as defined in reference 8, appeared to be the best single criterion for determining comparative lubrication behavior among fluids.

The objectives of this investigation were (1) to determine wear rates and friction coefficients with five C-ether formulations developed by Monsanto Research (refs. 6 and 7) during steady-state operation under boundary lubrication conditions at disk temperatures of 20°, 150°, and 260° C, and (2) to compare these results with those of the MIL-L-27502 candidate ester liquid lubricant and the C-ether base stock.

In the experiments annealed, pure-iron riders (99.99 percent iron) slid against M-50 tool steel disks in dry air (< 100 ppm H_2O) at a load of 1 kilogram (initial Hertz stress, 1×10^9 N/m^2) and at sliding velocities of 7.1 to 9.1 m/min. Test time intervals for wear measurements were usually at 10, 40, 70, 100, and 130 minutes.

Annealed, pure-iron riders were used instead of M-50 tool steel (as in previous studies, refs. 9 and 10) to achieve larger and more easily measured wear scars, the iron being much softer than the M-50 tool steel disks. Surface sliding velocities and loads were selected that avoided elastohydrodynamic and "mixed" lubrication regions (ref. 8). A dry-air test atmosphere was selected because it had been determined (ref. 9) that, in general, lower wear rates were observed when fluids were tested in moist air.

Apparatus

The sliding friction and wear apparatus used in this study is shown in figure 1. The test specimens were contained inside a stainless-steel chamber, and the moisture content of the chamber atmosphere was controlled. A stationary, 0.476-centimeter-radius, hemispherically tipped rider was placed in sliding contact with a rotating, 6.35-centimeter-diameter disk. Rider holders of three different lengths were used to permit three concentric wear tracks to be run on a single disk, thereby eliminating the need to refinish disks after each run. Sliding velocities ranged from about 7.1 to 9.1 m/min as disk rotational speed was maintained at 50 rpm for all three rider holders.

A normal load of 1 kilogram (initial Hertz stress, 1×10^9 N/m^2) was applied with a deadweight. Disks were made of consumable-vacuum-melted (CVM)

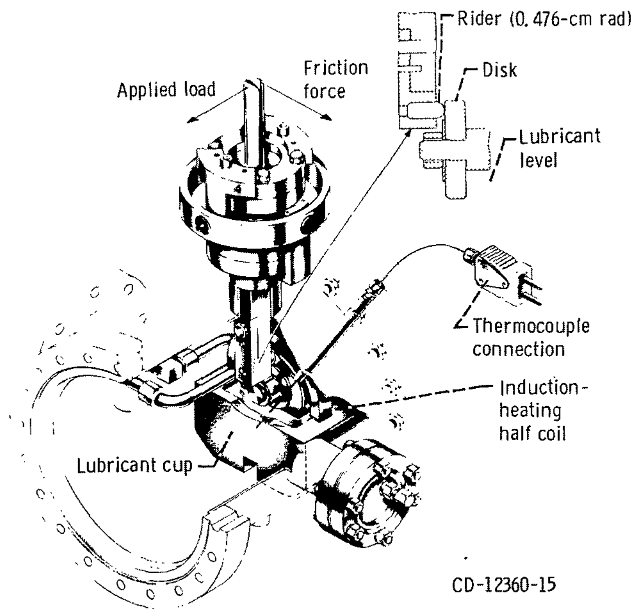


Figure 1. - Friction and wear apparatus.

M–50 tool steel and heat treated to a hardness of Rockwell C62 to C64. Riders were made of pure iron (99.99 percent iron) and were annealed to a hardness of 70 to 92 kg/mm^2 (diamond pyramid hardness number, DPH) as measured on an Eberbach microhardness tester at a 150-gram load.

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 an X–Y recorder.

The test atmosphere used in this study was dry air (<100 ppm H_2O) obtained by drying and filtering service air. The moisture concentration was monitored by a moisture analyzer with an accuracy of ±10 parts per million.

Procedure

Disks were ground and lapped to a surface finish of 1×10^{-7} to 2×10^{-7} meter (4 to 8 μin.) rms. Rider tips were machined and polished to a surface finish of 5×10^{-8} to 10×10^{-8} meter (2 to 4 μin.) rms. Specimens were scrubbed with a paste of levigated alumina and water, rinsed with tap water and distilled water, and then placed in a desiccator.

Test lubricants were degassed at approximately 150° C (302° F) at 2.7×10^2-N/m^2 pressure for 1 hour. Measurements made using the Karl Fisher technique indicate that this degassing procedure reduces dissolved water content in the test fluids to less than 20 ppm.

The specimens were assembled, and approximately 3×10^{-5} cubic meter (30 milliliters) of lubricant was placed in the lubricant cup. The test chamber (3.7×10^{-3}-m^3 volume) was purged with the dry-air test atmosphere for 10 minutes at a flow rate greater than 5×10^{-2} m^3/hr. During the high-temperature runs the disk was heated by induction to test temperature while rotating. The rider was then loaded against the disk with the deadweight, and this marked the start of the test run. The flow rate of the dry-air atmosphere was reduced to 3.5×10^{-2} m^3/hr, and a pressure of 6.9×10^{-3} N/m^2 (1 psig) was maintained in the test chamber. The lubricant was heated only by heat transfer from the disk. At disk temperatures of 150° and 260° C (302° and 500° F) the bulk oil temperatures stabilized at approximately 140° and 230° C (284° and 446° F), respectively.

Frictional force was continuously recorded. Bulk lubricant temperature and disk temperature were continuously monitored. Rider wear scar diameters were measured and recorded after each time interval. Disk wear with pure-iron riders was found to be so small that it was not measurable. During most test runs rider wear scars were measured at test times of 10, 40, 70, 100, and 130 minutes.

Experimental Lubricants

The experimental fluids used in this study were a fully formulated ester (used for reference), a C-ether base fluid (modified polyphenyl ether), and five C-ether formulated fluids (containing phosphorous ester, organic acid, and other additives). Some typical properties of the ester and the C-ether base fluid are given in table I. The formulated fluids, which contain no more than 0.10 percent by weight of any one additive, have essentially the same physical properties as the C-ether base fluid. Table II gives the additive contents, structures, and functions for all the test fluids.

Formulated Ester

The fully formulated ester is a special synthesized fluid whose base stock is a mixture of hindered polyol esters, polyester, and dipentaerythritol esters. It was developed by Monsanto Research (refs. 3 and 4) as a MIL–L–27502 specification candidate lubricant (−40° to 240° C operating range). Generic names for the additives are given in table II for this reference fluid where exact information is considered proprietary by the fluid manufacturer.

C-Ether Base Fluid

The C-ether base fluid used in this study was originally reported in reference 5 and more recently in references 6 and 7. This fluid is a blend of three- and four-ring components that are structurally similar to the polyphenyl ethers and contains a dimethyl silicone antifoaming additive.

C-Ether Formulations

The five specially formulated C-ether-base fluids were developed by Monsanto Research and subjected to extensive screening tests (ref. 7). The additive contents of these fluids are listed in table II along with the weight percentage of each used, their molecular structures, and the general function or purpose for each additive. An appropriate background reference for a general understanding of the mechanisms and purposes involved in using various chemical lubricant additives is given in reference 11. Also, a study by Jones (ref. 9) involved the use of phosphorous ester and organic acid

TABLE I. - TYPICAL PROPERTIES OF TEST FLUIDS

Property[a]	Formulated ester fluid[b]	C-ether base fluid
Kinematic viscosity, m^2/sec (cS):		
At 38° C (100° F)	3.96×10^{-5} (39.6)	2.5×10^{-5} (25)
At 99° C (210° F)	7.02×10^{-6} (7.02)	4.1×10^{-6} (4.1)
At 150° C (302° F)	2.80×10^{-6} (2.80)	1.9×10^{-6} (1.9)
At 260° C (500° F)	1.06×10^{-6} (1.06)	7.6×10^{-7} (0.76)
At 300° C (572° F)	[c]8.6×10^{-7} (0.86)	6.9×10^{-7} (0.69)
Pour point, °C (°F)	-51 (-60)	-29 (-20)
Flashpoint, °C (°F)	274 (525)	239 (445)
Fire point, °C (°F)	---------------	285 (540)
Density at 38° C (100° F), kg/m^3 (g/milliliter)	[d]0.994	1.19×10^3 (1.19)
Thermal decomposition (isoteniscope), °C (°F)[e]	298 (536)	390 (734)
Vapor pressure, N/m^2:		
At 220° C (428° F)	1.33×10^2	--------------
At 371° C (600° F)	---------------	1.86×10^4
Surface tension at 23° C (73° F), N/cm (dynes/cm)	---------------	[e]4.48×10^{-4} (44.8)

[a]Manufacturer's data.
[b]A specification MIL-L-27502 candidate lubricant with a base stock mixture of hindered polyol esters, polyester, and dipentaerythritol esters (refs. 3 and 4).
[c]Extrapolated.
[d]Specific gravity, 15.6° C/15.6° C (60° F/60° F).
[e]Measured in author's laboratory.

additives of the same general types of some employed in this study.

Additional comments on the rationale for selecting the additives shown in table II are presented for each C-ether formulation, as follows:

Formulation I.—This formulation contained two antiwear or boundary lubrication additives consisting of 0.07-weight-percent perfluoroglutaric acid (PFGA) and 0.05-weight-percent di[2-ethylhexyl] perfluoroglutarate (ester of PFGA). Chemical analyses during previous bearing test studies (ref. 6) with a C-ether-plus-PFGA lubricant showed a quick loss of additives from the fluid in most instances. Therefore, to provide a cushion or continuing source of additive, this formulation was devised to use a fast-reacting absorbed additive (the PFGA) in combination with a slowly reacting compound (the PFGA ester).

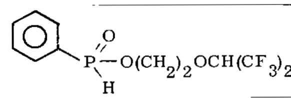
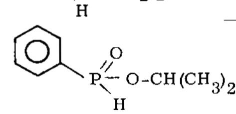
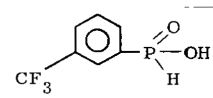
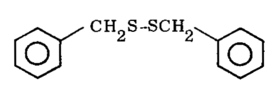
Formulation II.—The second formulation studied was the base fluid plus 0.10-weight-percent 2-[hexafluoro-i-propoxy] ethyl phenylphosphinate. This multipurpose additive is a boundary lubrication improver as well as an antisludge agent (both corrosion and oxidation inhibition).

Formulation III.—The third formulation chosen for study contains 0.10-weight-percent *i*-propylphenylphosphinate as a boundary additive plus 0.05-weight-percent trichloroacetic acid to improve fluid wettability.

Formulation IV.—The fourth formulation studied was the base stock plus 0.075-weight-percent *m*-trifluoromethylphenylphosphinic acid, which should serve as a boundary lubrication improver as well as an antisludge additive. In a previous study (ref. 6) one additive containing a pH group gave good bearing lubrication, but large amounts of sludge were formed. This sludge could come from reaction of the C-ether base stock at reactive sites on the metal. To prevent this, the phosphorous additive was partially fluorinated to form an even more protective absorbed film between the metal and the C-ether.

Formulation V.—The fifth formulation was the base fluid plus 0.10 weight percent of a commercial acid phosphate mixture (refer to structure in table II) and 0.05 weight percent of dibenzyl disulfide. This formulation has the same expected function as formulation IV and uses essentially the same

TABLE II. - ADDITIVE CONTENTS AND FUNCTIONS OF TEST FLUIDS

Test fluid	Additive	Additive content, wt%	Additive structure	Additive function
Formulated ester[a] (specification-MIL-L-27502 candidate)	Proprietary metal derivatives consisting of (1) a complexing agent and (2) a metal compound that is complexed by that agent[b]	(c)	(c)	Deposit inhibitor
	Alkylated amine		(a)	Oxidation inhibitor
	Aromatic amine		(a)	Oxidation inhibitor
	Triphenylphosphine oxide		(a)	Metal passivator (corrosion and oxidation inhibitor)
	Metal deactivator[d]		(d)	Magnesium corrosion inhibitor
C-ether base fluid	Dimethyl silicone (Grade, 350 cS at 25° C)	(e)	$(CH_3)_3SiO\left[(CH_3)_2SiO\right]_n Si(CH_3)_3$	Antifoaming agent
C-ether[f] formulation I	Perfluoroglutaric acid	0.07	$HO_2C(CF_2)_3CO_2H$	Fast-reacting boundary lubrication
	di (2-ethylhexyl) perfluoroglutarate	.05	$(C_4H_9\text{-}CH(C_2H_5)\text{-}CH_2\text{-}O\text{-}C(=O))_2\text{-}(CF_2)_3$	Slow-reacting boundary lubrication
C-ether formulation II	2-(hexafluoro-i-propoxy) ethyl phenylphosphinate	0.10		Boundary lubrication and antisludge agent
C-ether formulation III	i-propylphenylphosphinate	0.10		Boundary lubrication
	Trichloroacetic acid	.05	$CCl_3\text{-}C(=O)\text{-}OH$	Boundary lubrication (wettability agent)
C-ether formulation IV	m-trifluoromethyl-phenylphosphinic acid	0.075		Boundary lubrication and antisludge agent
C-ether formulation V	Commercial acid phosphate mixture	0.10	$C_9H_{19}\text{-}O\text{-}(CH_2CH_2O)_5\text{-}P(=O)(OX)\text{-}OH$ (X=H or ethylene oxide chain)	Boundary lubrication
	Dibenzyl disulfide	.05		Antisludge agent when combined with phosphorous additive

[a]Refs. 3 and 4.
[b]Description of complexing agent given in ref. 17.
[c]Proprietary information (refs. 3 and 4).
[d]More exact description is proprietary (ref. 4).
[e]Weight percentage of antifoaming agent is proprietary.
[f]All C-ether formulations contain antifoaming agent.

mechanism to accomplish the desired result. The difference from formulation IV is that an active sulfur compound is combined with a phosphorous compound to function as the metal deactivator.

Results and Discussion

Steady-State Wear

Typical results of wear tests for all reference and test fluids, plotted in figures 2 and 3, show a consistent linear relationship with sliding distance in the range of about 200 to 1100 meters (about 50 to 130 min test time). Wear rates were calculated as the slopes of these lines by using the linear regression fit formula (least-squares estimates) as described in references 12 and 13, and they are herein defined as the "steady-state wear rates."

The computed mean values of these wear rates are presented in table III for three test runs at each fluid-temperature combination. The correlation coefficients R for each corresponding wear rate are shown in table IV, and these are the approximate measure of the degree of fit for a linear relationship of the two variables (rider wear and sliding distance)

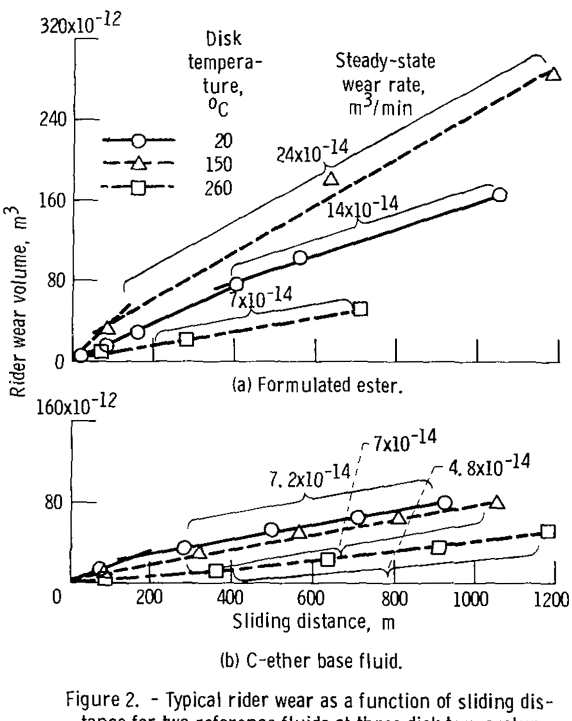


Figure 2. - Typical rider wear as a function of sliding distance for two reference fluids at three disk temperatures. Test conditions: load, 1 kg; disk speed, 50 rpm; sliding speed, 7.1 to 9.1 m/min; atmosphere, dry air (<100 ppm H_2O); rider, pure iron; disk, M-50 tool steel.

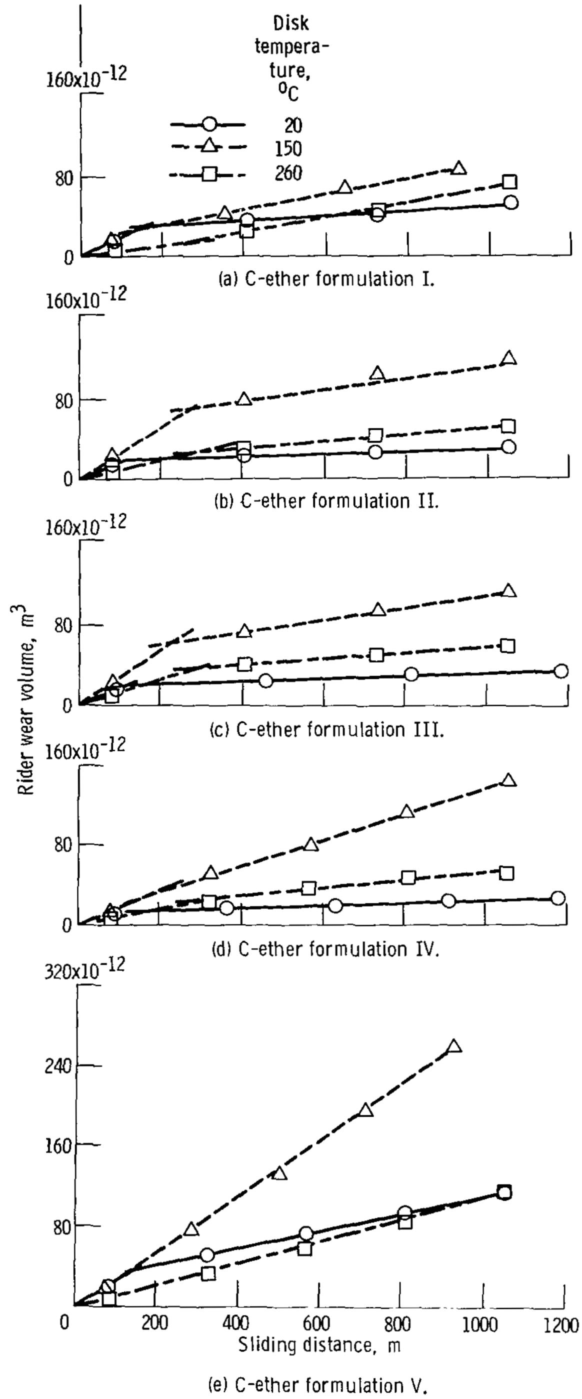


Figure 3. - Typical rider wear as a function of sliding distance for five C-ether formulations at three disk temperatures. Test conditions: load, 1 kg; disk speed, 50 rpm; sliding speed, 7.1 to 9.1 m/min; atmosphere, dry air (<100 ppm H_2O); rider, pure iron; disk, M-50 tool steel.

TABLE III. - SUMMARY OF FRICTION AND WEAR RESULTS FOR TEST FLUIDS

Disk temperature		Test fluid						
		Formulated advanced ester[a]	C-ether base fluid	C-ether formulation				
°C	°F			I	II	III	IV	V
Steady-state coefficient of friction[b]								
20	68	0.09(±0.07)	0.06(±0.045)	0.09(±0.06)	0.08(±0.06)	0.09(±0.06)	0.06(±0.055)	0.07(±0.06)
150	302	.16(±0.02)	.15(±0.02)	.15(±0.015)	.16(±0.025)	.16(±0.02)	.16(±0.015)	.12(±0.01)
260	500	.14(±0.01)	.17(±0.01)	.19(±0.02)	.14(±0.015)	.13(±0.025)	.14(±0.03)	.14(±0.02)
Steady-state rider wear rate[c], m^3/min								
20	68	15(±2.9×10^{-14}	6.9(±0.21×10^{-14}	2.1(±0.40)×10^{-14}	1.2(±0.27)×10^{-14}	1.5(±0.21)×10^{-14}	1.9(±1.4)×10^{-14}	8.5(±0.99)×10^{-14}
150	302	26(±24)	6.5(±1.3)	7.1(±0.74)	5.8(±1.4)	6.4(±0.91)	11.8(±1.3)	30(±3.3)
260	500	6(±1.3)	4.1(±1.0)	7.3(±1.2)	2.6(±1.3)	2.9(±0.70)	3.5(±1.7)	12(±1.8)
Run-in wear rate[c], m^3/min								
20	68	31(±10)×10^{-14}	16(±2.4)×10^{-14}	17(±3.8)×10^{-14}	16(±2.3)×10^{-14}	16(±2.8)×10^{-14}	8.4(±2.6)×10^{-14}	28(±3.5)×10^{-14}
150	302	25(±12)	12(±5.0)	15(±4.9)	18(±7.6)	23(±4.8)	18(±3.5)	25(±2.3)
260	500	8.1(±5.2)	3.3(±1.3)	7.1(±0.81)	3.3(±3.7)	8.6(±6.0)	7.5(±1.1)	8.1(±5.6)

[a]A mixture of hindered polyol esters, polyester, and dipentaerythritol esters formulated for use as a specification MIL-L-27502 candidate lubricant (refs. 3 and 4).

[b]Mean values. Scatter in parentheses.

[c]Mean values. Standard deviation in parentheses.

TABLE IV. - CORRELATION COEFFICIENTS FOR RIDER WEAR RATES AS CALCULATED BY LINEAR REGRESSION ANALYSIS FOR SLIDING FRICTION EXPERIMENTS

[Disk temperature, as shown; load, 1 kg; test atmosphere, dry air (<100 ppm H_2O); M-50 steel disk and pure-iron rider.]

Test fluid	Disk temperature, °C					
	20	150	260	20	150	260
	Correlation coefficient[a] at disk temperature, R			Square of correlation coefficient at disk temperature, R^2		
Formulated ester	0.9987	0.9945	0.9597	0.9974	0.9890	0.9211
C-ether base	.9979	.9980	.9937	.9959	.9961	.9874
C-ether formulation I	.9998	.9973	.9985	.9996	.9945	.9970
C-ether formulation II	.9599	.9860	.9893	.9215	.9722	.9787
C-ether formulation III	.9832	.9975	.9980	.9667	.9950	.9959
C-ether formulation IV	.9920	.9983	.9855	.9841	.9965	.9711
C-ether formulation V	.9998	.9990	.9992	.9996	.9979	.9984

[a]Ref. 12.

(ref. 12). Thus the consistently high absolute values of R, generally between 0.995 and 0.999 for the variables, indicate a high degree of association between them.

The square of the correlation coefficient R^2 is an even more significant parameter for determining these variable relationships. It measures the proportion of the total variation between the two parameters accounted for by the regression equation (ref. 14). Thus the data given in tables III and IV indicate that, in general, between 99.0 and 99.8 percent of the relationship between rider wear and sliding distance can be shown as a straight-line function.

Good reproducibility of the steady-state wear rate results in table III is shown by the fact that the ratio of standard deviations to mean wear values was less than 0.2 in most cases.

A discussion for each test fluid follows.

Formulated ester.—This reference fluid was used because it represents the most advanced ester known to date. Although it has not been fully qualified as a −40° to 240° C specification MIL-L-27502 lubricant, it is considered to be a prime candidate. Typical wear results for this fluid are shown in figure 2(a), and the slopes of these linear relationships at sliding distances of about 200 to 1100 meters (~ 50 to 130 min test time) are given as the steady-state wear rates. The average wear rates for three separate test runs are summarized in table III and shown graphically in figure 4 for each of the three disk operating temperatures.

The steady-state wear rates were found to be 15×10^{-14} and 26×10^{-14} cubic meter per meter of sliding distance for the two lower temperatures of 20° and 150° C, respectively. These wear results and the appearance of the rider wear surfaces indicate that lubrication was comparable to that in prior studies with a formulated type II ester (a MIL-L-23699 specification fluid) that was considered only marginally adequate lubrication (ref. 9). However, wear rates for the formulated ester of this study showed improved lubrication for the higher operating temperature of 260° C, where a value of 6.1×10^{-14} m^3/min was obtained. The increased effectiveness of the esters' additives at the highest temperature studied is probably due to their greater chemical reactivity, which could form protective surface films.

C-ether base fluid.—Typical wear results for this base fluid appear in figure 2(b), and the average steady-state wear rates for each temperature run are given in table III and shown graphically in figure 4. Wear rates decreased slightly with increasing temperature (from 6.9×10^{-14} m^3/m at 20° C to 4.1×10^{-14} m^3/m at 260° C). This indicates that the C-ether base fluid's molecules are more reactive at higher temperatures and apparently follow the general relationship that exists between wear and reactivity as described in reference 15. The C-ether base fluid had steady-state wear rates that were one-half the comparable values for the reference ester fluid or less at temperatures of 20° and 150° C and about two-thirds these values at 260° C.

C-ether formulations.—Typical wear results for

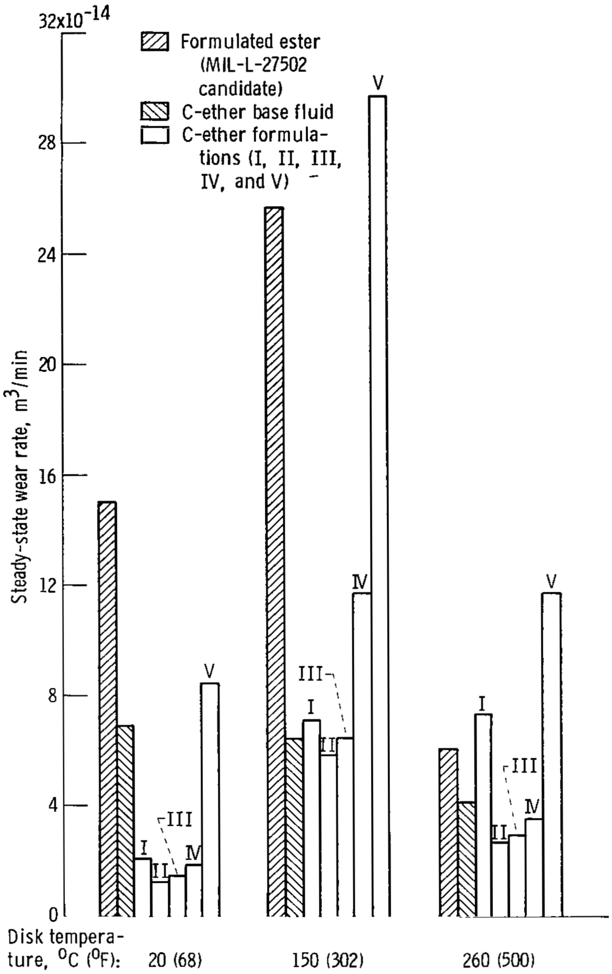


Figure 4. - Steady-state rider wear rate at three disk temperatures for formulated ester, C-ether base fluid, and five C-ether formulations. Test conditions: load, 1 kg; disk speed, 50 rpm; sliding speed, 7.1 to 9.1 m/min; atmosphere dry air (<100 ppm H_2O); rider, pure iron; disk, M-50 tool steel; maximum test duration, 130 min.

C-ether formulations I to V appear in figure 3, and the average steady-state wear rates for three separate test runs for each formulation at the three operating temperatures are shown in table III and comparatively in figure 4. In general, these fluids followed the same pattern of wear behavior with temperature, except at lower values, as the formulated ester fluid: that is, steady-state wear rates were low at 20° C (generally $<2\times10^{-14}$ m^3/m), reached maximum values at the intermediate temperature of 150° C (from 6×10^{-14} to 12×10^{-14} m^3/m), and decreased to lower values at 260° C (about 3×10^{-14} m^3/m). One exception to this general wear trend was observed for formulation I, where wear rate remained essentially constant at about 7×10^{-14} m^3/min at temperatures of 150° and 260° C.

Effectiveness of the various additives on wear is shown by the comparisons between the steady-state wear rates for the five formulations and the C-ether base fluid in figure 4. Formulations II and III yielded lower wear than the base fluid at all test conditions and gave the best overall wear results. Formulation IV gave somewhat less desirable wear behavior at the 150° C level than the other formulations. Formulation I exhibited lower wear rates only at the 20° C operating temperature. The most adverse wear behavior was shown by formulation V, which gave higher wear than the C-ether base fluid at all test conditions. Formulations II and III, which gave the best wear results, were the only two fluids containing esters of phenylphosphinic acids. Any further efforts in formulating C-ether fluids should include additional studies on these types of effective antiwear compounds.

Steady-State Coefficient of Friction

The friction coefficients that were measured during the stepwise wear tests at the three operating temperatures are compared in figure 5 for all the test

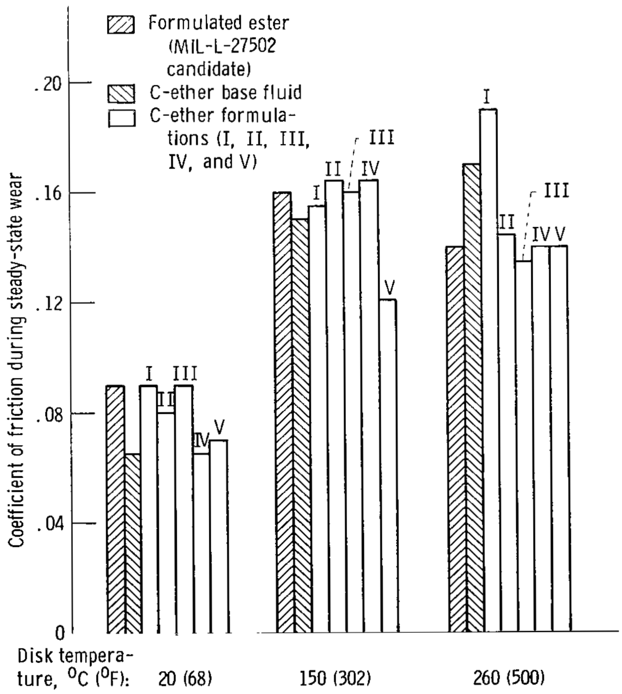
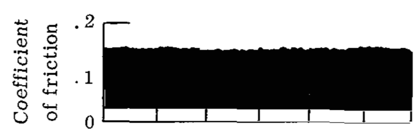
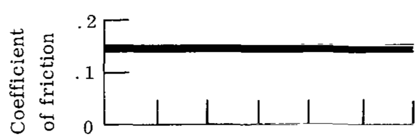
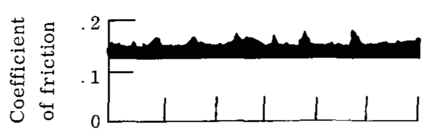
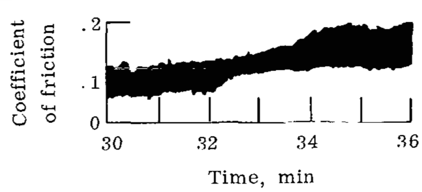


Figure 5. - Coefficient of friction during steady-state wear at three disk temperatures for formulated ester, C-ether base fluid, and five C-ether formulations. Test conditions: load, 1 kg; disk speed, 50 rpm; sliding speed, 7.1 to 9.1 m/min; atmosphere, dry air (<100 ppm H_2O); maximum test duration, 130 min.

TABLE V. - EXAMPLES OF FOUR TYPES OF FRICTION TRACES FROM SLIDING FRICTION EXPERIMENTS

[Test conditions: load, 1 kg; disk speed, 50 rpm; sliding speed, 8.1 m/min; atmosphere, dry air (<100 ppm H_2O.]

Friction type[a]	Friction trace segment	Test fluid	Disk temperature, °C	Steady-state coefficient of friction[b]
Smooth, wide band (S_w)		C-ether formulation III	20	0.09(±0.06)
Smooth, narrow band (S_n)		Formulated advanced ester	260	0.14(±0.01)
Erratic, spiked (E_s)		C-ether formulation V	260	0.14(±0.02)
Erratic, "wandering" (E_w)		C-ether formulation IV	260	0.14(±0.03)[c]

[a]Further variations include these types of friction accompanied by audible friction noise.

[b]Mean values. Scatter in parentheses.

[c]Mean value obtained over more extended period of time.

fluids. These values are also presented in table III, and they are the steady-state friction coefficients, defined in reference 8 as the coefficients of friction obtained during steady-state wear and after the run-in period, where initially higher coefficients were measured. They are analogous to the corresponding steady-state wear rates in that they occur during approximately the same test time interval. As shown in this figure the general trend of all fluids evaluated was for the steady-state friction coefficients to double when operating temperatures are increased from 20° to 150° C (average value going from about 0.08 up to 0.16 for most fluids). Further increasing the disk temperatures from 150° C up to 260° C resulted in slight decreases in friction coefficients (values going to 0.14) for the ester fluid and C-ether formulations II, III, and IV. The same temperature increase caused slight increases in friction coefficients (values increasing to about 0.18) for the C-ether base fluid and C-ether formulations I and V.

A qualitative evaluation of friction can be made by observing the friction traces during steady-state operating periods for each test fluid. There were four general types of friction traces recorded during the experimental runs. In addition, audible rubbing friction noise occurred at high temperatures in some runs when apparent fluid starvation in the system due to evaporation was evident. Examples of these types are illustrated and described in table V, and a listing is shown in table VI of those friction trace types encountered for each test fluid at each of the three operating disk temperatures studied. As indicated in these two tables the four types of friction traces obtained were (1) smooth, wide band S_w; (2) smooth, narrow band S_n; (3) erratic, spiked E_s; and (4) erratic, wandering E_w. These friction traces appear to be somewhat temperature related, but other test parameters not investigated here (e.g., speed, load, test component metallurgical combinations, rig stiffness) and fluid film properties may also affect results. Each type of trace is discussed separately below.

Smooth, wide band.—The smooth, wide-band type of friction trace was observed for all fluids only at the 20° C operating level, where lower coefficients of friction (0.06 to 0.09) were measured. Friction trace variation ranged from about ±0.05 to ±0.07.

Smooth, narrow band.—Five of the seven fluids exhibited the smooth, narrow-band type of friction at 150° C, and two of the fluids showed this type at 260° C. Friction trace variation ranged from ±0.01 to ±0.02.

Erratic, spiked.—The erratic, spiked friction trace was similar to the smooth, narrow-band trace in that normal variations were about ±0.02. However, there were periodic "spikes" or surges in the friction values to about twice the normal values. This frictional behavior was noted for several of the fluids at the 150° and 260° C operating temperatures. At 260° C it was usually accompanied by audible friction noise in the test components.

Erratic, wandering.—Erratic, wandering friction traces display a somewhat larger friction variation (about ±0.03) than does the erratic, spiked type of friction trace. It is the most erratic or irregular friction that was observed in all the experimental runs. Audible friction noise accompanied the two examples that were noted at the 260° C test conditions.

From this qualitative friction viewpoint, the formulated ester fluid gave the best results, with smooth friction traces over the entire temperature range. The C-ether formulation II fluid had erratic, spiked traces with audible noise at the two upper operating temperatures. The remaining fluids showed mixed results, with both smooth and erratic friction. There was no correlation between the type of friction trace and coefficient of friction values.

All the friction and wear results for all the test fluids at the three selected temperatures of 20°, 150°, and 260° C are summarized in table III, including a tabulation of the run-in wear rates for all tests. Run-in wear is the usually higher initial wear rate that is experienced before the onset of the linear steady-state

TABLE VI. - TYPES OF FRICTION TRACES FROM SLIDING FRICTION EXPERIMENTS

Test fluid	Disk temperature, °C		
	20	150	260
	Friction trace type[a]		
Formulated ester	S_w	S_n	S_n
C-ether base fluid	S_w	E_s	S_n
C-ether formulation I	S_w	S_n	E_s
C-ether formulation II	S_w	E_s	E_s, N
C-ether formulation III	S_w	S_n	E_w, N
C-ether formulation IV	S_w	S_n	E_w, N
C-ether formulation V	S_w	S_n	E_s, N

[a]Types of friction traces (as illustrated in table V):
S_w = Smooth, wide band
S_n = Smooth, narrow band
E_s = Erratic, spiked
E_w = Erratic, wandering
N = Audible friction noise

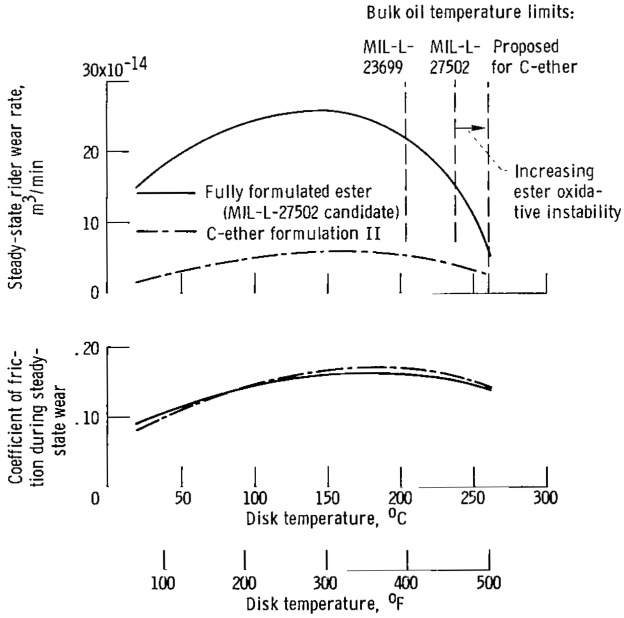


Figure 6. - Steady-state friction and wear as a function of disk temperatures from 20° to 260° C (68° to 500° F) for a formulated ester (MIL-L-27502 candidate) and C-ether formulation II. Test conditions: load, 1 kg; disk speed, 50 rpm; sliding speed, 7.1 to 9.1 m/min; atmosphere, dry air (<100 ppm H_2O); maxaimum test duration, 130 min.

wear after reaching the "transition point" (ref. 16). As defined and demonstrated in reference 8, run-in wear behavior of liquid lubricants in the boundary lubrication regime could be important if it is a significant part of the total wear since the total wear for a test run is the sum of the steady-state and run-in wear values. Over longer running periods, such as these tests, run-in wear is less significant than in previous studies of this type, where a test duration of 25 minutes was used (refs. 9 and 10).

Two problems observed for the C-ether fluids, the study of which was beyond the intended scope of this effort, were (1) the increased volatility of the fluids at the 260° C disk temperature that required additional fluid to be added to the test lubricant reservoir cup during the incremental testing, and (2) the formation of sludge material during friction and wear studies that is a potential filter-clogging agent in system applications (e.g., as encountered in the bearing tests of ref. 7).

Concluding Remarks

In conclusion, the susceptibility of C-ethers to selective additive treatment has been demonstrated in a series of sliding friction and wear studies at temperatures to 260° C. Based on steady-state wear rates, coefficient of friction values, and friction traces, three C-ether formulations (II, III, and IV) gave better boundary lubrication than the C-ether base fluid and a reference formulated ester in the temperature range of 20° to 260° C. Figure 6 shows comparative plots of friction and wear rate data for the ester and C-ether formulation II. This figure shows the increased thermal operating potential for formulated C-ethers in relationship to bulk oil temperature limits for MIL-L-23699 and MIL-L-27502 type esters. This difference in temperature operation above 220° C is even more significant because of the increasing ester oxidative instability at these higher temperatures.

Summary of Results

Steady-state wear and friction measurements were determined under boundary lubrication conditions in a pin-on-disk sliding friction and wear apparatus at disk temperatures of 20°, 150°, and 260° C with five C-ether formulations (containing phosphorous ester, organic acids, and other additives). Results were compared with those obtained under similar conditions for a fully formulated MIL-L-27502 candidate ester lubricant and the C-ether base stock as reference oils. Test component metallurgy was annealed, pure-iron riders sliding against rotating, hardened, consumable-vacuum-melted (CVM) M-50 tool steel disks in a dry-air (<100 ppm H_2O) atmosphere. Other test conditions were a load of 1 kilogram (initial Hertz stress, 1×10^9 N/m^2), a disk speed of 50 rpm, which results in sliding velocities of 7.1 to 9.1 m/min, and time sequences for each test run of 1 to 130 minutes. The major results were the following:

1. Three of the C-ether formulations gave better boundary lubrication than the C-ether base fluid and a reference formulated ester, based on steady-state wear rates and coefficients of friction. This was the case under most test conditions, but most significantly this occurred for three of the formulated C-ether fluids at the highest disk temperature of 260° C. These formulations all contained phosphorous acids or esters, including one that was a mixture of phenylphosphinic acid ester and trichloroacetic acid.

2. The other two C-ether formulations yielded higher wear rates and friction coefficients than the C-ether base fluid for most of the temperature range. One of these formulations contained glutaric acid and an ester of this acid, and the other contained phosphorous acid and dibenzyl disulfide.

3. Only one C-ether formulation showed consistently higher steady-state wear values than the formulated ester fluid, but the friction coefficients were the same or slightly lower over the entire temperature range. This formulation consisted of the base stock plus a phosphorous acid and dibenzyl disulfide.

4. A qualitative method for comparing friction behavior was devised where friction traces during steady-state testing were designated as one of the following: (a) smooth, wide band S_w; (b) smooth, narrow band S_n; (c) erratic, spiked E_s; and (d) erratic, wandering E_w. No correlation was found between this criterion and quantitative coefficient of friction values, but the trace type seemed to be temperature related. It varied from smooth, wide-band operation at 20° C for all fluids to an erratic (both spiked and wandering) behavior at 260° C for all five C-ether formulated fluids. The ester fluid gave a smooth friction trace over the entire temperature range.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, October 8, 1980

References

1. Bucknell, R. L.: Influence of Fuels and Lubricants on Turbine Engine Design and Performance. PWA-FR-5673, Pratt & Whitney Aircraft, 1973. (AFAPL-TR-73-52-VOL-2, AD-769309.)

2. Miner, John R.: Advanced Lubricating Fluids for Turbojet Engines. 1970 Air Force Materials Symposium, Session on Fluids and Lubricants, Air Force Systems Command, Wright-Patterson AFB, Ohio, 1970, Session 1F, Paper 2.

3. Clark, F. S.; Miller, D. R.; and Reid, S. L.: Development of a Gas Turbine Engine Oil for Bulk Oil Temperatures of −40° to 465° F, Part I. MRC-SL-477, Monsanto Research Corp., 1975. (AFML-TR-74-247, AD-A014808.)

4. Clark, F. S.; Herber, J. F.; and Reid, S. L.: Development of a Gas Turbine Engine Oil for Bulk Oil Temperatures of −40° to 465° F, Part II. MRC-SL-538-Pt. 2, Monsanto Research Corp., 1975. (AFML-TR-74-247-Pt. 2, AD-A027068.)

5. McHugh, Kenneth L.; and Stark, Louis R.: Properties of a New Class of Polyaromatics for Use as High-Temperature Lubricants and Functional Fluids. ASLE Trans., vol. 9, no. 1, Jan. 1966, pp. 13-23.

6. Clark, F. S.; Green, R. L.; and Miller, D. R.: Synthesis and Evaluation of C-Ether Formulations for Use as High-Temperature Lubricants and Hydraulic Fluids. (MRC-SL-460, Monsanto Research Corp.; NASA Contract NAS3-15333.) NASA CR-134643, 1974.

7. Clark, F. S.; and Miller, D. R.: Formulation and Evaluation of C-Ether Fluids as Lubricants Useful to 260° C. (MRC-SL-1007, Monsanto Research Corp.; NASA Contract NAS3-19746.) NASA CR-159794, 1980.

8. Loomis, William R.; and Jones, William R., Jr.: Steady-State Wear and Friction in Boundary Lubrication Studies. NASA TP-1658, 1980.

9. Jones, William R., Jr.: Boundary Lubrication of Formulated C-Ethers in Air to 300° C. Lubr. Eng., vol. 32, no. 10, Oct. 1976, pp. 530-538.

10. Jones, William R., Jr.; and Hady, William F.: Effect of Humidity and a Wettability Additive on Polyphenyl Ether Boundary Lubrication of Steel in Air and Nitrogen to 350° C. NASA TN D-6055, 1970.

11. Gunther, Raymond C.: Lubrication. Chilton Book Co., 1971, pp. 246-280.

12. Bowker, Albert H.; and Lieberman, Gerald J.: Engineering Statistics. Prentice Hall, Inc., 1959, p. 273.

13. Freund, John E.: Mathematical Statistics. Prentice Hall, Inc., 1962.

14. Atherton, Murle J.: Some Common Errors Associated with Regression Analysis. Technical Paper-679-OP, The International Nickel Company, Inc., 1970.

15. Rowe, C. N.: Wear: Corrosion and Erosion. Interdisciplinary Approach to Liquid Lubricant Technology, NASA SP-318, 1973, pp. 527-568.

16. Ferrante, John; and Brainard, William A.: Wear of Aluminum and Hypoeutectic Aluminum-Silicon Alloys in Boundary-Lubricated Pin-on-Disk Sliding. NASA TP-1442, 1979.

17. Thompson, Q. E.; Reid, S. L.; and Weiss, R. W.: Antioxidants for Ester-Base Functional Fluids. U.S. Patent 3,684,711, Aug. 1972.

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16. Abstract

Steady-state wear and friction studies were made at boundary lubrication conditions in a pin-on-disk (pure iron on rotating CVM M-50 steel) sliding friction apparatus with five C-ether-formulated fluids (modified polyphenyl ether containing phosphorous ester, organic acid, and other additives). Conditions included 20°, 150°, and 260° C disk temperatures, dry-air test atmosphere, 1-kilogram load, 50-rpm disk speed, and test times to 130 minutes. Results were compared with those obtained with a formulated MIL-L-27502 candidate ester and the C-ether base fluid. Three of the C-ether formulations gave better lubrication than both reference fluids under most conditions. The other two C-ether formulations yielded higher wear rates and friction coefficients than the C-ether base fluid for most of the temperature range. Only one C-ether formulation showed consistently higher steady-state wear rates than the ester.

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