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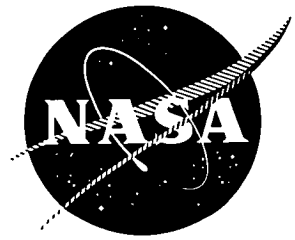

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FORMULATION AND EVALUATION OF C-ETHER FLUIDS AS LUBRICANTS USEFUL TO 260°C

by F. S. Clark and D. R. Miller

MONSANTO RESEARCH CORPORATION

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16. Abstract

Three base stocks were evaluated in bench and bearing tests to determine their suitability for use at bulk oil temperatures (BOT) from -40 to +260°C.

A polyol ester gave good bearing tests at a bulk temperature of 218°C, but only a partially successful run at 274°C. These results bracket the fluid's maximum operating temperature between these values.

An extensive screening program selected lubrication additives for a C-ether (modified polyphenyl ether) base stock. One formulation lubricated a bearing for 111 hours at 274°C (BOT), but this fluid gave many deposit related problems. Other C-ether blends produced cage wear or fatigue failures.

Studies of a third fluid, a C-ether/disiloxane blend, consisted of bench oxidation and lubrication tests. These showed that some additives react differently in the blend than in pure C-ethers.

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FOREWORD

This report describes work done under NASA contract NAS3-19746 by Monsanto Research Corporation. Except where noted otherwise, the location of the work was the Monsanto Company Research Center in St. Louis, Missouri. Subcontracted studies included thin-film oxidation tests run under the direction of Professor Elmer Klaus at The Pennsylvania State University, University Park, Pennsylvania, and high frequency rig tests directed by Professor Alastair Cameron at Imperial College, London, England. Mr. Lewis B. Sibley of SKF Industries, King of Prussia, Pennsylvania, supervised detailed failure analyses of used bearings. The NASA Project Manager, Mr. William R. Loomis, Structures and Mechanical Technologies Division, NASA Lewis Research Center, provided overall guidance and management for these studies.

Mr. Ralph A. Luebke and Mr. Alan J. Bindbeutel ran the bearing tests, and Mr. Luebke and Mr. Harold Kaatman II performed many of the bench screening tests.

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1. SUMMARY

The goal of this contract is a gas turbine engine lubricant/hydraulic fluid useful at a bulk temperature range of -40°C to +260°C (-40°F to +500°F).

We studied three types of fluids for this application:

-- an ester formulation especially blended for high temperature performance.

-- various formulations of a C-ether (modified polyphenyl ether) reference oil.

-- a -40°C pour point C-ether/disiloxane blend developed under an earlier NASA contract.

The ester performed smoothly in bearing tests at a bulk oil temperature (BOT) of 218°C. An attempt to raise the bulk temperature to ca. 274°C was partially successful in that no lubrication problems occurred after 70 hours. However, deposit formation in the sump and on the filters led to cessation of further running. Thus, the fluid's maximum BOT lies somewhere between 218 and 274°C. The ester survives bulk temperatures of 240°C in bench oxidation-corrosion tests and in bearings less mechanically demanding than those used in this study. This suggests the maximum BOT is at the upper end of the 218 to 274°C range.

Screening of the C-ether blends included macro oxidation-corrosion tests, friction and wear tests on a rub-block rig, slow and fast four-ball tests, high frequency reciprocating wear tests and thin-film oxidation tests.

The macro oxidation test served as a preliminary pass/fail screen. The ranking of passing additives involved their performance in lubrication tests, namely, the slow and fast four-ball and rub-block tests. Treatment of the data involved three steps. First, regression analyses based on bearing and bench tests from an earlier contract weighed or ranked the bench tests based on how well they correlated with bearing life. Relative performance of each additive in each bench test came from the test data. Finally, combination of performance and test weight gave overall ranking.

After this bench screening, tests on an 80-mm custom bearing rig evaluated five additive packages in the C-ether oil. The unformulated C-ether base stock will survive 1 to 15 hours at a bulk temperature of 274°C before cage wear failure occurs. We wanted to improve this performance to a 100-hour run free of lubrication failures and with a deposit rating analogous to esters at 218°C.

For comparison, we had bearing test data from an earlier contract on esters and other C-ether blends.

A bearing test reached 111 hours using one of the new formulations; however, deposits and filter pluggings marred this run. Cage wear failures or fatigue spalling ended the other tests. Moreover, one attempt at repeating a test gave a wide variation in bearing life, and so the statistical significance of individual runs is in doubt.

Characterization of the C-ether/disiloxane included only bench testing. Lubrication additive responses in this fluid can differ greatly from C-ethers.

2. INTRODUCTION

This report describes studies on high temperature lubricants and extends earlier work begun in NASA contract NAS3-15333. That contract sought to develop C-ether lubricants and hydraulic fluids for the space shuttle and for gas turbine engines; the present contract focuses on fluids for advanced air breathing aircraft engines and has a specific goal of defining a lubricant usable at bulk temperatures of 40°C to +260°C. Such performance would exceed the upper stability of many hindered esters by about 40°C and would allow operation in hot spots well above 260°C. Many presently available fluids are of limited use above 260°C for various reasons. Their shortcomings may embrace inherent instability, poor lubrication, high density, flammability or high pour point.

Polyphenyl ethers can be made thermally and oxidatively stable at 340°C; however, they have inconveniently high pour points (near 4°C). C-ethers (modified polyphenyl ethers, ref. 1) are stable to at least 260°C and to over 320°C in some tests. Bench tests predict they should have superior bearing fatigue life compared to polyphenyl ethers or esters. Ten 2000-hour bearing tests on JT3D bearings showed longer B10 fatigue life for C-ethers than for Type II esters (ref. 2). However, temperatures were relatively low (150°C oil-in for the C-ether and 120°C for the esters).

C-ethers have convenient pour points (near -29°C). Moreover, blending C-ethers with disoloxanes extends the pour point down to -40°C with only small changes in evaporation loss or oxidative stability (ref. 3). One such blend with a -40°C pour point became a candidate fluid in this contract.

Sometimes, polyphenyl ether related fluids show poor boundary lubrication. However, careful selection of metallurgy and/or additives can greatly improve their performance. For instance, excessive wear of steel/chrome-anodized aluminum journal bearings is greatly reduced by additives (ref. 4) or by using hard anodized aluminum. Reference 3 contains other examples of additive effects.

The history of bearing tests on C-ethers includes acceptable inerted runs on 25-mm bearings at 260°C (ref. 5) and 316°C (ref. 6) and a wear failure in air on a 125-mm bearing (ref. 7).

NASA contract NAS3-15333 (ref. 3) also covered the performance of C-ether formulations during very high temperature bearing tests. The test bearing was a custom 80-mm axially loaded ball bearing with a silvered 6415 cage riding on an inner race of M50 steel. At an outer race temperature of 316°C and an oil inlet temperature of 260°C, an unformulated C-ether base stock ran for

1-15 hours before catastrophic cage wear occurred. Additives extended the bearing life to over 90 hours, but several problems remained with these formulations. These included:

- excessive deposit formation. Even the cleanest C-ether formulation produced higher deposit ratings than esters run at lower temperatures.

- the peeling away during a 100-hour test of about 75% of the silver plating on the side of the cage facing the lubricant supply jet.

Still, this represented a considerable improvement in performance and the present contract continued these studies.

An alternate approach to a 260°C bulk temperature oil would be upgrading of esters. Many present-day polyesters can withstand extended operating periods at maximum bulk oil out and hot spot temperatures of about 180°C and 260°C, respectively, in current engines. Recent formulation studies performed by the Air Force have raised the stability of ester fluids to MIL-L-27502 levels, i.e., to a bulk temperature of 240°C. These products perform well in lightly loaded roller bearings at bearing temperatures (hot spots) of 300°C (ref. 8).

Thus, three types of fluids have emerged as primary candidates for the main goal of this contract - a 260°C bulk temperature oil: (1) formulations of C-ethers, (2) an ester formulation especially blended for high temperature performance, and (3) a -40°C pour point C-ether/disiloxane blend developed under another NASA contract. We hoped to:

- improve C-ether performance in the custom bearing rig with complete elimination of boundary wear failures and reduction of deposits.

- begin characterization of C-ether/disiloxane fluids in bench and bearing tests.

- evaluate the performance of the new ester blends in more stringent bearings.

Secondarily, we sought correlations between screening tests and bearing life along with information on the basic lubrication chemistry of additives and base stocks. Time allowed few mechanism studies. Work on one additive, bis(trimethylsilyl) phosphonate, is reported in Appendix C.

3. RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

3.1 ESTERS (MCS 1892)

1. The formulated polyol ester lubricated the bearing at bulk temperatures of 218°C (100 hours) and 274°C (70 hours). Smooth, uninterrupted running and low levels of solid formation at 218°C contrasted with frequent filter pluggings and sump deposits at 274°C. Even at this harsher temperature, bearing deposits were not excessive and wear was negligible. *Thus the useful maximum bulk temperature of MCS 1892 lies between 218°C and 274°C.* Thermal cracking of the base stock is believed to set this upper limit.

2. Previous work showed that MCS 1892 has bulk oxidative stability for 72 hours in a bench oxidation test at 240°C (ref. 8). Also, it operates lightly loaded roller bearings at a BOT of 240°C for 48 hours. Hence, the useful operating temperature probably lies between 240°C and 274°C.

3.2 C-ETHERS: RESULTS AND CONCLUSIONS

1. Formulation of C-ethers can lead to significant extension of bearing life to 100 or more hours; however, no contract formulation completely eliminated cage wear and deposit problems. For example, of five fluids studied in this contract:

   - one ran for 111 hours without gross wear failure, but deposits caused many filter pluggings and a high deposit rating.
   - three failed because of gross cage wear.
   - duplicate runs on a fifth fluid failed by different mechanisms. One lasted 81 hours and then suffered gross fatigue and spalling failure, while the second lasted only 1 hour due to excessive cage wear.

2. Because of the above poor reproducibility, statistical inference based on individual runs is difficult.

3. Prediction of bearing life proved very difficult, suggesting an erratic failure mode. The bearing design, individual bearing fabrication, cage metallurgy, corrosion, and/or additive depletion may all influence bearing performance, as may water and oxygen levels.

4. The flow four-ball test using steel on silvered steel (the cage metallurgy) provided insights into additive

mechanisms and culled ineffective additives. The thin-film oxidation test produced fluid degradations typical of those encountered in the bearings. These were the most useful screening tests.

5. The most effective additive was a trifluromethylated phenylphosphinic acid. This produced the longest bearing life (111 hours). It generated less deposits than the unsubstituted phenylphosphinic acid, but much more than perfluoroglutaric acid after 100 hours.

6. Occasional peeling of silver from the side of the cage at the point of fluid impingement is probably not fluid related. It may result from poor adhesion of the silver to the underlay.

3.3 C-ETHERS: RECOMMENDATIONS

1. In future testing, use smaller, more available bearings. Such units will allow more test runs and much easier duplication, thereby giving more statistically significant tests.

2. Modify the bearing design to minimize cage wear by:

   a. Use of a wider land surface area (ref. 5).

   b. Use of an outer race riding retainer. This leads to less imbalance on the cage and hence more uniform wear.

   c. Using a higher oil flow rate (ref. 9).

   d. Changing the cage metallurgy.

3. If using silvered steel cages, employ a nickel rather than a copper strike to plate the steel.

4. Install a centrifugal filter to supplement the normal aircraft filters.

3.4 C-ETHER/DISILOXANES (MCS 1305)

Time and funding limitations precluded bearing tests on this oil. Bench testing showed:

1. This fluid is stable at least to 278°C in the absence of copper.

2. Some additives react very differently in C-ether/disiloxane mixtures than in C-ethers despite the similarities of these base stocks.

4. MATERIALS

4.1 BASE STOCKS

Some properties of the three base stocks are given in Table 1. All work on esters in this contract used MCS 1892. The previous contract (ref. 3) utilized another polyol ester designated Skylube® 450, and some of the tables in this report refer to test results on that product. The C-ethers are a proprietary family of jet engine lubricants. Chemically, these fluids are modified, all-aromatic polyphenyl ethers.

TABLE 1. - PROPERTIES OF BASE STOCKS

Property	MCS 524	MCS 1305	MCS 1892	Skylube 450
Chemical class	C-ether	C-ether/ disiloxane	Ester	Ester
Viscosity, cs				
37.8°C (100°F)	25.2	18.7	39.6	27.8
98.9°C (210°F)	4.1	3.5	7.0	5.5
260°C (500°F)	0.81	0.77	1.06	
$T_{D'}$ °C (°F)	367 (692)	391 (736)	312 (594)	
AIT, °C (°F)	504 (940)	471 (880)	427 (800)	435 (815)
Pour point, °C (°F)	-29 (-20)	-39 (-39)	-51 (-60)	-59 (-75)
Evap. loss, % [204°C (400°F), 6.5 hr]	10	11	0.93	2.7

4.2 ADDITIVES

The additives studied in this contract are listed in Table 2 with their sources. Table 3 codes some of these additives.

TABLE 2. - ADDITIVES

Additive	Abbreviation	Chemical Class	Source
Additive A-88	A-88		Monsanto Company
Bis(2-ethylhexyl) perfluoroglutarate; i.e., bis(2-ethylhexyl)-2,2,3,3,4,4-hexafluoropentanedioate	PFGE		Synthesized for the contract; see Appendix D.
Bis(3-{[3-(phenylthio)phenyl]thio}-phenyl)disulfide			Synthesized for the contract; see Appendix D.
Bis(trimethylsilyl) perfluoroglutarate; i.e., bis(trimethylsilyl)-2,2,3,3,4,4-hexafluoropentanedioate	SPFGA		Synthesized for the contract; see Appendix D.
Bis(trimethylsilyl) phosphonate			Synthesized for the contract; see Appendix D.
Dibenzyl disulfide			Commercial sample
Diphenyl disulfide			Commercial sample
Emcol PS-236		Organic phosphate ester	Witco Chemical
HITEC E-611		Calcium sulfonate	Edwin Cooper
HITEC E-644		Succinimide	Edwin Cooper
2-Mercapto-5-benzilideneimino-1,3,4-thiadiazole			Synthesized for the contract; see Appendix D.
1-Methylethyl phenylphosphinate	MEP		Synthesized for the contract; see Appendix D.
Methyl polysilicate cluster			Olin
Perfluoroglutaric acid; i.e.,2,2,3,3,-4,4-hexafluoropentanedioic acid	PFGA		Commercial sample
Phenylboric acid			Aldrich
Phenylphosphinic acid	PPA		Aldrich
[3-(Phenylthio)phenyl]phosphinic acid			Synthesized for the contract; see Appendix D
3-{[3-Phenylthio)phenyl]thio}benzoic acid			Synthesized for the contract; see Appendix D.
Potassium 3-(3-phenoxyphenoxy) phenate			Synthesized for the contract; see Appendix D.
Tetrahydro-2H-thiopyran-4-yl phenyl-phosphinate			Synthesized for the contract; see Appendix D.
Tetraphenyltin			Commercial sample.
Trichloroacetic acid	TCA		Commercial sample.
[3-(Trifluoromethyl)phenyl]phosphinic acid	FPPA		Synthesized for the contract; see Appendix D.
2-[2,2,2-Trifluoro-1-(trifluoromethyl)-ethoxy]ethyl phenylphosphinate			Synthesized for the contract; see Appendix D.

TABLE 3. - CODING OF ADDITIVES

CONTRACT NAS3-19746

A = 0.1% A-88 + 0.05% [3-(phenylthio)phenyl]phosphinic acid

B = 0.1% Emcol PS-236 + 0.05% dibenzyl disulfide

C = 0.1% 2-[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]ethyl phenylphosphinate

D = ∿0.07% perfluoroglutaric acid + 0.05% bis(2-ethylhexyl) perfluoroglutarate

E = 0.1% phenylboric acid

F = 0.1% 1-methylethyl phenylphosphinate

G = 0.1% 1-methylethyl phenylphosphinate + 0.05% trichloroacetic acid

H = 0.075% [3-(trifluoromethyl)phenyl]phosphinic acid

I = 0.1% [3-(trifluoromethyl)phenyl]phosphinic acid

J = 0.1% A-88 + 0.05% dibenzyl disulfide

K = 0.1% 2-mercapto-5-benzilideneimino-1,3,4-thiadiazole (filtered)

L = ∿0.07% perfluoroglutaric acid + 0.06% phenylphosphinic acid

CONTRACT NAS3-15333

PFGA = ∿0.07% perfluoroglutaric acid

TCA = 0.05% trichloroacetic acid

A-88 = 0.1% proprietary additive

5. LUBRICANT SCREENING TESTS

The screening dealt with the bearing problems of the aromatic base stocks: wear, deposits, and "peeling" loss of silver from the cage during longer test runs. The main effort went into predicting bearing life (usually cage wear failures), estimating deposits, and ranking additives.

Initially, the program had two parts. In the first, candidate fluids passed or failed macro oxidation-corrosion tests at 260°C and 278°C as well as checks on viscosity and pour points. Subsequently, five wear screening tests qualified eight additives and led to ranking and selection of the best three. The screening tests were:

Slow Four-Ball: M50 on M50
Slow Four-Ball: M50 on silvered 6415 (cage metallurgy)
Fast Four-Ball: M50 on silvered 6415
Rub-Block: M50 on M50:
(a) slow-speed friction
(b) fast-speed wear

All of these tests related to lubrication performance. The fast four-ball test additionally served as a deposit test.

Accumulated data eventually showed that the slow four-ball test on the cage metallurgy correlated best with bearing life. Hence, this test was used to cull blends likely to produce lubrication failures from more promising formulations.

Finally, when accurate prediction of bearing performance still remained elusive, we augmented the screening program with high frequency rig* and thin-film oxidation tests.

No single or combination of tests completely reflected bearing experience and, in particular, estimates of bearing life remained uncertain. Nevertheless, the screening provided valuable insights to critical performance properties. Consider, for example, the slow four-ball and thin-film oxidation tests. The former showed the exact temperature of additive reactions on metal surfaces and suggested specific types of additive reactions. The latter produced fluid changes typical of those encountered in the bearing and showed catalytic effects of silver and steel on fluid breakdown.

Appendix A describes each of the test rigs and their overall usefulness. It also contains the screening test data on C-ether fluids and MCS 1892, while Appendix B has the data on formulations of MCS 1305, the C-ether/disiloxane.

*A new reciprocating wear test. See Appendix A, part 5.

The peeling of cage silver at the point of fluid impingement may have originated in substandard plating. According to bearing failure analyses at SKF Industries, the plating on one bearing which showed this effect had inferior bonding to the underlay. This phenomenon, then, may not involve the fluids *per se*.

6. SELECTION OF ADDITIVES FOR BEARING TESTS

Nine candidate additives (A through H and L) which passed the preliminary screening are listed and coded in Table 3. Subsequent characterization included the bench tests listed in section 5.

The interpretation of these data and ranking of the additives encompassed the following steps:

(a) A weighting factor was assigned to each test to indicate its estimated significance in bearing life tests. Specifically,

Slow four-ball	= 12
Fast four-ball	= 3
Rub-block (friction)	= 3
Rub-block (wear)	= 3

Of these tests, the slow four-ball, M50 on silvered steel correlated best with bearing life and so received the largest factor. Regression analysis showed no correlation with the alternate metallurgy (M50 on M50), so this test received a factor of zero.

(b) A judgemental score described the performance of each additive in each test. The best performance was ten and the worst was zero.

(c) The product of the score per test times the weight of the test gave the rating per test.

(d) The sum of all the ratings per test produced the final rating of the additives for the entire screening program.

The results of this selection analysis are in Table 4 which, for comparison, includes several additives of known bearing life. Compound C was not bearing tested since its slow four-ball curve changed as a function of time and also with the amount of various impurities in the additive.

This selection technique is a Kepner-Tregoe decision analysis method (ref. 10).

TABLE 4. - SELECTION ANALYSIS OF ADDITIVES[a] IN MCS 524

Additive:		C	H	L	G	PFGA	B	D	A-88 + TCA	F	A	E	None
Test	Weight	Score (score x wt.)											
Slow four-ball	12	10 (120)	9 (108)	9.5 (114)	9 (108)	9.5 (114)	8 (96)	9.5 (114)	7 (84)	9 (108)	4 (48)	6 (72)	0 (0)
Fast four-ball	3	8 (24)	10 (30)	not run	7 (21)	8 (24)	6 (18)	7 (21)	8 (24)	5 (15)	5 (15)	3 (9)	0 (0)
Rub-block torque	3	9 (27)	9.5 (29)	9.5 (29)	9 (27)	8 (24)	4 (12)	4 (12)	(23)	3 (9)	8 (24)	2 (6)	4 (12)
Rub-block wear	3	9 (27)	10 (30)	9 (27)	9 (27)	not run	10 (30)	0 (0)	(15)	0 (0)	10 (30)	6 (18)	0 (0)
		198	197	170 + fast four-ball	182	162 + rub-block wear	156	147	146	132	117	105	12

[a] See Tables 2 and 3 for coding of additives.

7. BEARING TESTS

7.1 DESCRIPTION OF TEST APPARATUS, BEARINGS, AND CONDITIONS

Bearing tests took place in a custom designed high speed rig depicted schematically in Figure 1. Figure 2 is a simplified version of Figure 1 showing the positions of temperature measurements. The drive train consisted of an Erdco universal test stand (ref. 11) modified by the substitution of a 10:1 helical-geared speed increaser for the original 3:1 speed increaser. This change permitted the 50-horsepower drive motor to turn test bearings at continuously variable speed to past 30,000 rpm.

Consultations with bearing specialists at NASA, Pratt and Whitney and Midwest Aero Industries Corporation* fixed the bearing design. It is an 80-mm bore, ABEC Class 7 angular (25°) contact 18-ball bearing typifying current aircraft engine practice. Ball-to-raceway conformity is 52%. The cage, designed to ride on the inner race, has an imbalance limit of 3 g-cm at the land riding surface. Inner (split) and outer races are fabricated of M50 tool steel with a specified R_C 60 hardness and rms roughness of 15.2×10^{-6} cm (6×10^{-6} in.). The balls (1.428 cm or 0.5625 in. diameter) are also M50 steel of R_C 60 hardness. Their specified rms roughness is 5.08×10^{-6} cm (2×10^{-6} in.). The cage is fabricated of AMS 6415 steel of R_C 28-30 hardness silver plated to a depth of 2.54×10^{-3} to 5.08×10^{-3} cm (0.001-0.002 in.).

Marlin Rockwell Corporation manufactured the bearings acquired for this contract from a single heat and stabilized them for 340°C running.

Reference 3 gives details of the test head, lubricant system and test procedures.

The test conditions included:

	Contractual
Test duration	100 hours or prior lubrication failure
Bearing speed	2×10^6 mm-rpm (DN)
Contact stress	1.38×10^9 N/m² (200,000 psi) maximum, inner race
Test oil inlet temperature	204°C or 260°C for MCS 1892 260°C for C-ether oils
Bearing outer race temperature	260°C or 316°C for MCS 1892 316°C for C-ether oils

*Then of Royal Oak, Michigan; more recently a division of Pure Carbon Company of St. Mary's, PA.

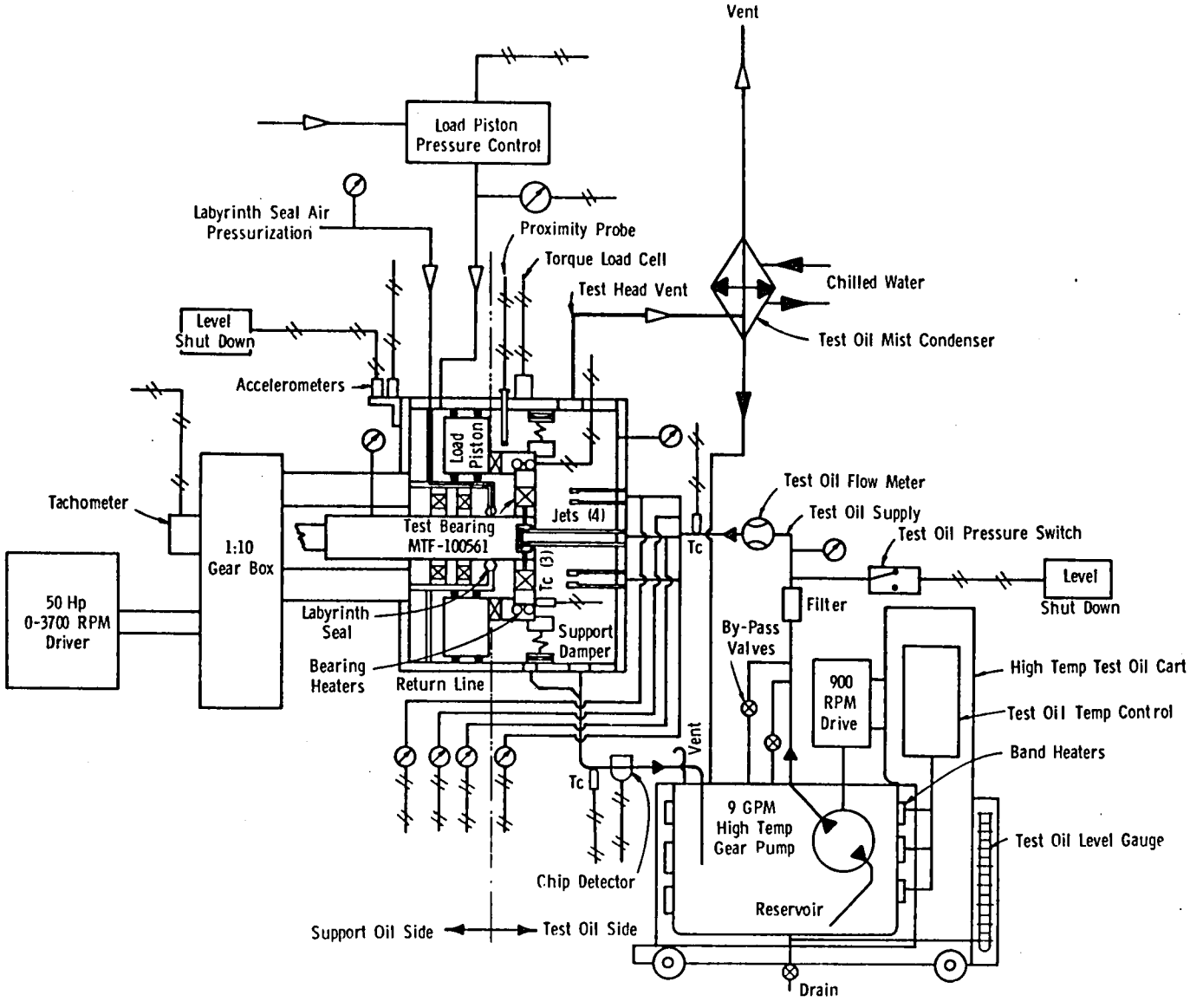


Figure 1. Bearing Test Rig

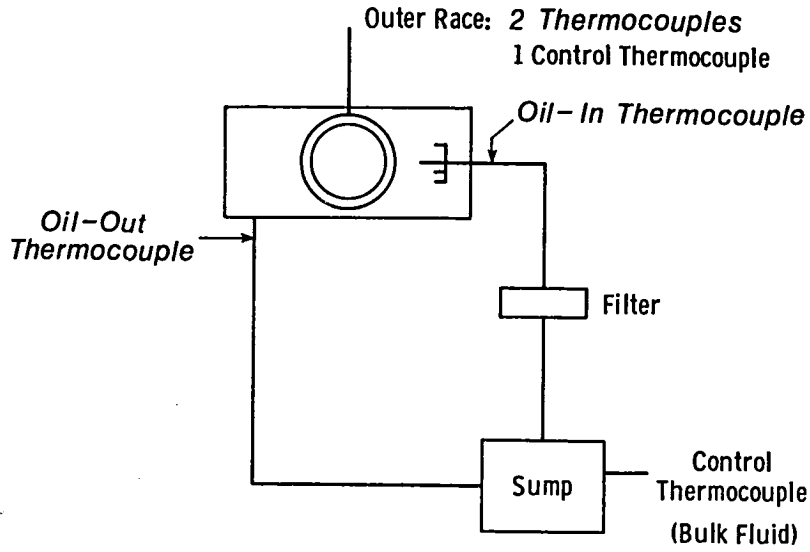


Figure 2. Simplified Schematic of the Test Bearing. Points of direct temperature measurements are shown in italics. Bulk temperature exceeds oil-in temperature by about 14°C.

	Noncontractual
Test oil flow rate	5.17×10^{-5} m³/s (0.82 gpm)
Test oil flow through jet	60% of above
Initial test oil charge	7000 cc
Test oil filter	10 μm (nominal), tests 16-19
	10 μm (nominal), replaced @66 hr by 200 μm SS screen, test 20
	10 μm + 1.5 μm (nominal) in parallel, test 21
	two 10 μm filters in parallel, tests 22-24

We will call the conditions of the oil inlet temperature at 260°C, the outer race temperature at 316°C, and the BOT around 274°C Type III conditions since these values closely match the Type III designation used by engine manufacturers to classify the severity of engine tests. Type II conditions in this report refer to an oil inlet of 204°C, a race temperature of 260°C and a BOT of about 218°C.

7.2 CALCULATION OF BEARING DEPOSIT RATINGS

The demerit rating on each item is a product of three factors:

area factor x rating factor x severity factor, OR

(% coverage) x (type of deposit) x (5.0)

The area factor is the percentage coverage. The rating factors for each type of deposit are given in Table 5. The severity factor is 5.0. Thus, for a part toally covered with light varnish, the deposit rating is:

$$1 \times 1 \times 5 = 5.0$$

The average of all 12 items is the overall deposit rating.

TABLE 5. - DEPOSIT RATING SCALE

Deposit Type	Rating Factor
Discoloration	0
Light varnish (translucent)	1
Medium varnish (opaque)	3
Heavy varnish (dark, has depth)	5
Light sludge <1/64"	6
Medium sludge 1/64" - 3/64"	7
Heavy sludge >3/64"	8
Light smooth carbon <1/64" (Chips when cutting edge applied.)	9
Medium smooth carbon 1/64" - 3/64"	10
Heavy smooth carbon >3/64"	11
Light crinkled carbon	12
Medium crinkled carbon	13
Heavy crinkled carbon	14
Light blistered carbon	15
Medium blistered carbon	16
Heavy blistered carbon	17
Light flaky carbon	18
Medium flaky carbon	19
Heavy flaky carbon	20

7.3 TEST RESULTS: MCS 1892

Three bearing tests characterized this ester. A large leakage of support oil into the MCS 1892 clouded the results from the first test at Type II conditions (about 218°C bulk). After a second successful 100-hour test at Type II conditions, the question arose: What performance is possible at higher temperatures given the known stability of this fluid?

To obtain a direct comparison with C-ethers, the third test employed Type III conditions (about 274°C bulk). Repeated filter pluggings ended this test after 70 hours, but only modest deposits formed on the bearing.

Table 6 reviews the salient highlights of the three bearing tests run on MCS 1982. Standout features include: *low deposit ratings and smooth bearing lubrication at all temperatures.* The data on Skylube® 450 allow comparison with performance by another ester.

TABLE 6. - BEARING TESTS ON MCS 1892

Test 16--Type II Conditions (218°C bulk)
Test 17--Type II Conditions
Test 18--Type III Conditions (274°C bulk)
Skylube 450 (ref. 3): Test 7--Type II Conditions

	Test 16 (100 hr)	Test 17 (100 hr)	Test 18 (70 hr)[a]	Skylube 450 (88 hr)[b]
Deposit rating	7.4	5.0	11.3	6.0
Viscosity increase, %	140	216	282	37
TAN	4.1	5.6	2.7	3.8
Metal uptake	Si, Mg	Mg	Fe, Mg	
Support oil leakage, %	6.4	0.26		
Bearing Serial No.	18	19	20	6

[a]Test terminated by filter pluggings.

[b]Test terminated due to a drive system malfunction.

The deposit ratings for MCS 1892 under Type II conditions were as low or lower than those previously obtained with Skylube 450. Even under the stringent Type III conditions which led to fluid degradation elsewhere in the system, the bearing deposit rating rose to only 11.3 - a rise caused by small amounts of carbon deposits. (Filter residues are not included in the rating.)

All of these tests were free of boundary or other lubrication problems. The fluid deposits which formed under Type III conditions produced filter pluggings but did not interfere with bearing lubrication. Thus, esters can provide wear-free lubrication up to race temperatures of 316°C.

The viscosity increase of MCS 1892 under Type II conditions exceeded that of the reference ester, as did the uptake of certain metals. This happened despite the superior performance of MCS 1892 in macro oxidation-corrosion tests.

Detailed descriptions of the three tests follow.

7.3.1 Bearing Test No. 16:* MCS 1892 at Type II Conditions

There were no wear failures after 100 hours at an outer race temperature of 260°C. The resulting fluid and bearing data were as follows:

Deposit rating	7.4
Viscosity increase	140%
Total acid number	4.08
Gravimetric analysis	54.0 mg/liter
Oil consumption	15.5 cc/hr

Deposit Rating

The deposit rating of 7.4 compares favorably with the rating of 6.0 for an 87-hour test on Skylube 450. While this is quite satisfactory, this rating is somewhat higher than expected based on the oxidation-corrosion properties of MCS 1892. Table 7 gives a detailed description of the deposits found in the bearing.

During this test, the front heater wires fatigued, and heat input came only from the rear heater. This may have produced a temperature gradient across the bearing. Deposits in the rear areas did exceed those in forward areas. Figures 3 through 5 are photos of the bearing and cage.

Viscosity Increase

The viscosity increase of 140% exceeded that of the Skylube 450 (37%). Because of this, and because of the low oil consumption observed during this test, suspicions grew that considerable contamination of the test oil by the support oil may have occurred. Infrared/liquid chromatography analysis of the 100-hr test oil showed 6.4% support oil in the ester. It is quite possible that this pollution catalyzed the viscosity increase as much as any inherent instability in the MCS 1892. Moreover, the viscosity of the support oil is quite a bit higher than that of the MCS 1892 (187 cs @ 38°C vs 30.6 cs). At a level of 6.4% of support oil in the ester, the final viscosity increase of the ester would be 97% rather than 140%. Viscosity increase as a function of time during the test is given in Table 8.

Lubricant Analyses

The fluid metal content, viscosity increase, and total acid number as a function of time are given in Table 8. The corresponding figures for Skylube 450 after 87 hours are also given.

*The numbering sequence continues from contract NAS3-15333.

TABLE 7. - DETAILED DEPOSIT RATING OF BEARING TEST NO. 16

Test Lubricant: MCS 1892

Item	Description	Area x Rating	Severity Factor	Demerits
Balls	100% clean (discolored)	0	5	0
Cage Periphery	50% discolored	0		
	40% light varnish	0.4	5	3.5
	10% medium varnish	0.3		
rear	90% light varnish	0.9	5	6.0
	10% medium varnish	0.3		
front	65% discolored	0		
	30% light varnish	0.3	5	2.25
	5% medium varnish	0.15		
inside	20% clean	0		
	30% light varnish	0.3		
	30% medium varnish	0.9	5	11.0
	20% heavy varnish	1.0		
	(5 ball widths light burnished)			
Outer Ring Path	50% discolored	0		
	40% light varnish	0.4	5	3.5
	10% medium varnish	0.3		
rear	50% medium varnish	1.5	5	20.0
	50% heavy varnish	2.5		
front	60% light varnish	0.6	5	9.0
	40% medium varnish	1.2		
Inner Ring Rear annulus	20% clean	0	5	24.0
	80% light hard sludge	4.8		
path	100% discolored	0	5	0
Inner Ring Front annulus	50% clean	0		
	20% light varnish	0.2	5	10.0
	30% light hard sludge	1.8		
path	100% discolored	0	5	0
			Total demerits =	89.25

Overall rating = 89.25/12 = 7.4

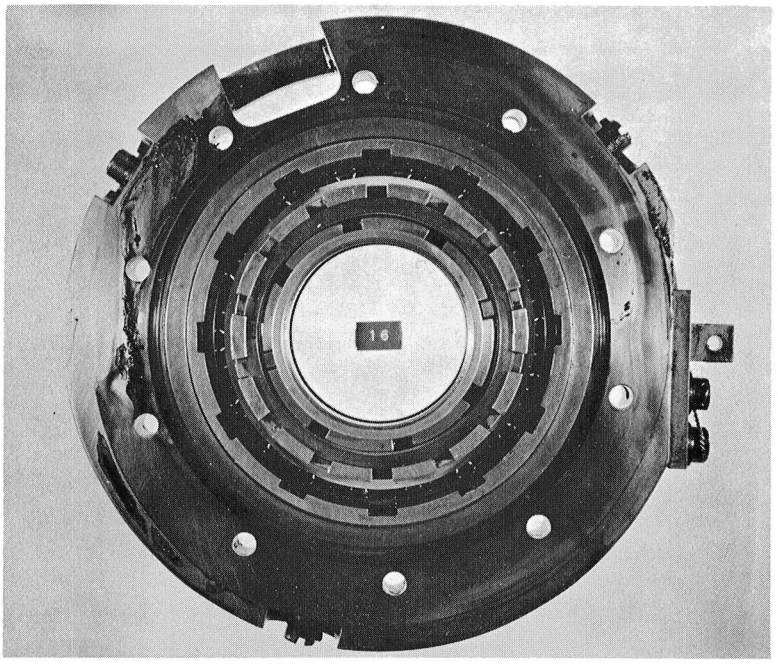


Figure 3. Bearing Test 16. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

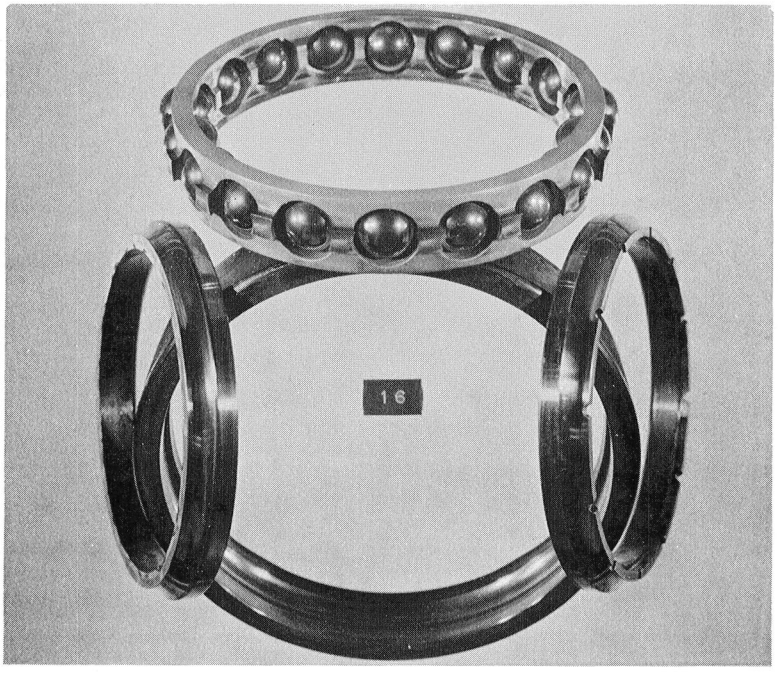


Figure 4. Bearing Test 16. Composite View of Test Bearing

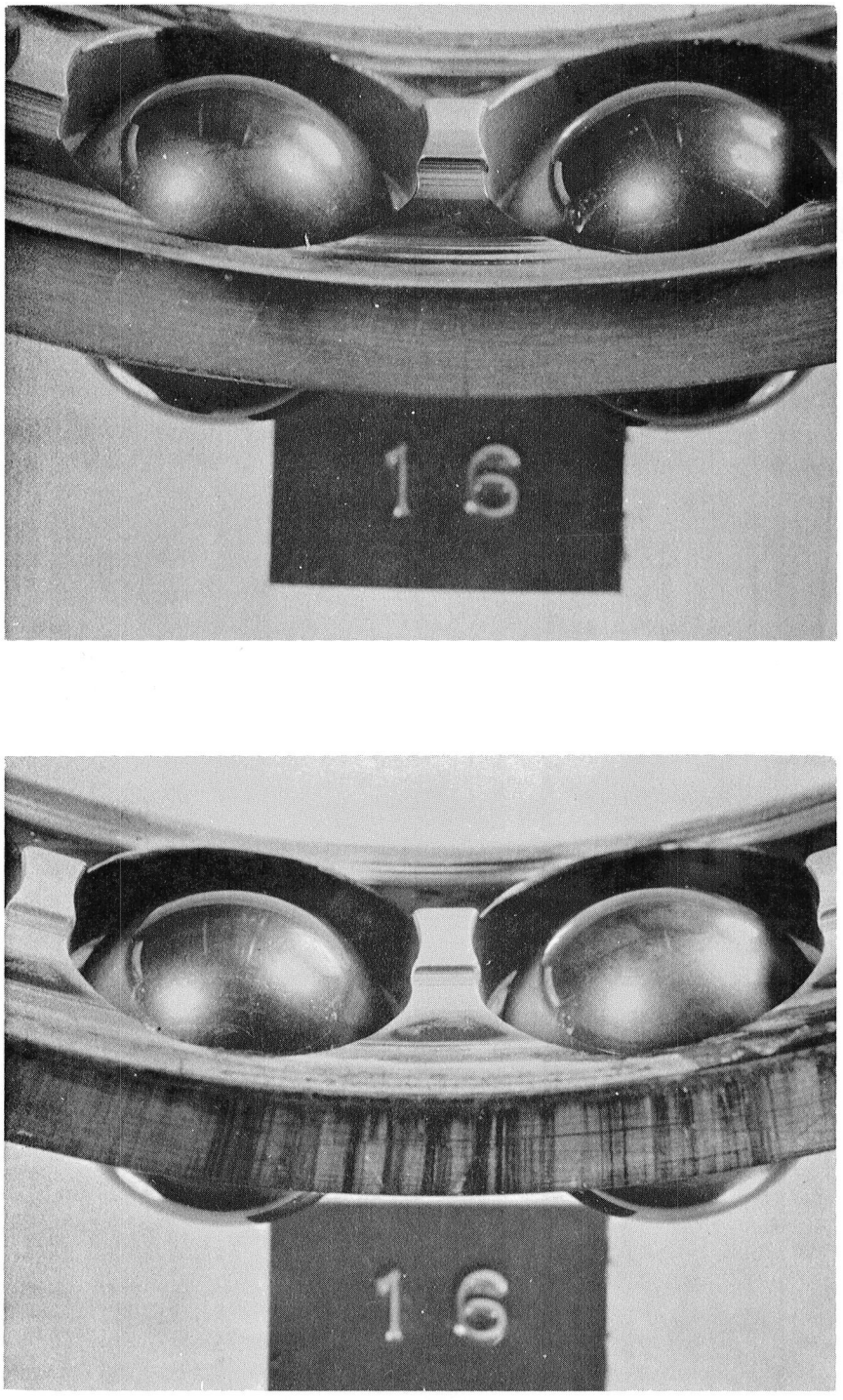


Figure 5. Bearing Test 16. Two Views of the Bearing Cage

TABLE 8. - LUBRICANT ANALYSES OF BEARING TEST NO. 16

Test lubricant:	MCS 1892						Skylube 450[a]	Support Oil
Sample number:	1	2	3	4	5	6		
Time taken, hours:	0	2.0	23.0	51.0	74.5	100.2	87	0
Metal content, ppm:								
Ni	0.9	1.1	1.3	1.3	1.4	1.7	0.1	0.1
Fe	5.2	6.5	7.0	8.2	10.0	15.7	10.2	4.5
Mg	1.2	1.1	1.8	4.8	5.9	6.6	0.4	0.4
Cu	<0.1	0.5	1.8	2.0	2.2	2.4	0.3	4.3
Ag	<0.1	0.3	0.8	1.6	4.4	5.1	<0.1	0.4
Cr	1.2	1.2	1.2	1.2	1.2	1.4	0.9	<0.1
Al	0.3	0.2	0.2	0.3	0.4	0.7	0.4	0.7
Si	7.8	33.4	51.0	56.4	57.5	51.0	4.7	83.4
Ti	0.2	0.2	0.5	0.5	0.5	0.5	<0.1	0.2
Zn	0.3	0.7	1.2	1.5	1.8	2.0		0.7
Kinematic viscosity, centistokes, at 37.8°C (100°F)		39.7	47.1	60.0	75.8	95.2		187.2
Viscosity increase, %		0.0	18.9	51.5	91.4	140.4	37.4	
TAN, mg KOH/g		0.29	0.88	1.69	2.90	4.08	3.76	0.14
Gravimetric analysis, mg solid/liter fluid						54.0		

[a]Bearing test No. 7, contract NAS3-15333.

As mentioned earlier, the viscosity increase for MCS 1892 was greater than that for Skylube 450. So also was the uptake of metals. This was true for every metal analyzed, but strikingly so for silicon which reached a maximum of 57 ppm after 74 hours. This cannot be explained totally by the uptake of 6% of support oil.

In conclusion, the performance of the MCS 1892 in this test was quite satisfactory. The fluid shortcomings were viscosity increase and metal uptake. However, the degradation was doubtlessly accentuated by the contamination of the MCS 1892 with support oil. This leakage occurred because of the misalignment of a seal plate gasket.

7.3.2 Bearing Test No. 17: MCS 1892 at Type II Conditions

Because support oil leakage created doubts about test 16, we repeated a Type II test on MCS 1892. The results closely matched those of test 16:

Deposit rating	5.0
Viscosity increase	221%
Total acid number	5.63
Gravimetric analysis	92 mg/liter
Oil consumption	38.5 cc/hr

The low deposit rating - the lowest observed - reflected the overall cleanliness of the bearing (Figures 6 through 8). Table 9 delineates the bearing deposits.

As before, the viscosity increase was on the high side. The support oil leakage during the test amounted to only 0.26% and so probably did not contribute much to the viscosity rise.

To check on leakage during the test, we turned to a new analytical method, namely, introduction of a radioactive compound into the support oil. Radioactivity in the test fluid would then measure any leakage.

The radioactive tracer, a synthetic hydrocarbon, was put into the support oil at 30.5 hours and counting showed that a small amount of leakage subsequently took place. The data in Table 10 reveal a break in viscosity at about this time. However, this is believed to be fortuitous because of the very small amount of tracer, less than 1 gram. Or, stated another way, if the support oil leakage is not significant, leakage of a tracer is even less likely to be decisive.

Table 10 gives the metal content, viscosity increase and total acid number as a function of time along with the corresponding figures for Skylube 450. MCS 1892 had higher metal levels particularly for iron and magnesium.

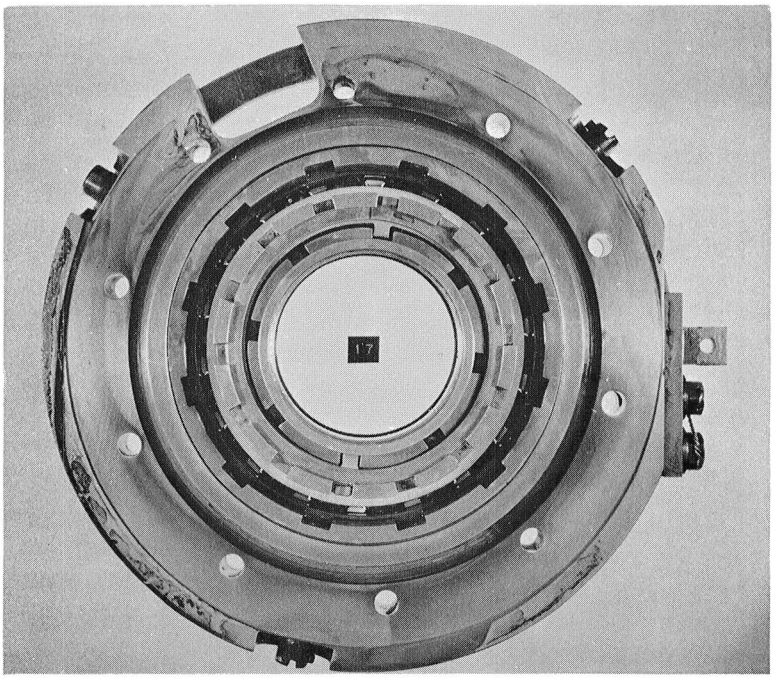


Figure 6. Bearing Test 17. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

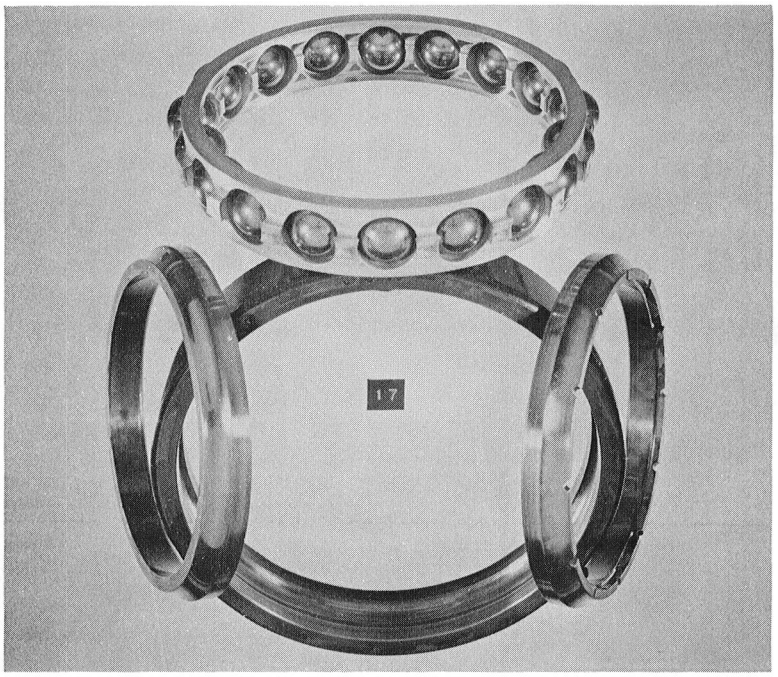


Figure 7. Bearing Test 17. Composite View of Test Bearing

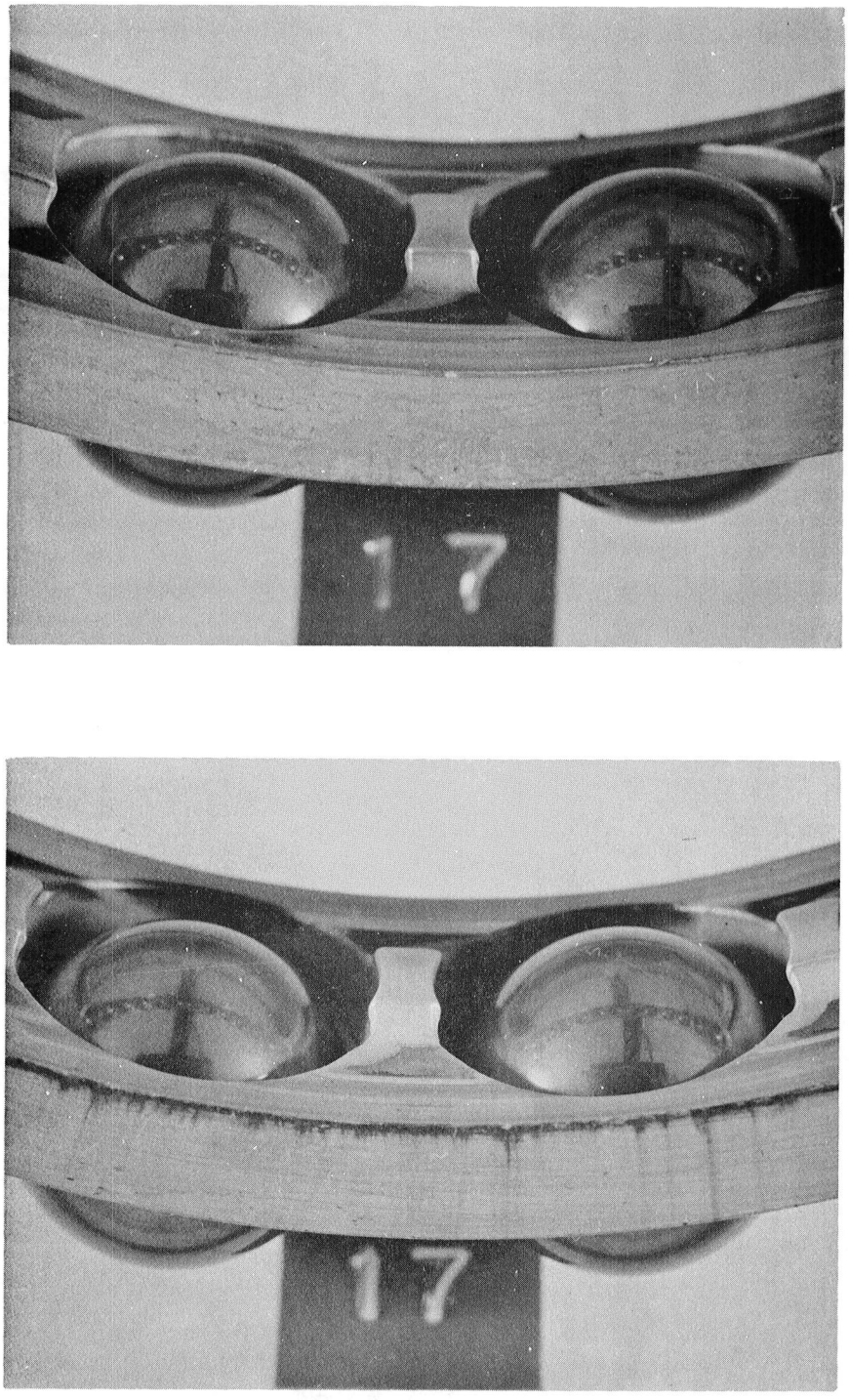


Figure 8. Bearing Test 17. Two Views of the Bearing Cage

TABLE 9. - DETAILED DEPOSIT RATING OF BEARING TEST NO. 17

Test Lubricant: MCS 1892

Item	Description	Area x Rating	Severity Factor	Demerits
Balls	100% clean (some discoloration)	0	5	0
Cage Periphery	50% discolored	0		
	30% light varnish	0.3	5	4.5
	20% medium varnish	0.6		
rear	97% light varnish	0.97	5	5.3
	3% medium varnish	0.09		
front	95% clean	0	5	0.25
	5% light varnish	0.05		
inside	40% clean	0		
	30% light varnish	0.3	5	7.0
	20% medium varnish	0.6		
	10% heavy varnish	0.5		
Outer Ring Path	40% discolored	0		
	40% light varnish	0.4	5	5.0
	20% medium varnish	0.6		
rear	60% medium varnish	1.8	5	19.0
	40% heavy varnish	2.0		
front	80% light varnish	0.8	5	7.0
	20% medium varnish	0.6		
Inner Ring Rear annulus	50% clean	0		
	40% light hard sludge	2.4	5	15.5
	10% medium hard sludge	0.7		
path	100% discolored	0	5	0
Inner Ring Front annulus	80% discolored	0	5	6.0
	20% light hard sludge	1.2		
path	80% clean	0	5	0
	20% discolored	0		

Total demerits = 59.55

Overall rating = 59.55/12 = 5.0

TABLE 10. - LUBRICANT ANALYSES OF BEARING TEST NO. 17

Test lubricant:	MCS 1892					Skylube 450[a]
Sample number:	1	2	3	4	5	
Time taken, hours:	1	2.2	47	74	100	87
Metal content, ppm:						
Ni	1.1	1.1	1.3	1.5	1.7	0.1
Fe	6.6	8.0	17.9	26.2	34.0	10.2
Mg	1.3	3.1	8.4	28.5	48.6	0.4
Cu	0.7	2.1	2.3	2.9	3.3	0.3
Ag	0.2	0.5	0.5	0.4	0.4	<0.1
Cr	1.2	1.2	1.4	1.9	2.1	0.9
Al	0.2	0.3	0.3	0.3	0.3	0.4
Si	8.2	8.9	10.0	10.5	10.7	4.7
Ti	0.1	0.1	0.1	0.1	0.1	<0.1
Kinematic viscosity, centistokes, at 37.8°C (100°F)	40.3	44.0	76.4	102.4	127.1	
Viscosity increase, %	1.8	11.1	92.9	158.6	221.0	37.4
TAN, mg KOH/g	0.27	0.67	5.57	5.61	5.63	3.76
Gravimetric analysis, mg solid/liter fluid					92	

[a]Bearing test No. 7, contract NAS3-15333.

7.3.3 Bearing Test No. 18: MCS 1892 at Type III Conditions (Figures 9 through 11)

To directly compare esters and C-ethers, the third bearing test on MCS 1892 used Type III conditions:

Bulk temperature	274°C (∿525°F)
Test oil inlet temperature	260°C (500°F)
Outer race temperature	316°C (600°F)
Test duration	100 hours or prior failure
Bearing speed	2×10^6 mm-rpm (DN)
Contact stress	1.38×10^9 N/m² (200,000 psi), max. Hertz, inner race

These conditions represent a typical bearing environment for C-ethers, but they are very severe for esters which give heavy deposits in oxidation-corrosion tests at 260°C. Indeed, the bulk temperature exceeds that at which inherent rupture of carbon-oxygen bonds in esters can occur. Moreover, there was the possibility that deposits could induce lubrication failure.

In spite of this, the Type III test lasted 70 hours. No lubrication problems interrupted the test, and the general cleanliness exceeded expectations. The deposit rating of 11.3 was roughly double that of the previous tests and resulted primarily from small carbon deposits. In addition, the sump stayed relatively clean. However, considerable fluid degradation occurred as evidenced by the following:

- Viscosity increase (282%)
- Six filter pluggings
- Carbon pluggage of the condenser drain line
- Dirty mounts
- Large uptake of iron and magnesium

Solid formation in the fluid caused the filter to plug at 7.2, 29, 33.5, 51.8, 63.7 and 70.5 hours, and these delays finally terminated the test. In contrast, the sump was fairly clean and deposit free. The gravimetric analysis of 75.0 mg/liter was not excessive.

The extra thermal-oxidative stress put on the ester by the Type III conditions doubtless led to the above decomposition-related problems. Still, the overall bearing cleanliness was tolerable, and there were no wear problems and no evidence of incipient boundary failure. Thus, esters can lubricate the bearing at a bearing temperature of 316°C.

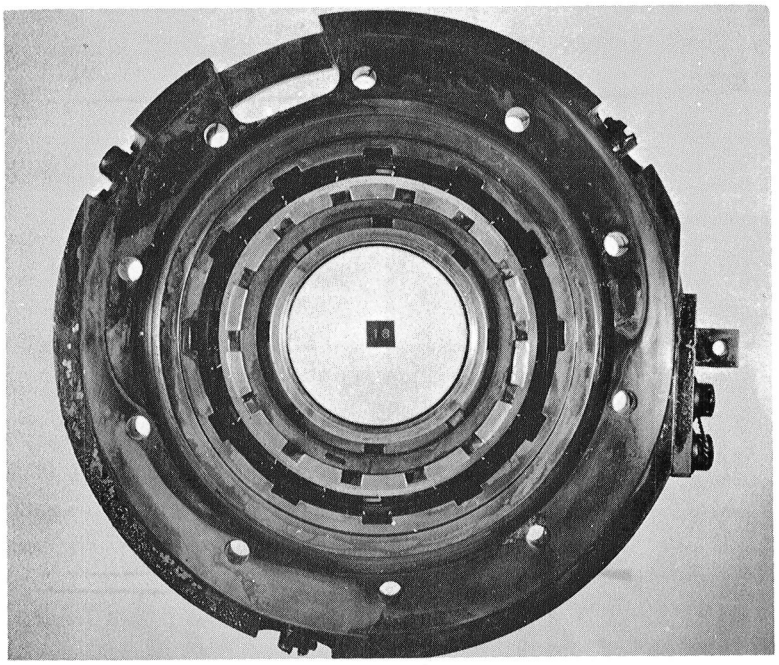


Figure 9. Bearing Test 18. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

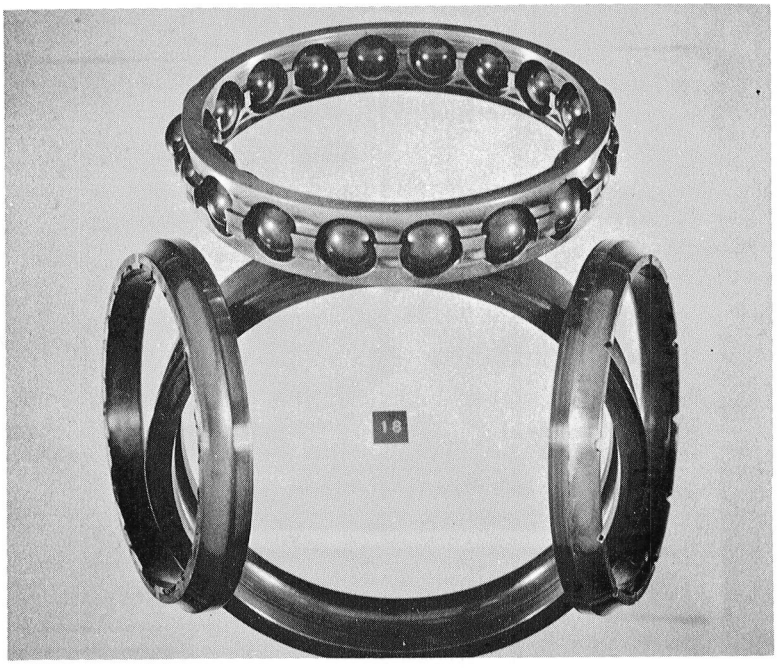


Figure 10. Bearing Test 18. Composite View of Test Bearing

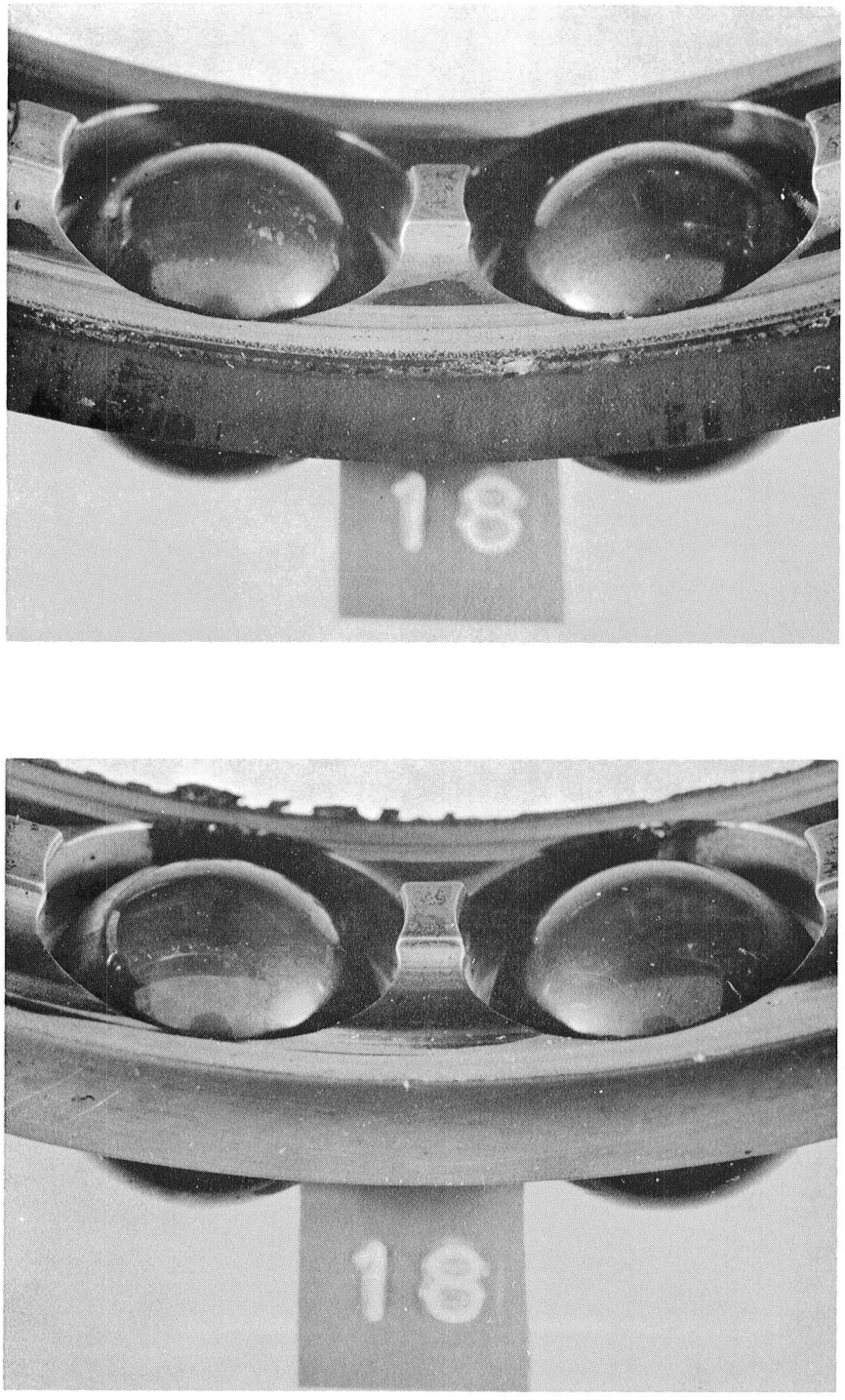


Figure 11. Bearing Test 18. Two Views of the Bearing Cage

Further details of various test parameters are provided below.

Deposit Rating (Table 11)

The deposit rating, 11.3, was about twice that of previous tests. Unlike before, carbon deposits appeared in four areas, and this, of course, raised the overall rating.

Viscosity Increase

The large viscosity increase, 282%, reflected the harsh environment of the test. Moreover, this increase is deceptive in that it does not take into account the extra charges of make-up fluid. All told, the make-up amounted to 5.5 liters and partially offset the viscosity and acid increases of the original oil. The viscosity increase as a function of time is given in Table 12.

Lubricant Analyses

The time increments of viscosity, acid number and metal uptake are shown in Table 12 as is the gravimetric analysis on the 70-hour sample. Note the large uptake of iron and magnesium (494 and 67 ppm, respectively). Surprisingly, the gravimetric analysis was not particularly high and did not reflect continued filter pluggings. Indeed, it was smaller than the analysis from test 17 which had no filter pluggings at all.

The filter residues consisted predominantly of inorganic matter such as iron salts plus smaller amounts of carboxylate salts. Breakdown of the base stock generated the carboxylates.

7.4 TEST RESULTS: C-ETHERS

Six bearing tests characterized five new C-ether formulations. Despite deposit-related interruptions, one fluid ran for 111 hours without catastrophic cage failure.

Drastic cage-to-race wear failures ended runs at 25, 16 and 13 hours, but one of these failures may have resulted from rig-related problems.

In the fifth test, the outer race and five balls suffered fatigue spalling after 81 hours, and a repeat of this run gave a cage failure after 1 hour. Table 13 summarizes these results.

The reference points here are the wear-free bearing tests on esters and the tests on the unformulated C-ether base stock. The latter ran for only 1 hour before the bearing overheated. Further running is possible, but steady, unremitting wear continued, and very massive retainer damage resulted after 15 hours

TABLE 11. - DETAILED DEPOSIT RATING OF BEARING TEST NO. 18

Test Lubricant: MCS 1892

Item	Description	Area x Rating	Severity Factor	Demerits
Balls	100% (discolored)	0	5	0
Cage Periphery	20% discolored	0		
	50% light varnish	0.5		
	25% medium varnish	0.75	5	7.5
	5% heavy varnish	0.25		
rear	80% light varnish	0.8		
	5% medium varnish	0.15		
	5% heavy varnish	0.25	5	10.5
	10% light smooth carbon	0.90		
front	80% clean	0		
	10% light varnish	0.1	5	2.0
	10% medium varnish	0.3		
inside	30% light varnish	0.3		
	30% medium varnish	0.9		
	20% heavy varnish	1.0	5	20.0
	20% light smooth carbon	1.8		
Outer Ring Path	30% clean	0		
	70% light varnish	0.7	5	3.5
rear	60% medium varnish	1.8		
	40% heavy varnish	2.0	5	19.0
front	40% discolored	0		
	60% light varnish	0.6	5	3.0
Inner Ring Rear annulus	20% discolored	0		
	10% medium varnish	0.3		
	40% light smooth carbon	3.6	5	39.0
	30% medium crinkled carbon	3.9		
path	60% discolored	0		
	40% light varnish	0.4	5	2.0
Inner Ring Front annulus	20% discolored	0		
	20% light varnish	0.2		
	20% medium varnish	0.6		
	10% heavy varnish	0.5	5	25.0
	20% light crinkled carbon	2.4		
	10% medium crinkled carbon	1.3		
path	60% discolored	0		
	20% light varnish	0.2	5	4.0
	20% medium varnish	0.6		

Total demerits = 135.5

Overall rating = 135.5/12 = 11.3

TABLE 12. - LUBRICANT ANALYSES OF BEARING TEST NO. 18

Test lubricant:	MCS 1892								Skylube 450[a]
Sample number:	1	2	3	4	5	6	7	8	
Time taken, hours:	0	4.5	12.0	25.3	31.3	44.0	58.2	70.5	87
Metal content, ppm:									
Ni	0.8	1.0	1.1	1.4	1.2	1.8	2.0	2.6	0.1
Fe	6.8	10.0	25.8	57.2	74.0	132.3	190.0	493.5	10.2
Mg	1.1	3.2	5.9	10.7	13.6	42.6	55.2	67.2	0.4
Cu	<0.4	1.6	2.3	2.7	1.8	2.3	2.5	2.9	0.3
Ag	<0.2	0.4	0.7	0.8	0.6	0.8	0.9	1.1	<0.1
Cr	1.3	1.5	1.6	2.0	1.7	1.7	2.0	2.5	0.9
Al	0.2	0.3	0.2	0.4	0.5	0.8	0.9	1.1	0.4
Si	3.8	5.4	4.9	6.4	6.2	7.9	7.1	8.7	4.7
Ti	0.2	0.3	0.6	0.6	0.5	1.1	1.3	2.6	<0.1
Kinematic viscosity, centistokes, at 37.8°C (100°F)				54.8	50.5	64.3	80.2	151.4	
Viscosity increase, %				38.4	27.5	39.6	102.5	282.3	37.4
TAN, mg KOH/g	0.35	0.71	0.78	2.01	1.27	1.48	1.89	2.67	3.76
Gravimetric analysis, mg solid/liter fluid								75.0	

[a]Bearing test No. 7, contract NAS3-15333.

TABLE 13. - RESULTS OF C-ETHER BEARING TESTS

Test No.	Fluid[a]	Bearing Serial No.	Outer Race Temp., °C	Hours Run	Failure Mode; Comments
19	MCS 524 + G	21	316	13	cage wear
20	MCS 524 + H	22	316	111	no failure
21	MCS 524 + ∿0.07% PFGA + 0.06% PPA	23	316	25	cage wear
22	MCS 524 + ∿0.07% PFGA + 0.06% PPA + 0.1% SPFGA	24	316	16	cage wear
23	MCS 524 + ∿0.07% PFGA + 0.3% SPFGA	25	316	81	fatigue
24	Same as test 23	26	316	1	cage wear

[a]See Tables 2 and 3 for coding of the additives.

(ref. 3). In contrast, most formulations lubricated the bearing very smoothly without appreciable wear until shortly before a failure. This failure pattern suggests additive depletion effects.

Despite these numerous cage-related failures, C-ethers have in fact lubricated silvered cages but under conditions quite different from those used in this contract. For example:

- The ten 2000-hour fatigue tests on the Pratt & Whitney JT3D engine bearings used silvered 6415 cages. The outer race temperature reached about 195°C (ref. 2).
- Silvered M-1 steel cages survived inerted tests on polyphenyl ethers and C-ethers at 260°C. However, best results came from cages with wider than standard guide lands. Later inerted tests with this metallurgy ran at 315°C (ref. 5 and 6).

However, extrapolations from these environments to a high temperature air system and different bearing designs are difficult. In the present study, cage wear represents a weak link, the point of most lubrication failures, and even the most successful fluids of this contract did not totally preserve the cage silver in the cage imbalance contact zone. This wear may have resulted from low film thickness or because the fluid's low viscosity at 316°C induced cage instability and extraneous motion. Reference 5 outlines other factors important to lubrication above 260°C. Finally, chemical effects peculiar to

aromatic oils, steel and silvered steel will influence the wear rate, and critical chemical reactions appear necessary to overcome boundary or elastohydrodynamic wear. Some reactions which may specifically or distinctly involve a silvered cage in contact with steel include:

- Formation on the silver and/or the race steel of surface coatings or soaps by additives or base stocks. Unformulated C-ethers apparently can't protect silver by this mechanism.
- Formation by air of ion oxides. This reaction varies with oxygen concentration and increases the friction and wear of silver-iron couples (ref. 12). Some C-ether bearing tests have had better success inerted than in air (ref. 5, 6 and 7).
- Silver catalyzed deposit formation. The thin-film oxidation tests (Appendix A, section 2) show silver generates two to five times more fluid degradation than steel.

Both fluid breakdown and the wear process itself can generate deposits. Just how such particles interrelate with overall wear is not known, but presumably their effects would be destructive. However, the literature (ref. 13) describes a beneficial breakdown process for polyphenyl ethers. Both the bearing tests and thin-film oxidation tests of this contract show that for C-ethers the deposits vary markedly with additives.

The following sections describe the six C-ether bearing tests in detail. They include a descriptive history of each run, visual analyses of the bearings, deposit ratings for tests of 100 hours or more, and chemical and physical analyses of the test fluids. Appendix F contains post-test failure analyses of some of the bearings.

7.4.1 Bearing Test No. 19: MCS 524 + 0.1% 1-Methylethyl Phenylphosphinate + 0.05% Trichloroacetic Acid (Test Duration 13 Hours)

Despite doing well in the bench screening program where it ranked fourth of nine C-ether formulations, this blend lubricated the bearings for only 13 hours. Moreover, early filter pluggings occurred at 1.5 and 3.1 hours. At 12.9 hours, solids suddenly and completely blinded the filter. Apparently this stopped any fluid flow, and some starvation may have resulted during the idle down (approximately 30 seconds). The chip detector bridged during the subsequent heatup, thereby terminating the test.

Excessive, drastic cage wear on the inner race directly caused the test failure. Distortions of the bearings revealed

the great stress felt during the failure. At the conclusion of the test, cage expansion against the race prevented normal disassembly of the bearing, and deformation had enlarged many of the ball sockets (Figures 12 through 14).

No attempt was made to perform a deposit rating on the bearing since the test lasted only 13 hours. The fluid viscosity rose by 9.9%. Further details of the fluid analyses are presented in Table 14. The most notable metal uptake was that of silver which rose to 69 ppm. The gravimetric analysis at the end of the test was 338 mg/liter, reflecting the large amount of wear that occurred. The support oil leak amounted to 800 ppm; this analysis also showed a contamination of 30 ppm of ester lubricant presumably from the preceding bearing test.

TABLE 14. - LUBRICANT ANALYSES OF BEARING TEST NO. 19

Test lubricant:	MCS 524 + G[a]				
Sample number:	1	2	3	4	5
Time taken, hours:	Unused	0.5	5.3	12.9	∿13
Metal content, ppm:					
Ni		2.4	2.4	2.8	3.1
Fe		17.0	13.5	57.3	64.3
Mg		0.7	0.7	0.6	0.6
Cu		1.6	1.0	1.3	1.3
Ag		0.8	3.6	8.7	9.5
Cr		0.2	0.5	0.8	0.8
Al		0.6	0.5	0.5	0.5
Si		33.2	41.0	56.2	69.0
Ti		0.1	0.1	0.1	0.1
K		150	240	263	258
Kinematic viscosity, centistokes, at 37.8°C (100°F)	24.3	24.7	25.3		26.7
Viscosity increase, %		1.6	4.1		9.9
TAN, mg KOH/g		0.28	0.11		0.11
Gravimetric analysis, mg solid/liter fluid					338

[a]Coded in Table 3.

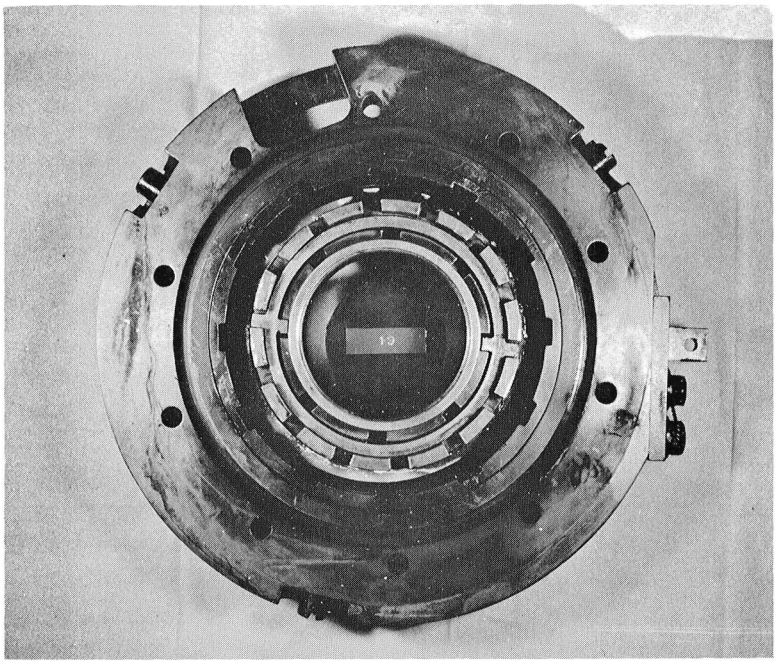


Figure 12. Bearing Test 19. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

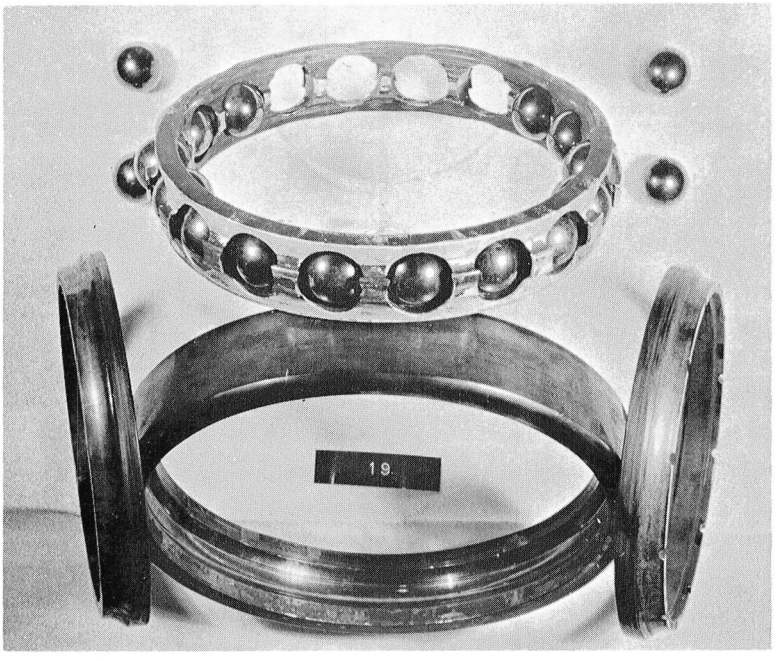


Figure 13. Bearing Test 19. Composite View of Test Bearing

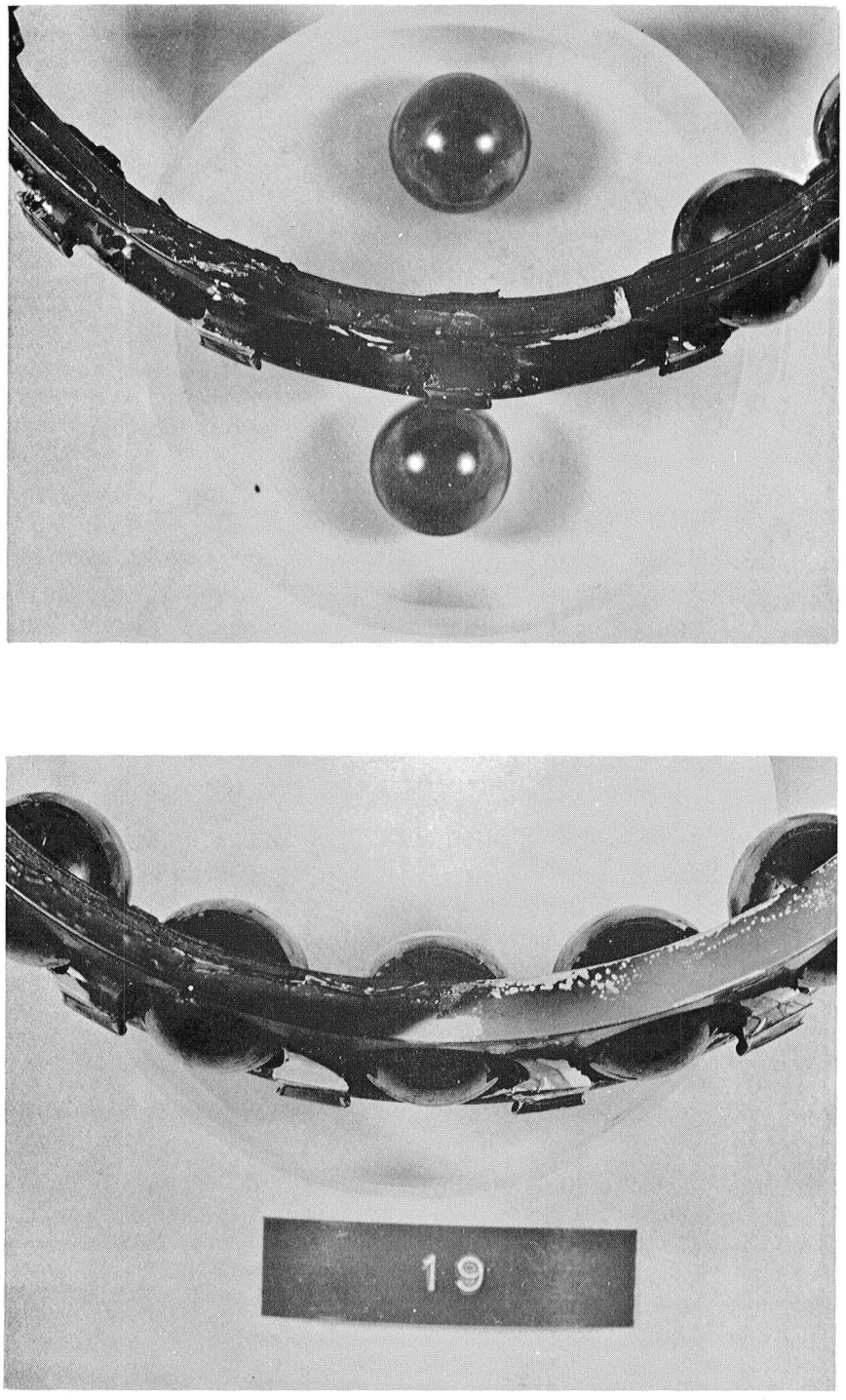


Figure 14. Bearing Test 19. Two Views of the Bearing Cage

Chemical Analysis of Filter Residues

Solids from the first filter plugging contained large amounts of carbon, iron, potassium, and phosphorus. Typical values for these elements would be 50, 5, 5, and 9%, respectively. Solids from the third filter plugging contained much less carbon (16%) and phosphorus (3%) and much more iron (19%) and silver (2%). Apparently, the initial solids involved the phosphorus ester additive; the later solids are much higher in wear debris.

Additive Depletion

Phosphorus analysis showed the drain fluid had lost 69% of the phosphinate ester. The chlorine in the drain fluid exceeded the theoretical amount contributed by trichloroacetic acid, possibly because of the presence of chlorine-containing impurities in the base stock.

7.4.2 Bearing Test No. 20: MCS 524 + 0.075% [3-(Trifluoromethyl)phenyl]phosphinic Acid (Test Duration 111 Hours)

This test fluid accomplished the contract goal of a 100-hour run without lubrication failure. Indeed, because of an error in the test log, the test ran for 111 hours instead of the usual 100 hours. While covered with considerable deposits, the silver coating on the inside of the cage contacting the inner race remained basically intact. However, bearing imbalance wear removed silver from four adjacent ball pockets in the cage. A post-test analysis of the bearing is included in Appendix F.

Despite this promising result, numerous problems bedeviled this run. Inordinate deposits caused five filter pluggings and a high deposit rating; intermittent foaming stopped the test at one point; silver eventually peeled from the side of the cage.

Problems

The problems are discussed in greater detail below, followed by a discussion of the test results.

Filter Pluggings--
These occurred at 8.7, 24.4, 32.7, 55 and 66 hours. The second of these may have been an artifact caused by concurrent foaming of the fluid. However, the remainder were bona fide pluggings.

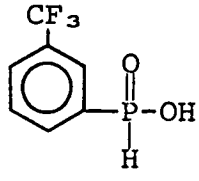
After the plugging at 66 hours, we replaced the 10-micron (nominal) Purolator filter with a 100-mesh screen. The bearing ran for the next 45 hours without further filter problems, but the amount of particulate matter in the fluid increased tremendously. The sedimentary analysis at 33 hours was 11.4 mg/liter, while that at 111 hours was 53,013 mg/liter.

Silver stripped or peeled from the cage did not plug the first three filters since visual inspection showed this peeling did not start until past the half-way mark of the test. Likewise, really excessive cage wear did not occur and so could not have caused the filter problems.

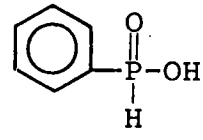
Deposits--

This was not a clean test. Carbon deposited on parts of the cage and elsewhere, producing a deposit rating of 25.3. In contrast, esters would have a rating of 11 after 70 hours. Details of the types and locations of the deposits are given in Table 15, and Figures 15 through 17 are photos of the bearing. (See also Figures F1 and F2 of Appendix F.)

The extent of deposits is doubly critical because we selected the additive to minimize deposits. The additive is a fluorinated derivative of phenylphosphinic acid which had been used in bearing test No. 12 (ref. 3).



Additive in Test 20



Additive in Test 12

Large amounts of sludge quickly formed during a Type III bearing test on the unsubstituted acid in MCS 524, and overheating of the bearing eventually resulted. We turned to a fluorinated, oleophobic chain and lower concentration to avoid this. In fact, window observation of the bearing showed a reasonably clean run until about the time of the installation of the 100-mesh screen. The overall cleanliness at the end of the test was unsatisfactor however, though an improvement over the earlier test.

Solids from the filters, the bearing hub annulus, and the bearing assembly face all contained large amounts of carbon (30 to 73%), modest amounts of iron (0.5 to 3.2%) and some silver (0.4 to 7.4%). The high carbon content suggests the solids are fluid or additive related rather than wear products.

Peeling of Silver from the Edge of the Cage--

The test removed virtually all of the silver on the front edge of the cage, the position of fluid impingement on the cage. This loss may not involve the fluid, but rather the quality of silver plating (see Appendix F, page 126).

TABLE 15. - DETAILED DEPOSIT RATING OF BEARING TEST NO. 20

Test Lubricant: MCS 524 + 0.075% CF_3-$\emptyset PO_2H_2$ (FPPA)

Item	Description	Area x Rating	Severity Factor	Demerits
Balls	100% light varnish	1	5	5.0
Cage Periphery	∿30% silver removed			
	85% light varnish	0.85	5	8.75
	15% light sludge	0.9		
rear	40% clean	0	5	37.75
	5% light smooth carbon	0.45		
	15% light crinkled carbon	1.8		
	30% medium crinkled carbon	3.9		
	10% heavy crinkled carbon	1.4		
front	95% silver removed			
	90% discolored	0	5	3.0
	10% light sludge	0.6		
inside	4 ball pockets silver removed (∿20%)			
	20% discolored	0	5	25.5
	5% light varnish	0.05		
	10% medium varnish	0.3		
	20% heavy varnish	1.0		
	10% light sludge	0.6		
	35% light smooth carbon	3.15		
Outer Ring Path	60% light varnish	0.6	5	18.0
	20% medium varnish	0.6		
	20% light crinkled carbon	2.4		
rear	10% medium varnish	0.3	5	56.0
	80% light crinkled carbon	9.6		
	10% medium crinkled carbon	1.3		
front	50% medium varnish	1.5	5	37.5
	50% light crinkled carbon	6.0		
Inner Ring Rear annulus	15% medium varnish	0.45	5	60.0
	5% medium smooth carbon	0.5		
	5% heavy smooth carbon	0.55		
	75% heavy crinkled carbon	10.5		
path	60% discolored	0	5	3.0
	30% light varnish	0.3		
	10% medium varnish	0.3		
Inner Ring Front annulus	15% clean	0	5	34.5
	20% discolored	0		
	5% light varnish	0.05		
	5% heavy varnish	0.25		
	5% light sludge	0.30		
	30% light crinkled carbon	3.6		
	10% medium crinkled carbon	1.3		
	10% heavy crinkled carbon	1.4		
path	10 light varnish	0.1	5	14.0
	90% medium varnish	2.7		
			Total demerits =	303

Overall rating = 303/12 = 25.3

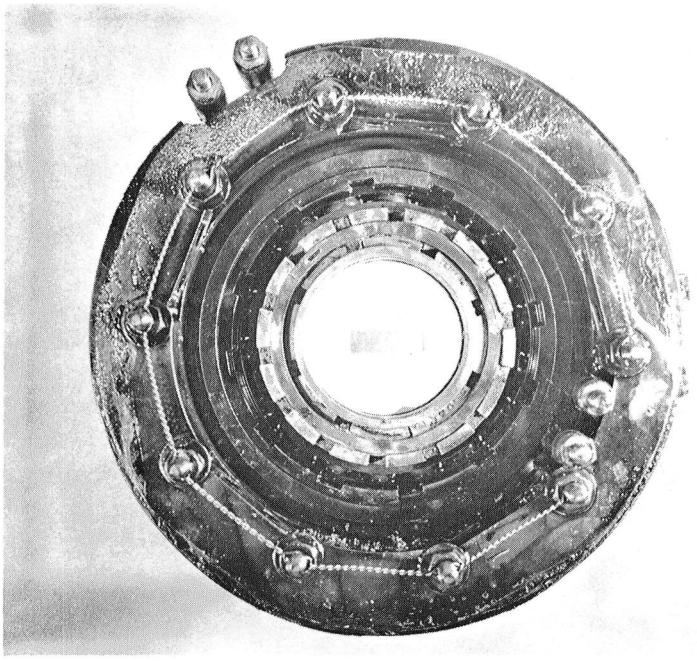


Figure 15. Bearing Test 20. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

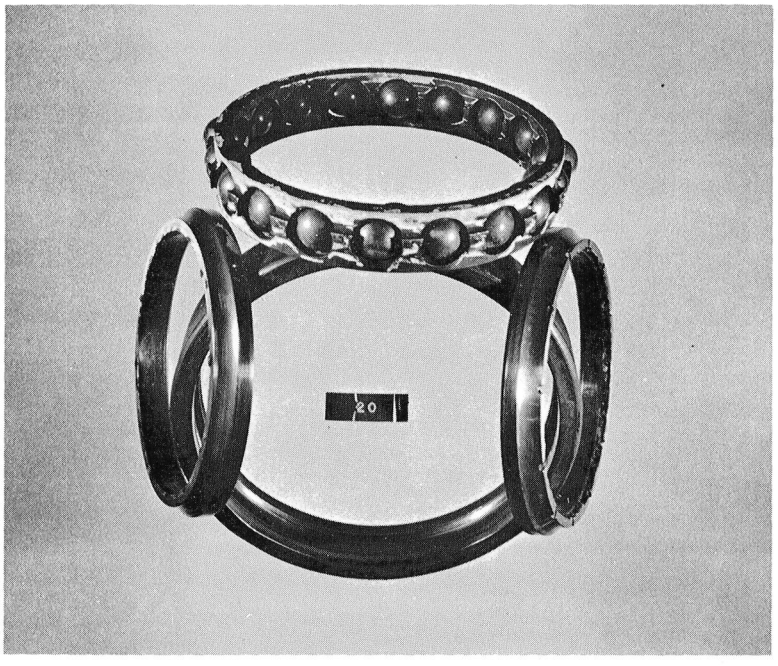


Figure 16. Bearing Test 20. Composite View of Test Bearing

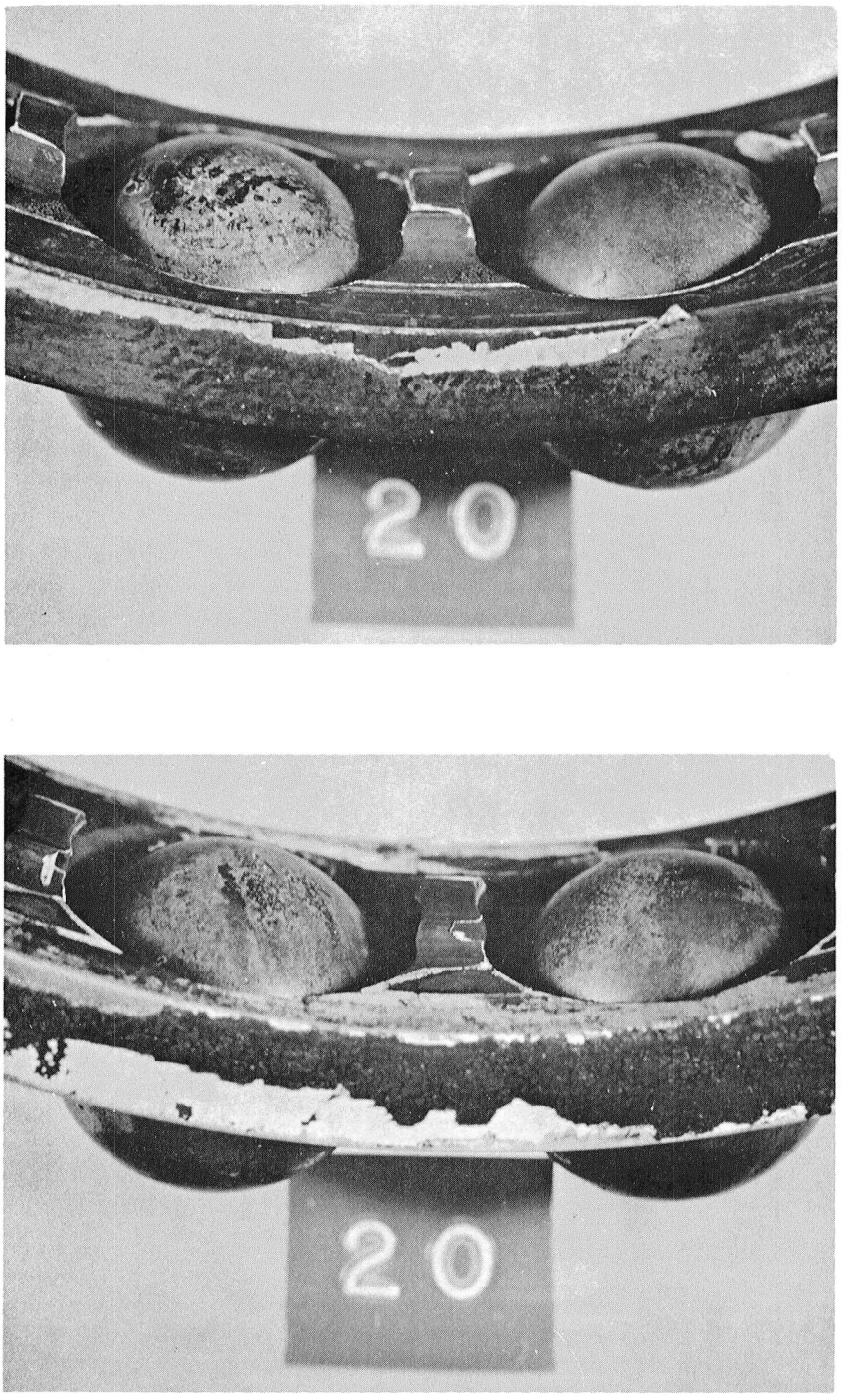


Figure 17. Bearing Test 20. Two Views of the Bearing Cage

Intermittent Foaming--

Excessive foaming halted the test at 32.7 hours. Filtration of the test fluid through Dicalite Speedplus and the addition of more antifoam reduced foaming for the rest of the test.

The sudden eruption of foaming after 30 hours of smooth running is very unusual, and no such problem occurred in any other bearing test. Electron phase microscopy revealed that silicone particles were still in the fluid before the filtration.

Test Results

Deposit Rating--

See Table 15 and the discussion in the subsection entitled Deposits, above.

Viscosity Increase--

The viscosity increase after 111 hours was 237%. The rate of increase over the first 35 hours was modest and linear; thereafter, a sharp rate of increase of viscosity took place. The data are given in Table 16.

Lubricant Analyses--

Table 16 also contains the time increments of acid number and metal uptake. The concentration of iron and silver increased initially but then subsided. After 56.5 hours, large increments in virtually all of the metals occurred. Moreover, there was an extremely large sedimentary analysis at the conclusion of the test, whereas this analysis at 33 hours was a very reasonable 11 mg/liter. This doubtless reflects the use of the 100-mesh screen rather than a fine filter.

Additive Depletion--

After 33 hours, only 16% of the original acid charge remained in the fluid. As in other long-time tests (Nos. 11 and 12) and many short tests, a lot of depletion took place.

Support Oil Leakage--

The drain fluid contained 725 ppm of aliphatic oil.

Concluding Comments

This is only the second C-ether bearing test to run for 100 hours. The previous test (perfluoroglutaric acid additive, test 11 of ref. 3) was both cleaner and had fewer filter pluggings. Its deposit rating was only 9.2 (Table 17). The bench screening program predicted the satisfactory lubrication of test 20, and the thin-film oxidation tests suggested deposit problems (after the fact).

TABLE 16. - LUBRICANT ANALYSES OF BEARING TEST NO. 20

Test lubricant:	MCS 524 + 0.07% CF_3-$\emptyset PO_2H_2$ (FPPA)									
Sample number:	1	2	3	4	5	6	7	8	9	10
Time taken, hours:	0	0.75	8.7	19.1	31.2	32.7	53.2	56.5	84.8	111.0
Metal content, ppm:										
Ni	2.4	2.8	2.5	2.5	2.4	2.4	2.6	2.9	24.3	36.7
Fe	1.9	9.1	12.0	5.8	3.0	2.4	3.1	4.4	391.5	556.7
Mg	0.3	0.4	0.3	0.2	0.1	0.1	0.4	0.6	0.5	0.4
Cu	0.3	2.6	1.9	1.2	1.6	1.3	3.0	3.0	12.6	18.1
Ag	0.1	3.0	27.0	29.4	14.5	14.5	73.2	82.0	162.0	345.8
Cr	0.4	0.4	0.2	0.3	0.3	0.2	0.6	0.3	19.1	34.6
Al	1.1	1.2	1.2	1.1	1.1	1.1	1.6	2.4	2.4	2.4
Si	15.5	16.9	15.2	16.4	19.0	19.5	17.7	20.0	47.1	51.4
Ti	<0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.3	0.8	1.5
K	2.3	14.8	7.2	6.1	6.1	4.8	3.2	4.2	10.1	14.0
Kinematic viscosity, centistokes, at 37.8°C (100°F)	23.2	24.6	26.3	28.3	30.3	30.4	44.7	49.2	76.9	78.2
Viscosity increase, %		6.0	13.4	22.0	30.6	31.0	79.7	112.1	231.5	237.1
TAN, mg KOH/g	0.18	0.17	0.11	0.10	0.17	0.17	0.63	0.63	0.64	0.64
Gravimetric analysis, mg solid/liter fluid						11.35				53,013

TABLE 17. - DETAILED DEPOSIT RATING OF BEARING TEST NO. 11 (REF. 3)

Test Lubricant: MCS 524 + ∿0.07% PFGA[a]

Item	Description	Area x Rating	Severity Factor	Demerits
Balls	20% clean 80% discolored	0	5	0
Cage Periphery	100% clean (∿5% silver removed)	0	5	0
rear	100% light varnish	1.0	5	5
front	100% clean (∿95% silver removed)	0	5	0
inside	100% light varnish (∿25% silver removed)	1.0	5	5
Outer Ring Path	50% clean 25% light varnish 25% medium varnish	0 0.25 0.75	5	5
rear	95% medium varnish 5% heavy varnish	2.85 0.25	5	15.5
front	50% light varnish 50% medium varnish	0.5 1.5	5	10.0
Inner Ring Rear annulus	40% light varnish 20% medium smooth carbon 40% heavy smooth carbon	0.4 2.0 4.4	5	6.8
path	50% discolored 50% light varnish	0 0.5	5	2.5
Inner Ring Front annulus	40% light varnish 60% light smooth carbon	0.4 5.4	5	29.0
path	25% medium varnish	0.75	5	3.75
			Total demerits =	109.75

Overall rating = 109.75/12 = 9.2

[a]See Table 2 for abbreviations.

7.4.3 Bearing Test No. 21: MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.06% Phenylphosphinic Acid (Test Duration 25 Hours)

Test Results

This formulation displayed excellent lubrication in all bench tests and in some noncontract rigs; thus, we have observed the following:

- Very low boundary coefficient of friction on the slow four-ball test (M50 on silvered 6415 steel).
- Large reduction in the boundary coefficient of friction in the slow four-ball test (316 stainless steel on 316 steel).
- A very small wear scar from the fast-speed rub-block test (M50 on M50).
- Very low torque readout during the low-speed rub-block test (M50 on M50).

Nevertheless, the bearing failed relatively quickly, a failure marked by the overheating of both the bearing and the fluid. The bearing temperature rose to 393°C, the fluid temperature to 302°C. The severe temperature distorted the cage and welded two balls against the race. Extreme wear damaged about one-half of the cage, and the failure stripped considerable silver from the front and back of the cage. Figures 18 through 20 are photos of the bearing; Appendix F describes a failure analysis of the test bearing.

Before the failure, the only problem consisted of a filter pluggage at 23 hours. The filter system for this test comprised three filters as opposed to the previous use of one filter. We aligned two Purolator AN6235-4-10 filters and one APM AC-3255 E-16 filter in parallel. With a pressure drop of 50 psi needed to stop the test, the overall filter capacity exceeded that of previous runs. This did not eliminate filter pluggages.

Prior to the filter stoppage, the bearing heat wattage remained constant, and the fluid did not degrade. However, upon resumption of the test after the shutdown, the wattage dropped sharply, signaling increased frictional heating and the upcoming failure.

Table 18 contains data for the fluid metal uptake, viscosity increase, acid number, and gravimetric analyses. While the drain fluid contained a fair amount of iron (178 ppm), the test fluid digested only a modest quantity of silver. The acid number dropped during the course of the test, while the viscosity rose slightly. The final gravimetric analysis was 376 mg per liter. Overall, the fluid properties changed remarkably little prior to the bearing failure.

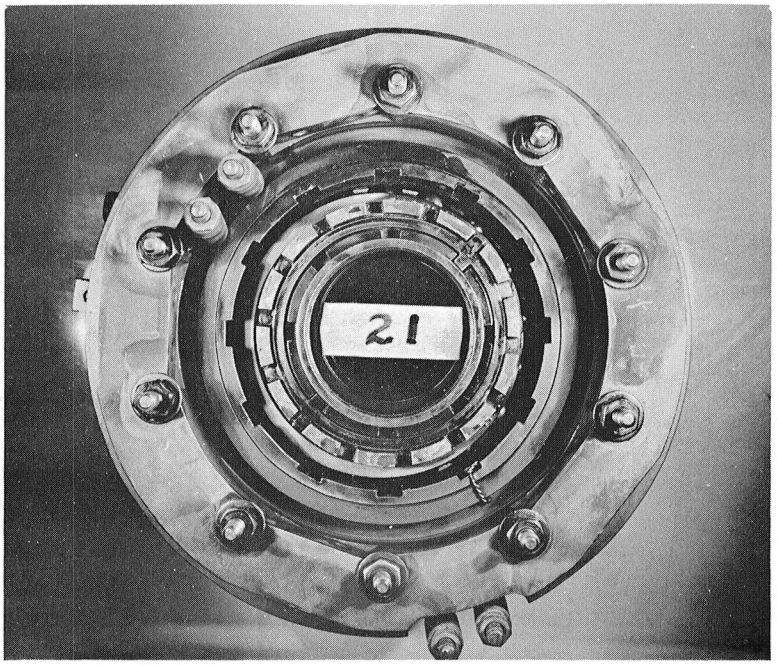


Figure 18. Bearing Test 21. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

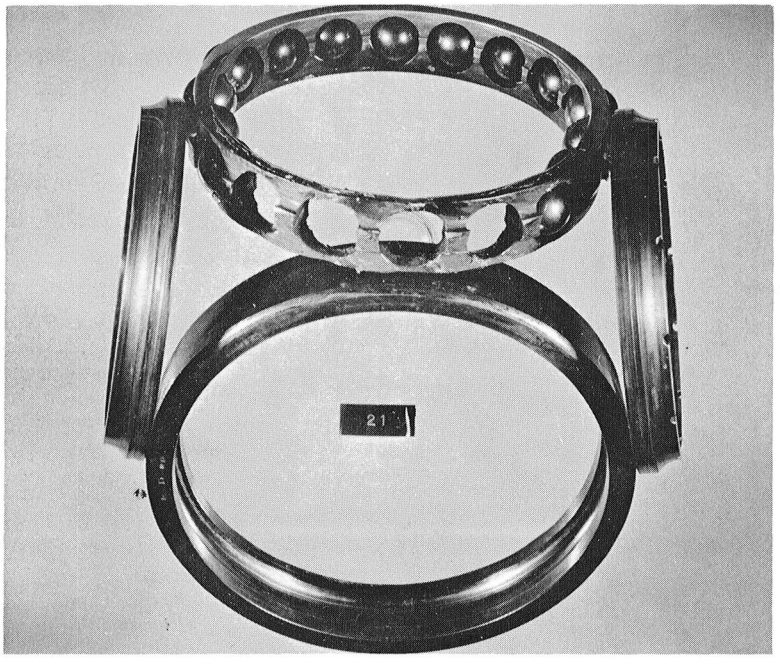


Figure 19. Bearing Test 21. Composite View of Test Bearing

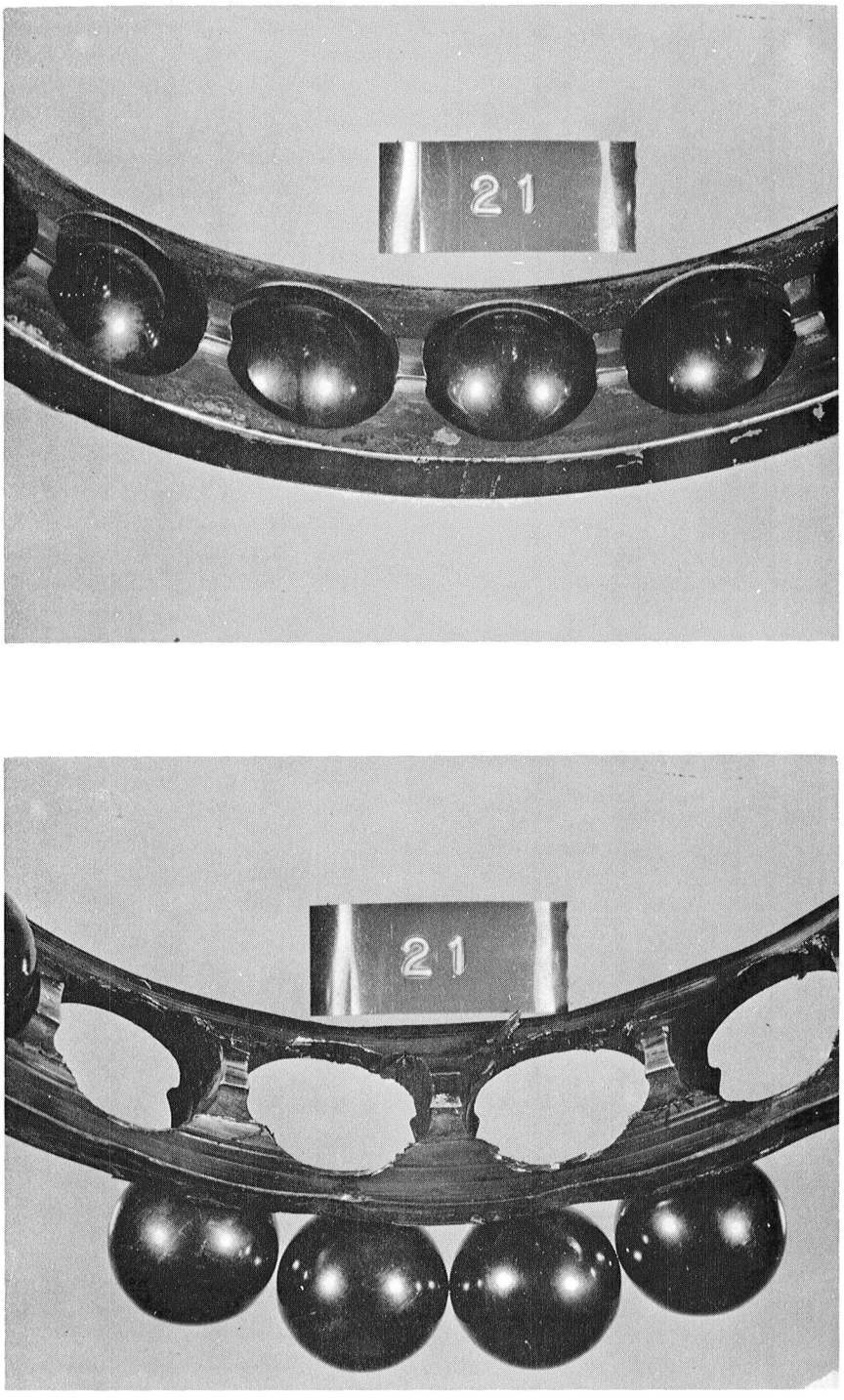


Figure 20. Bearing Test 21. Two Views of the Bearing Cage

TABLE 18. - LUBRICANT ANALYSES OF BEARING TEST NO. 21

Test lubricant:	MCS 524 + ∿0.07% PFGA + 0.06% PPA[a]				
Sample number:	1	2	3	4	5
Time taken, hours:	Unused	0	8.8	18.0	25.4
Metal content, ppm:					
Ni	3.2	3.9	4.4	2.4	5.0
Fe	1.6	2.0	4.9	2.8	178.4
Mg	0.4	0.3	0.3	0.2	0.2
Cu	0.3	1.3	1.3	0.7	1.7
Ag	0.2	5.0	12.1	13.6	13.9
Cr	<0.1	0.3	0.5	0.2	1.0
Al	1.0	0.6	0.6	0.6	0.6
Si	21.0	17.0	19.4	17.6	19.0
Ti	<0.1	<0.1	<0.1	<0.1	0.6
K	3.9	0.5	0.7	0.6	0.9
Kinematic viscosity, centistokes, at 37.8°C (100°F)	24.9	24.5	25.6	26.1	26.7
Viscosity increase, %			2.8	4.8	7.2
TAN, mg KOH/g	0.47	0.39	0.13	0.09	0.08
Gravimetric analysis, mg solid/liter fluid					376.0
Support oil leakage, ppm					1400

[a]See Table 2 for abbreviations.

Both lubrication additives were depleted from the fluid after running for 25 hours. From this we could conclude that additive depletion caused the test failure. However, we must recall the disconcerting fact that an additive depletion in previous runs has not always led to bearing failures. For example, consider the test conducted on MCS 524 plus only perfluoroglutaric acid. After 53 hours, the amount of acid was less than 0.004%, yet the blend performed for 100 hours without a bearing failure. Or, consider phenylphosphinic acid as a single additive. Its concentration in MCS 524 dropped from 216 ppm to 25 ppm during the heating period prior to starting the bearing;

still, 94 hours elapsed before failure. All of these data leave the question: Why did failure occur using the acid combination but not using each additive separately?

One possible explanation could be additive depletion by way of additive interference.

One approach to overcoming such depletion would be to include additives which will generate perfluoroglutaric acid or phenylphosphinic acid as a function of time. An analogous situation in aliphatic oils would be the generation of acid phosphates by tricresyl phosphate. Work on this approach led to studies of silylated perfluoroglutaric acid (bearing tests 22, 23 and 24).

The evidence for additive depletion included the following:

- Initial fluorine concentration = 269 ppm
  Final fluorine concentration = 29 ppm
- Initial phosphorus concentration = 84 ppm
  Final phosphorus concentration = 4 ppm
- Unused fluid: low four-ball test friction
  Used fluid: high four-ball test friction
- Reduction of the acid number during the course of the test

7.4.4 Bearing Test No. 22: MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.06% Phenylphosphinic Acid + 0.1% Bis(trimethylsilyl) Perfluoroglutarate (Test Duration 16 Hours)

This test ran smoothly for 16 hours. At that point, excessive vibration and cage wear suddenly terminated the test.

The post-test clean-up showed that we had failed to connect the safety shut-down signal based on oil pressure. This raises the possibility that the test failure was related to the rig, not the fluid. For if the bearing continued to run after a filter plugging at 16 hours, starvation may have led to gross cage wear. The evidence as to whether this happened is not clearcut, hence it is not possible to conclusively define the failure mode. There are three likely causes:

- inherently poor boundary lubrication by the test fluid
- additive depletion
- starvation

Some facts give credence to starvation effects. For example, the abruptness of the failure (no more than 2 minutes) and the

negligible metal uptake by the oil would normally signal starvation. Usually, cage wear failures produce a rather large increase of silver and/or iron in the fluid.

On the other hand, the strip chart showed reduced but still positive jet pressure, so at least some oil was going through the filter. Other evidence regarding the failure mode from the strip chart was inconclusive. Thus, starvation remains a possible but not proven failure avenue for this test.

Figures 21 through 23 show the test bearing; other aspects of the run are described below.

Additive Depletion

This definitely occurred as shown by the data in Table 19. Less than 10% of each additive remained at the end of the test. This means that the silylated perfluoroglutaric acid did not act as an acid sink. Rather, it reacted directly on the metal surfaces.

TABLE 19. - ADDITIVE DEPLETION DURING BEARING TEST NO. 22

	Fluorine, ppm	Phosphorus, ppm
Unused fluid	613 (100%)	129 (100%)
5-hr Sample	97 (16%)	21 (16%)
16-hr Sample	52 (8%)	9 (7%)

Lubricant Analyses

Table 20 (on page 57) summarizes the fluid degradation data. The viscosity increase, total acid number, and metal uptake were all quite small. Chromatography/infrared analysis showed support oil contamination of 300 ppm.

7.4.5 Bearing Test No. 23: MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.3% Bis(trimethylsilyl) Perfluoroglutarate (Test Duration 81 Hours)

This test lasted 81 hours. It ended with successive chip detector bridgings at 78.5 and 80.7 hours. These in turn resulted from debris from heavy fatigue spalling of five balls and the outer race. However, the cage was in reasonably good shape with silver removed only from the cage-race imbalance contact zone. The bearing and cage are shown in Figures 24 through 26 and a spalled ball in Figure F7, Appendix F.

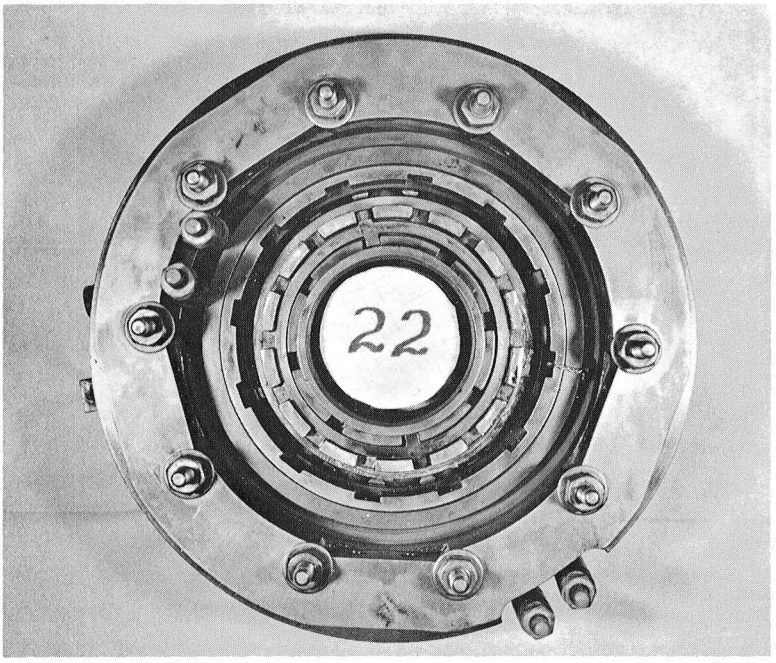


Figure 21. Bearing Test 22. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

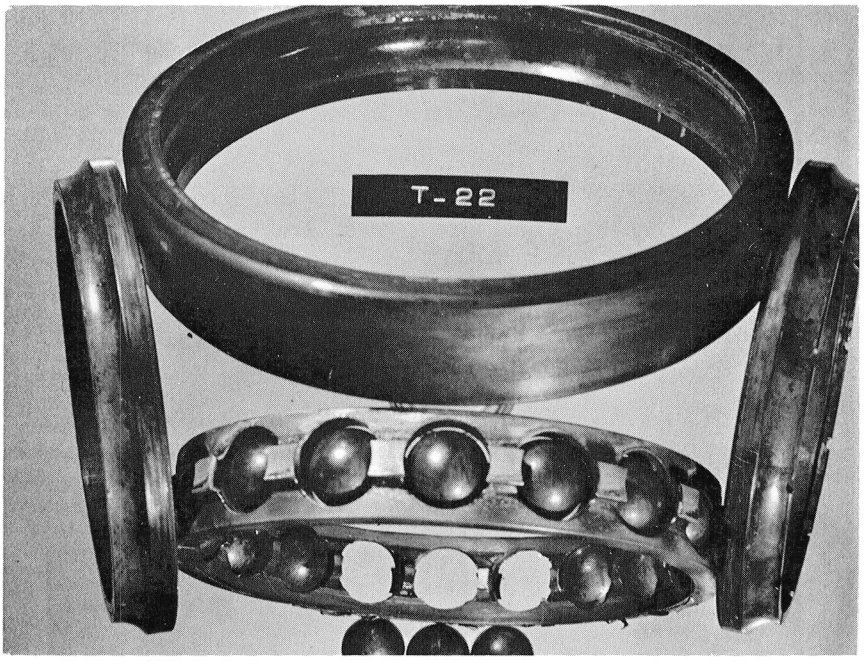


Figure 22. Bearing Test 22. Composite View of Test Bearing

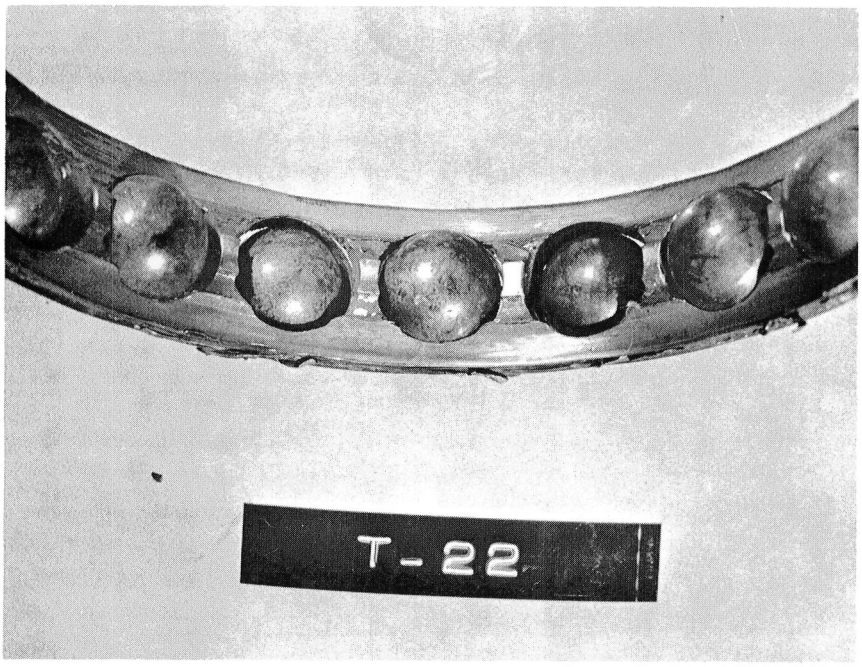


Figure 23. Bearing Test 22. View of the Bearing Cage

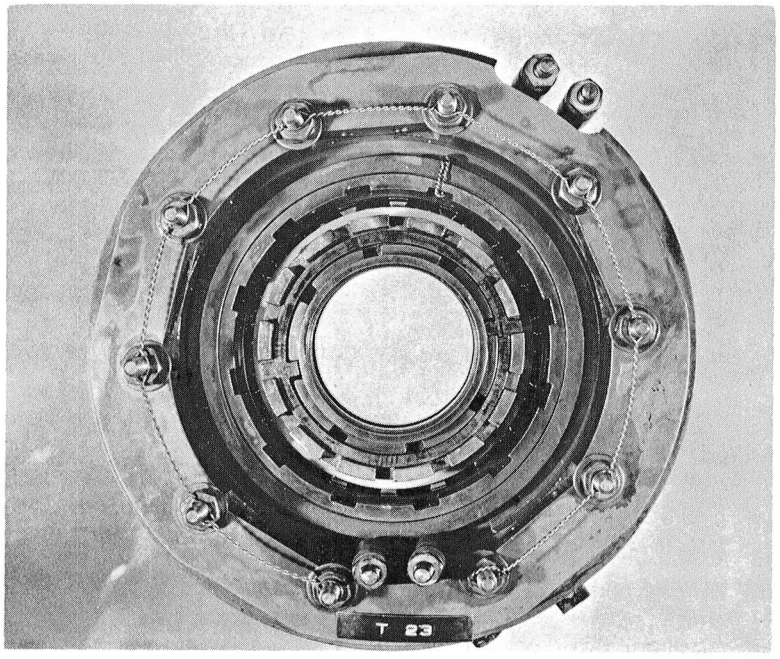


Figure 24. Bearing Test 23. Overall View of Bearing and Housing Viewed from the Direction of Test Oil Supply

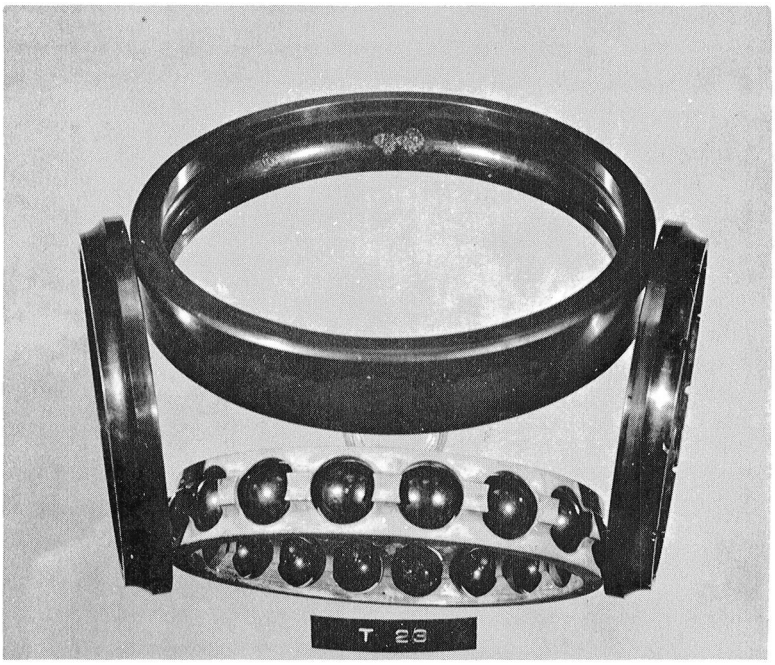


Figure 25. Bearing Test 23. Composite View of Test Bearing

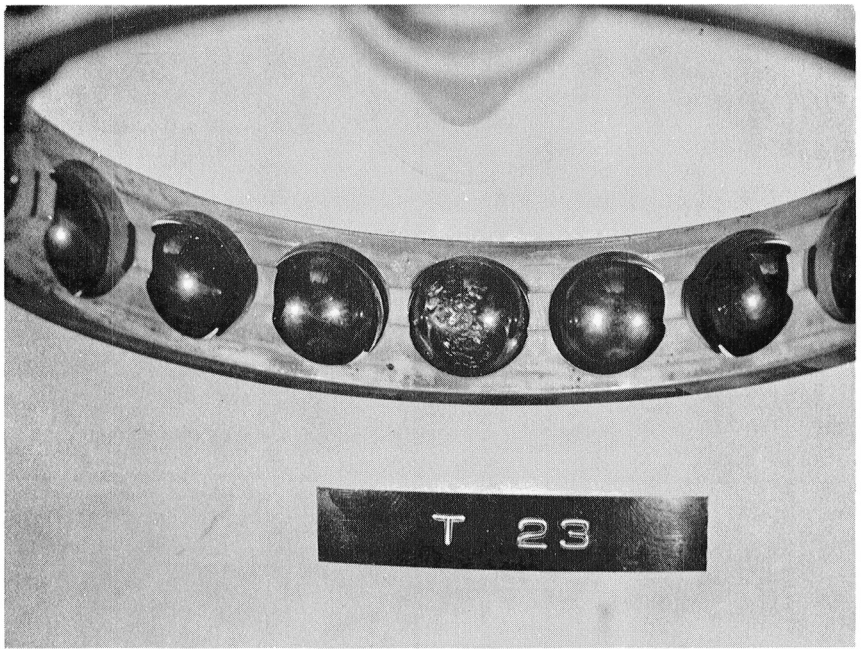


Figure 26. Bearing Test 23. View of the Bearing Cage

TABLE 20. - LUBRICANT ANALYSES OF BEARING TEST NO. 22

Test lubricant:	MCS 524 + ∿0.07% PFGA + 0.06% PPA + 0.1% SPFGA[a]		
Sample number:	1	2	3
Time taken, hours:	Unused	5.0	16.3
Metal content, ppm:			
Ni	2.8	6.5	5.0
Fe	4.4	3.7	11.0
Mg	0.5	0.3	0.2
Cu	0.2	0.7	0.8
Ag	0.4	5.8	10.0
Cr	0.1	0.2	0.2
Al	0.3	0.5	0.2
Si	269.0	45.5	35.5
Ti	0.1	0.1	0.1
K	0.4	1.2	0.8
Kinematic viscosity, centistokes, at 37.8°C (100°F)	25.2	25.8	27.2
Viscosity increase, %		2.4	7.9
TAN, mg KOH/g	0.67	0.12	0.05
Gravimetric analysis, mg solid/liter fluid			87.0

[a]See Table 2 for abbreviations.

This was the best test to date in terms of bearing cleanliness (Table 21), number of filter pluggings (one), and fluid cleanliness. The log listed various secondary interruptions:

chip detector bridging	5.2 hr
recorder failure	16.3 hr
foaming	around 22 hr (reduced to a low level by adding antifoam to make-up oil)
wattage starts to fall	∿65 hr
chip detector bridges	78.5 hr
chip detector bridges	80.7 hr (see Figure 27 on page 62)

TABLE 21. - DETAILED DEPOSIT RATING OF BEARING TEST NO. 23

Test Lubricant: MCS 524 + ∿0.07% PFGA + 0.3% SPFGA[a]

Item	Description	Area x Rating	Severity Factor	Demerits
Balls	100% discolored	0	5	0
Cage Periphery	100% light varnish	1.0	5	5.0
rear	80% light varnish	0.8	5	8.5
	5% medium varnish	0.15		
	15% heavy varnish	0.75		
front	100% light varnish	1.0	5	5.0
inside	95% light varnish	0.95	5	5.5
	5% medium varnish	0.15		
Outer Ring Path	100% discolored (large fatigue areas)	0	5	0
rear	100% light varnish	1	5	5
front	80% light varnish	0.8	5	7
	20% medium varnish	0.6		
Inner Ring Rear annulus	30% light varnish	0.3	5	24.5
	30% light sludge	1.8		
	40% medium sludge	2.8		
path	100% discolored	0	5	0
Inner Ring Front annulus	70% light varnish	0.7	5	13.5
	10% medium varnish	0.3		
	10% heavy varnish	0.5		
	10% light crinkled carbon	1.2		
path	70% light varnish	0.7	5	8
	30% medium varnish	0.9		
			Total demerits =	82

Overall rating = 82/12 = 6.8

[a]See Table 2 for abbreviations.

Bearing failure analysis by SKF Industries, Inc. did not resolve why the bearing fatigued. The spalls followed the grain flow patterns, i.e., the forming lines. Such spalling could result either from an excessively corrosive oil or weak steel. The analysis found no unusual inclusions, e.g., of retained austenite, but these may have been removed by the spalling. Reactive additives can lower fatigue life in aliphatic oils (ref. 14). More details of the failure analysis are in Appendix F.

The modest changes experienced by the test fluid are in Table 22. The drain oil contained 300 ppm of support oil.

7.4.6 Bearing Test No. 24: MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.3% Bis(trimethylsilyl) Perfluoroglutarate (Test Duration 1 Hour)

Although test 23 ran for 81 hours, severe cage wear brought this run to a halt after only 1 hour. The lubricant analyses are in Table 23; Figures 28 and 29 are photographs of the bearing.

This disturbing result raises a question about reproducibility: Are individual runs measuring chemical effects or variations in bearing fabrication?

Two changes in test 24 may have influenced the failure. Erratic oil flow probably supplied 5 to 10% less fluid than the normal break-in flow. Second, clearing a plugged condenser by blowing air back up through the condenser forced air over the bearing. This appears trivial, but oxygen will increase the wear of silver against iron (ref. 12). In run 23, the condenser was removed, cleaned and reinstated.

Support oil leakage was 620 ppm, surprisingly high considering the shortness of the test.

See Appendix F for the failure analysis of the test bearing.

TABLE 22. - LUBRICANT ANALYSES OF BEARING TEST NO. 23

Test lubricant:	MCS 524 + ∿0.07% PFGA + 0.3% SPFGA[a]								
Sample number:	1	2	3	4	5	6	7	8	9
Time taken, hours:	0	5.2	16.3	24.1	42.0	55.0	73.5	78.5	80.7
Metal content, ppm:									
Ni	0.4	2.2	2.2	2.2	2.2	2.4	2.7	2.8	3.0
Fe	0.7	1.4	1.6	1.6	1.9	1.3	1.9	2.6	6.1
Mg	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	<0.1	1.5	1.2	1.2	1.1	1.2	0.9	1.0	1.0
Ag	0.2	4.4	23.1	27.6	59.4	66.0	71.6	80.5	77.5
Cr	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.4
Al	0.1	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.2
Si	1020	41.0	35.0	29.4	52.5	68.0	39.4	43.5	70.2
Ti	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
K	38.6	4.7	1.4	2.7	2.5	28.4	1.8	2.1	2.8
Kinematic viscosity, centistokes, at 37.8°C (100°F)	27.0	26.5	26.2	29.0	30.1	31.2	33.5	34.7	26.1
Viscosity increase, %		-2.1	-2.9	7.1	11.4	15.5	23.9	28.4	33.6
TAN, mg KOH/g	0.79	0.05	0.03	0.03	0.03	0.05	0.03	0.06	0.05
Gravimetric analysis, mg solid/liter fluid									97

[a]See Table 2 for abbreviations.

TABLE 23. - LUBRICANT ANALYSES OF BEARING TEST NO. 24

Test lubricant:	MCS 524 + ∿0.07% PFGA + 0.3% SPFGA[a]	
Sample number:	1	2
Time taken, hours:	0	1
Metal content, ppm:		
Ni	2.4	2.8
Fe	1.4	35.0
Mg	<0.1	0.1
Cu	0.1	1.3
Ag	0.1	16.3
Cr	0.1	0.3
Al	0.4	0.6
Si	1020	<0.1
Ti	88.5	0.1
K	29.8	3.1
Kinematic viscosity, centistokes, at 37.8°C (100°F)	27.1	28.4
Viscosity increase, %		4.8
TAN, mg KOH/g	0.68	0.09
Gravimetric analysis, mg solid/liter fluid		85

[a]See Table 2 for abbreviations.

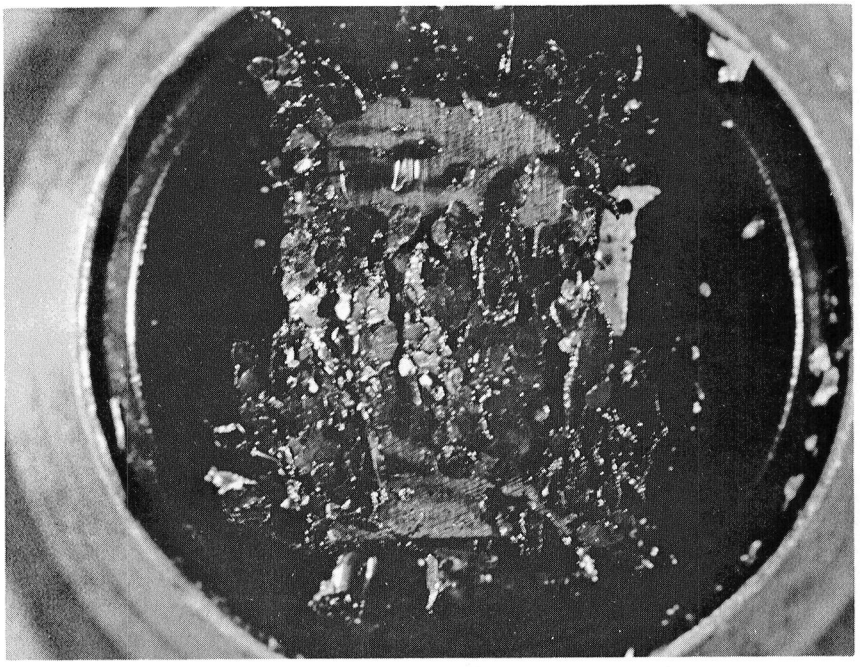


Figure 27. Bearing Test 23. Post-Test Chip Detector

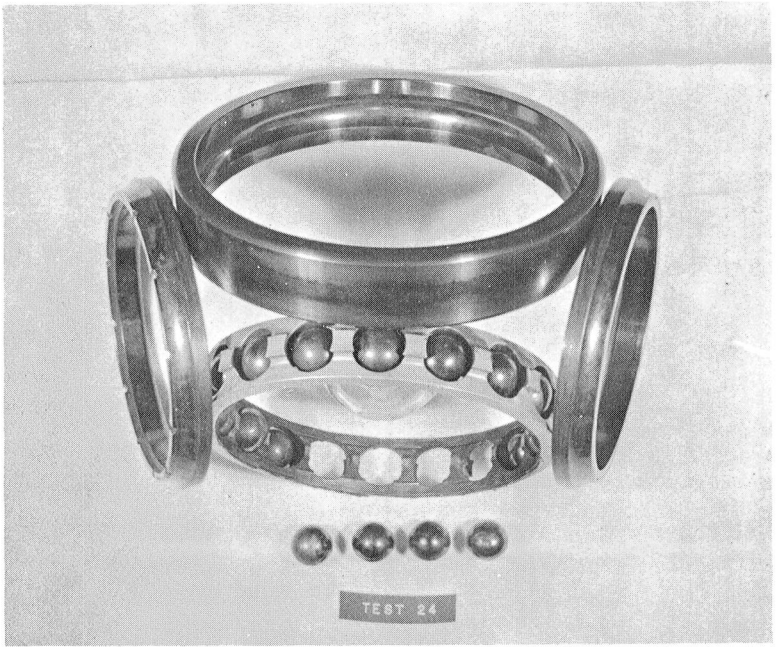


Figure 28. Bearing Test 24. Composite View of Test Bearing

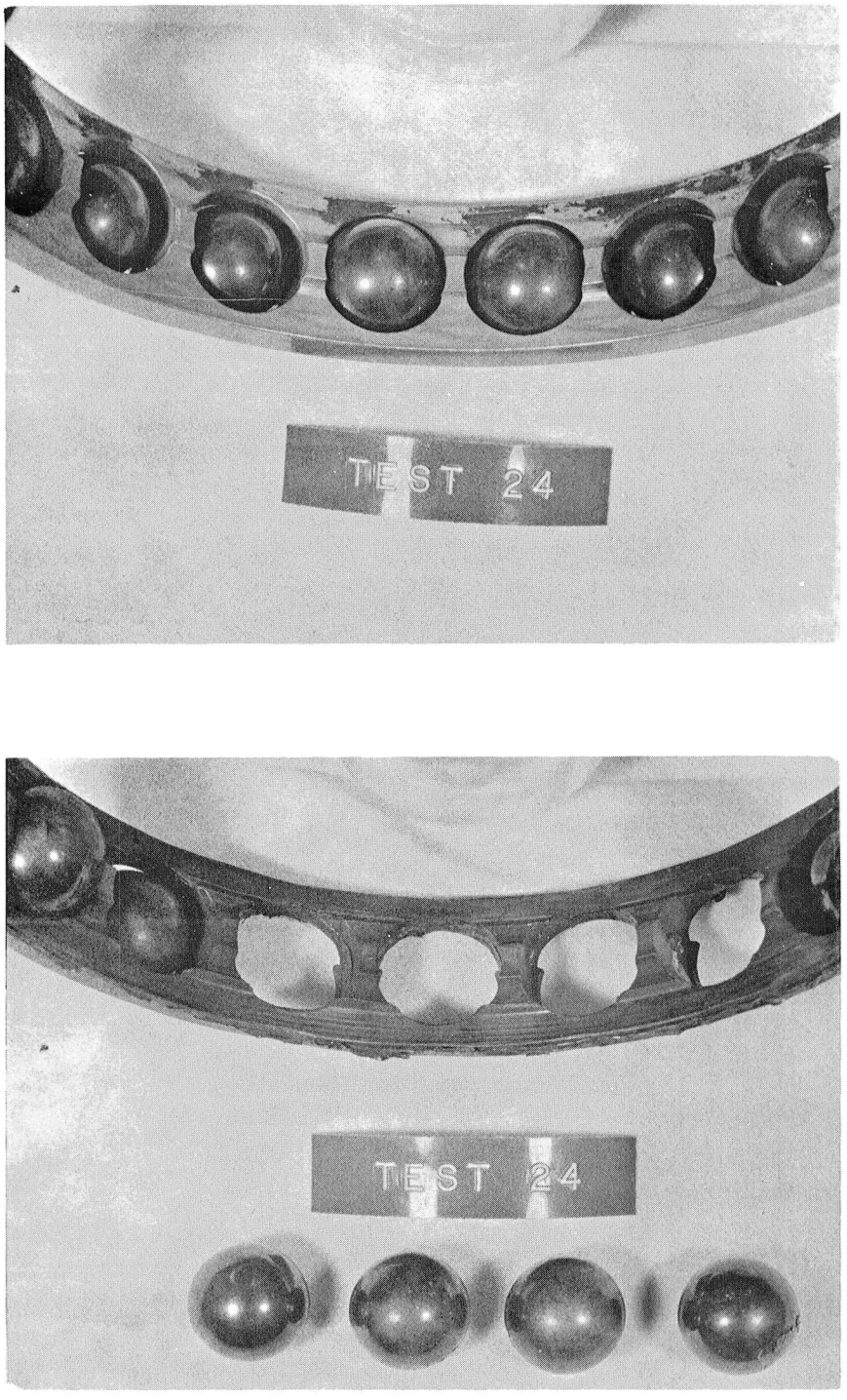


Figure 29. Bearing Test 24. Two Views of the Bearing Cage

APPENDIX A

SCREENING TESTS: C-ETHERS AND MCS 1892

1. MACRO OXIDATION-CORROSION TEST

A. C-Ethers

This test showed whether an additive triggered excessive fluid degradation or metal corrosion in a high temperature, static, oxidizing environment. Also, it screened the effectiveness of copper inhibitors. Test results determined whether additives merited further bench testing.

A blend containing phenylphosphinic acid characteristically showed satisfactory oxidation-corrosion results, but in subsequent bearing tests deposits quickly formed and eventually led to failures (ref. 3).

Presumably the generation of solids in the bearing involved chemistry resulting from dynamic interactions of the system components. Alternatively, mass transfer effects could mask deposit formation in the oxidation test. This lack of correlation with bearing tests led to the use of the fast four-ball and thin-film oxidation tests to screen for deposits.

Table A1 lists the first group of additives screened in the macro test at 260°C and 278°C. Failure resulted from excessive viscosity increase, metal corrosion or formation of medium amounts of coke or sludge. Data for compounds tested later are in Table A2.

B. MCS 1892

Table A3 shows that MCS 1892 - the formulated ester - produced heavy deposits both at 260°C and 278°C. This does not mean this will produce large deposits at bearing hot spots above 260°C provided the bulk temperature is lower.

For example, the following conditions were used in a 48-hour MIL-L-27502 bearing test on MCS 1892:

235°C (455°F)	oil-in temperature
240°C (464°F)	sump temperature
300°C (572°F)	bearing temperature
220°C (428°F)	oil-out temperature

TABLE A1. - MACRO OXIDATION-CORROSION TESTS ON MCS 524 BLENDS

(48 hours, 5 liters/hour)[a]

Additives[b]	Viscosity Increase, %		Copper Weight Loss, mg/cm²		Silver Weight Loss, mg/cm²		Deposits	
	260°C	278°C	260°C	278°C	260°C	278°C	260°C	278°C
None	5	6	-2.3	-2.0	-0.8	-0.9	none	none
		6		(c)		-0.4	none	none
A	9	9	-5.4	-5.9	-0.9	-1.0	lt. sludge	lt. coke and sludge
B	11	11	-5.0	-5.5	-1.1	-1.8	v. lt. coke	none
C	11	9	-7.4	-4.3	-0.3	-0.2	none	none
D	27	14	-7.2	-5.3	-1.2	-3.2	lt. sludge	lt. coke
E	5	11	-0.2	-1.4	-0.3	-0.3	none	none
F	8	10	-3.1	-3.0	-0.7	-0.9	none	none
G	16	25	-2.5	-3.5	0.0	-0.1	none	none
H	11	13	-4.7	-3.6	-0.4	-0.3	lt. coke lt. sludge	lt. sludge
			FAILURES					
I	8	37	-6.9	-10.0	-0.6	-2.3	none	med. coke
J	5	7	-5.9	-6.7	-1.0	-1.1	lt. coke lt. sludge	lt. coke lt. sludge
K	102		-3.9		-0.9		none	

[a]Negligible weight loss for magnesium, aluminum, titanium and iron.

[b]See Table 3 for coding and concentrations of additives.

[c]No copper coupon present.

TABLE A2. - OXIDATION-CORROSION TESTS ON MCS 524 BLENDS

(48 hours, 5 liters air/hr)[a]

Additives[b]	Viscosity Increase, %		Copper Weight Loss, mg/cm²		Silver Weight Loss, mg/cm²		Deposits	
	260°C	278°C	260°C	278°C	260°C	278°C	260°C	278°C
0.1% Potassium 3-(3-phenoxy-phenoxy) phenate	+2	+8	-1.2	-1.5	-0.2	-0.1	none	v. lt. coke
0.1% Potassium 3-(3-phenoxy-phenoxy) phenate + 0.05% bis(trimethylsilyl) phosphonate	+3	+10	-1.7	-2.1	-0.1	-0.3	v. lt. coke	lt. coke
0.1% Bis(trimethylsilyl) phosphonate	+6	+8	-4.5	-3.6	-0.5	-0.8	med. coke	lt. coke
∿0.07% PFGA + 0.06% PPA	+7	+8	-3.3	-4.2	-0.6	-1.6	lt. coke; lt. sludge	lt. coke; lt. sludge
∿0.07% PFGA + 0.06% FPPA	+11	+21	-5.3	-8.1	-0.9	-1.8	med. coke med sludge	med. coke
0.2% HITEC E644	+17	+21	-8.3	-8.2	-1.5	-2.3	v. lt. coke	v. lt. coke
0.1% HITEC E611	+7	+10	-2.6	-3.7	-1.6	-1.9	v. lt. coke	med. coke
∿0.07% PFGA + 0.1% PFGE + 0.06% PPA	+6	+10	-3.5	-4.2	-0.7	-1.1	lt. coke lt. sludge	lt. coke lt. sludge
0.1% SPFGA + ∿0.07% PFGA + 0.06% PPA	8		-4.7		-1.0		lt. coke lt. sludge	
0.3% SPFGA + ∿0.07% PFGA	39		-5.6		-1.5		v. lt. coke	

[a]Negligible weight loss for magnesium, aluminum, titanium and iron.

[b]See Table 2 for abbreviations.

Some test results are given below:

	MCS 1892	MIL-L-27502 Spec.
Overall deposit rating	31.1	80 (max)
Viscosity increase, %	30.8	100 (max)
TAN increase	1.04	2.0 (max)
Metal corrosion, mg/cm²	<±0.06	±0.2 (max)

Thus the fluid gave very good performance at a bulk temperature of 240°C (ref. 8).

TABLE A3. - OXIDATION-CORROSION TESTS ON MCS 1892

Oxidation-Corrosion Test at 260°C (48 hours)	
Viscosity increase, %	76
Metal corrosion, mg/cm²	
Aluminum	none
Titanium	+0.0
Iron	none
Copper	-1.2
Silver	+0.0
Deposits	heavy coke heavy sludge

Oxidation-Corrosion Test at 278°C (48 hours)	
Viscosity increase, %	1385
Metal corrosion, mg/cm²	
Aluminum	none
Titanium	none
Iron	+14.4
Copper	-0.1
Silver	none
Deposits	heavy coke heavy sludge

2. THIN-FILM MICRO OXIDATION TESTS (REF. 15)

We turned to thin-film tests because deposit-related problems such a filter pluggings continued to plague the bearing tests and neither macro oxidation-corrosion nor fast speed four-ball tests simulated these residues.

The thin-film approach quantifies the oxidation and evaporation of gas turbine lubricants. It minimizes problems associated with diffusion limitation by the use of a small sample (20-200 µl) with a relatively large fixed area of fluid-gas contact. Analysis via gel permeation chromatography (GPC) measures the quantity of fluid reacted and the amount of oxidized products formed. GPC is particularly useful in that it gives some information about the entire range of oxidation products.

The present study first compared new and used samples of four C-ether blends. Ultraviolet detection showed changes in molecular weight even in those samples taken from bench lubrication tests but much more noticeably in those from long-time bearing tests. Subsequently, micro oxidation tests for 1 hour at 353°C (667°F) produced changes in the unused fluids typical of those encountered in the bearings. These tests showed that silver generates two to five times more oxidation products than steel.

A. Description of the Rig (See Figure A1)

Test fluid holders are constructed from 19-mm diameter cold-rolled steel bar stock. The upper surface of the steel fluid holder (metal catalyst) has a flat depression or cup to contain the lubricant. Forty microliters of lubricant on the fluid holder surface theoretically form a slightly concave film approximately 150 µm thick. By a simple lathe machining procedure, a used steel specimen holder can be reworked to produce a fresh catalytic surface for reuse. The metal fluid holders are stored in thiophene-free benzene immediately after preparation to maintain the catalytic surface until used. Catalysts stored in benzene up to 10 days showed no change in activity.

To begin a test, a fresh holder held with a tong was rinsed with acetone, dried with dry air, and placed into a clean reactor. The reactor was then submerged in the metal bath and fastened into place with a transite holder. A nitrogen line was immediately connected to the gas inlet and the reactor flushed with 20 cm^3 per minute of nitrogen until the test system reached the steady state temperature.

Twenty-five minutes is required for the metal surface to reach constant temperature. The temperature was monitored by measuring the temperature at the metal surface with a copper-constantan thermocouple at the beginning of each day and by continually checking the temperature of the Cerrobase metal. To

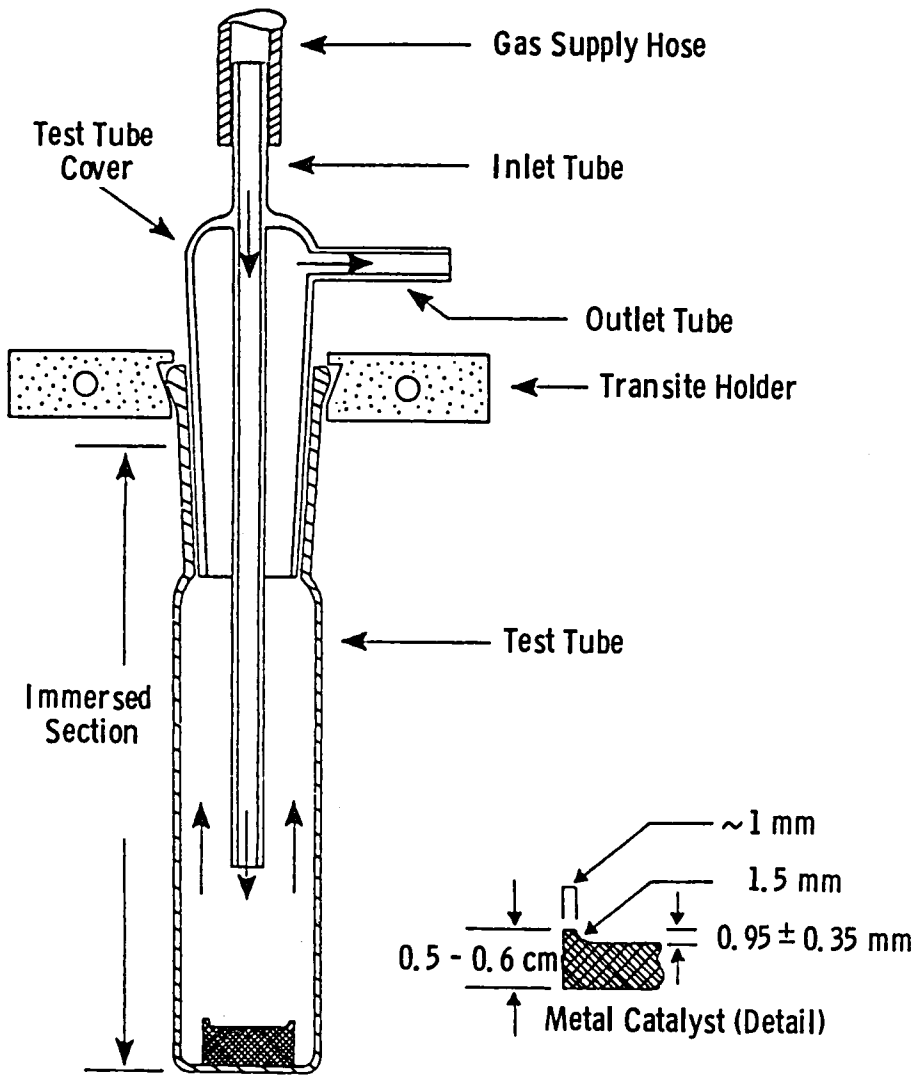


Figure A1. The Microtest Oxidation Apparatus

be sure of obtaining a steady state temperature, 45 minutes was allowed for preheating.

After the steady state temperature was reached, the nitrogen line was disconnected and a lubricant sample was injected onto the surface of the metal sample holder. For this purpose, a 100-microliter syringe with a fixed needle 230 mm long with an inner diameter of 0.46 mm is used. The long injection inlet tube guides the needle so that injection occurs on the center of the holder. At this point the measurement of test time was begun. For volatility tests, the nitrogen flow was continued following injection. For oxidation tests, flushing of the reactor with air (predried by an alumina tower) at 20 cm^3 per minute was begun 10 minutes prior to injection of the sample and continued following the injection. In the case of oxidation tests, it was found that there was no difference in test results between nitrogen flushing until sample injection and a 10-minute preflush of air before sample injection. In the latter case, the catalyst was visibly discolored by oxide formation, but the oxidation rate was not affected measurably.

To end the test, the gas inlet hose was removed and the reactor was removed from the metal bath and cooled rapidly in a high velocity stream of air. Calculations of the oxidation rate versus temperature during the air quench showed that the relative oxidation after removal from the bath was negligible.

After cooling the catalyst and reactor to room temperature, the fluid remaining in the catalyst surface was diluted with 2-3 ml of tetrahydrofuran (THF).

Successive washings of the catalyst surface with THF were used to obtain complete transferral of the solution portion of the sample to a 10-ml graduated cylinder. The final volume of the solvent diluted sample was 6 ml (40-µl injection sample) or 9 ml (60-µl injection sample). Only 2 ml of solution were necessary to fill the gel permeation chromatograph sample loop. The rest of the sample was used for flushing the loop and in some cases part of it was retained for further analysis.

The chromatograph used for this work was a double detector unit with differential refractive index (RI) and ultraviolet light adsorption (UV) detectors. A full description of the unit is available in the manufacturer's literature (Waters Associates, Inc., 1972). Operating conditions were selected to optimize the separation in the least time. A solvent flow rate of 3.0 ± 0.02 ml/min was used for most of this work. The GPC column [8 feet of 60 Å and 4 feet of 1000 Å polystyrene (PVB) packing] was capable of separating compounds in the molecular weight range of 200 to 50,000.

B. Test Data

Table A4 lists the test fluids and their deposit-related ratings in bearing and macro oxidation-corrosion tests.

TABLE A4. - BEARING AND MACRO OXIDATION DEPOSITS OF TEST FLUIDS

Fluid	Bearing Life, hr	Bearing Deposits	Macro Oxidation-Corrosion Test Deposits (260°C)
MCS 524	1-15 (wear failure)		small
MCS 524 + FPPA	111 (no failure)	heavy (deposit rating = 25)	light, coke, light sludge
MCS 524 + MEP + TCA	13 (wear failure)	-	negligible
MCS 524 + PFGA	100 (no failure)	moderate (deposit rating = 9.2)	pass
MCS 524 + PPA	94	very heavy	pass

Figures A2 through A6 contrast the unused and used C-ethers. The latter samples came from bearing tests or from a bench pin on disc machine run for 130 min at 260°C. These figures use UV detection. This proved more sensitive than Rl and and showed oxidative changes semiquantitatively.

In all instances, the GPC-UV picked up evidence of fluid change. Even in the bench test samples, a change in apparent molecular weight distribution took place with the formation of a small but measurable material of slightly higher molecular weight. A used sample from a short bearing test (13 hours) had comparable changes (Figure A2).

Fluids undergoing long bearing tests - MCS 524 + FPPA, MCS 524 + PFGA, and MCS 524 + PPA* - had about the same relative amounts of higher molecular weight products. In all three fluids, the high molecular weight products ranged from the molecular weight of the original fluid to 100,000 apparent molecular weight. The sample MCS 524 + FPPA in addition to some product at 100,000 apparent molecular weight exhibits a substantial peak above the

*See Table 2 for coding.

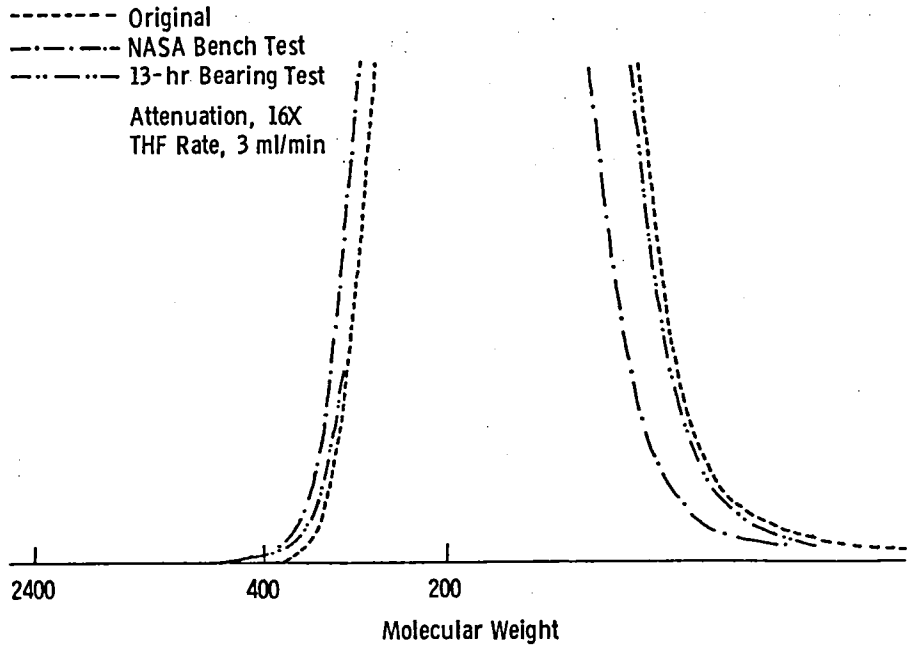


Figure A2. GPC Analysis of MCS 524 + MEP + TCA Before and After Use in Bearing and Bench Pin on Disc Tests

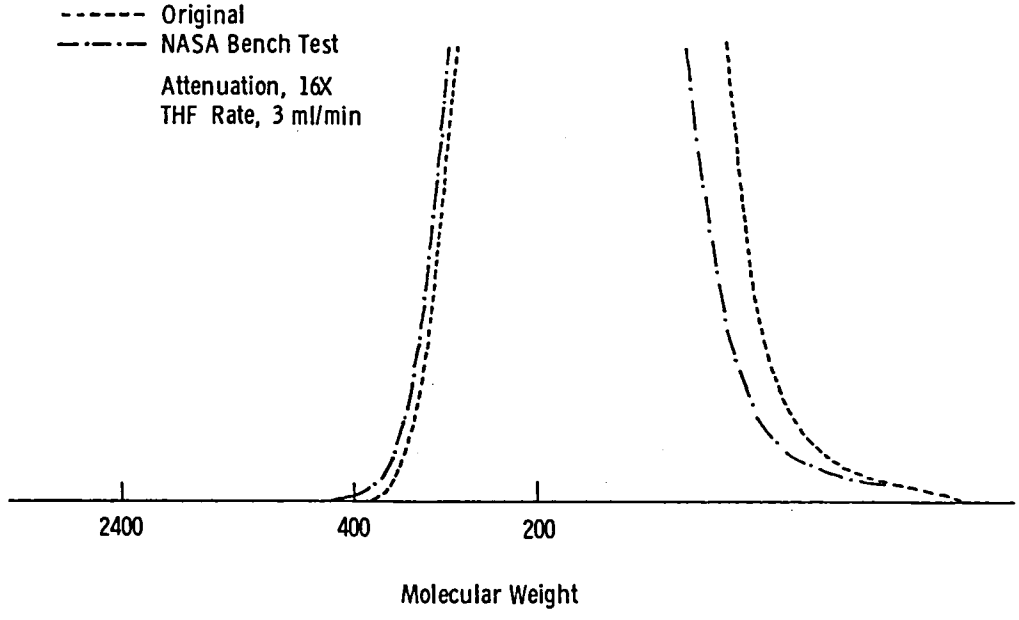


Figure A3. GPC Analysis of MCS 524 Before and After Pin on Disc Test

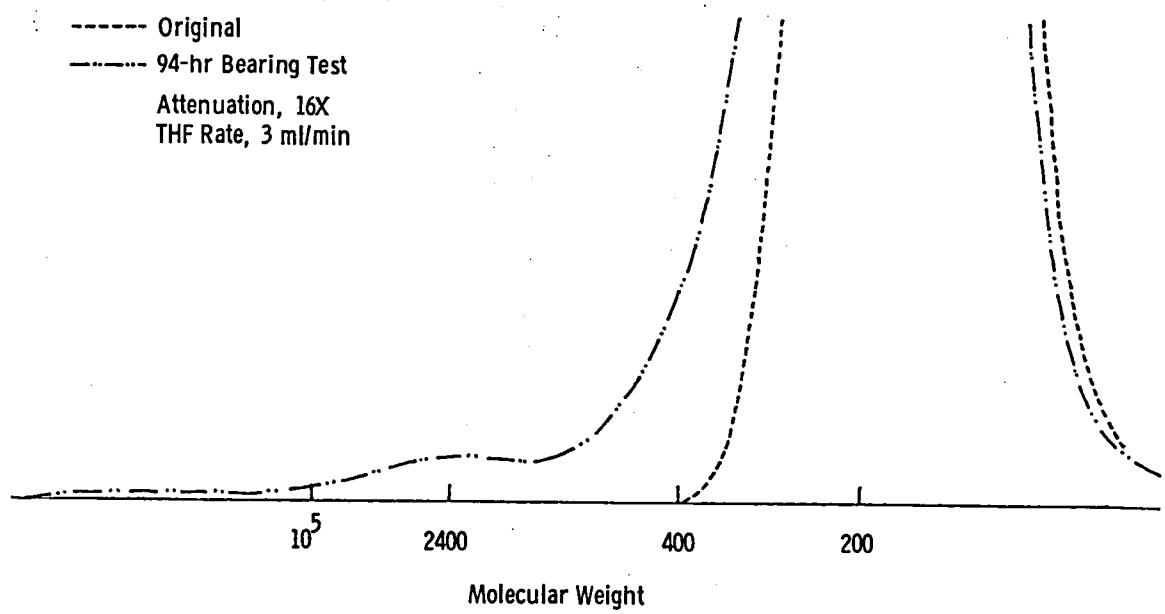


Figure A4. GPC Analysis of MCS 524 + PPA Before and After a 94-Hour Bearing Test

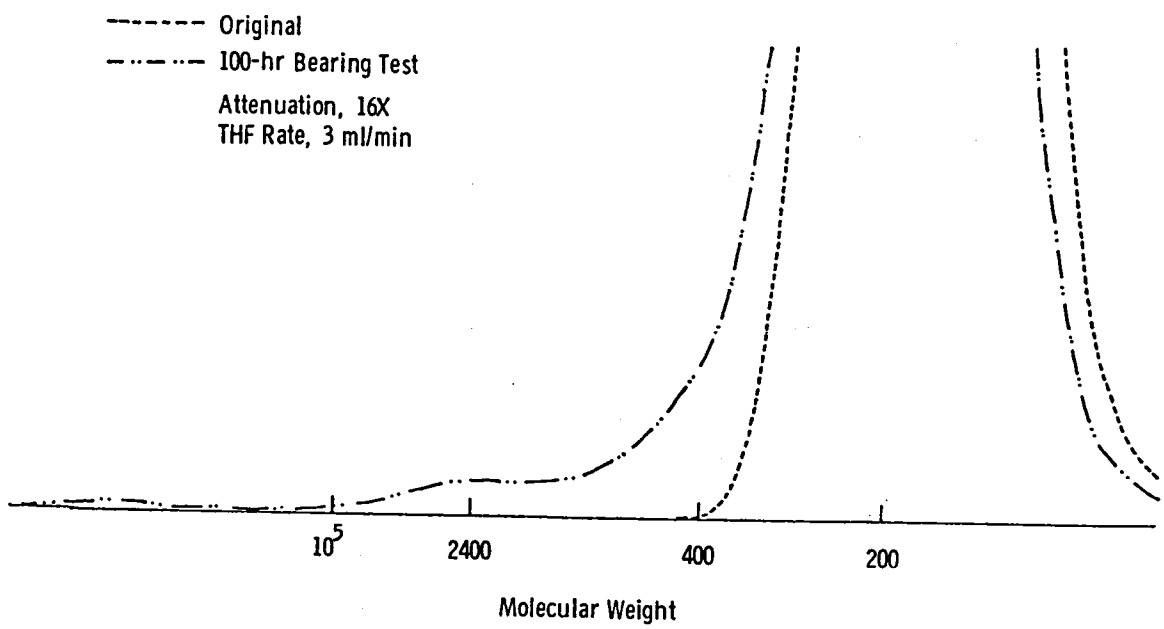


Figure A5. GPC Analysis of MCS 524 + PFGA Before and After a 100-Hour Bearing Test

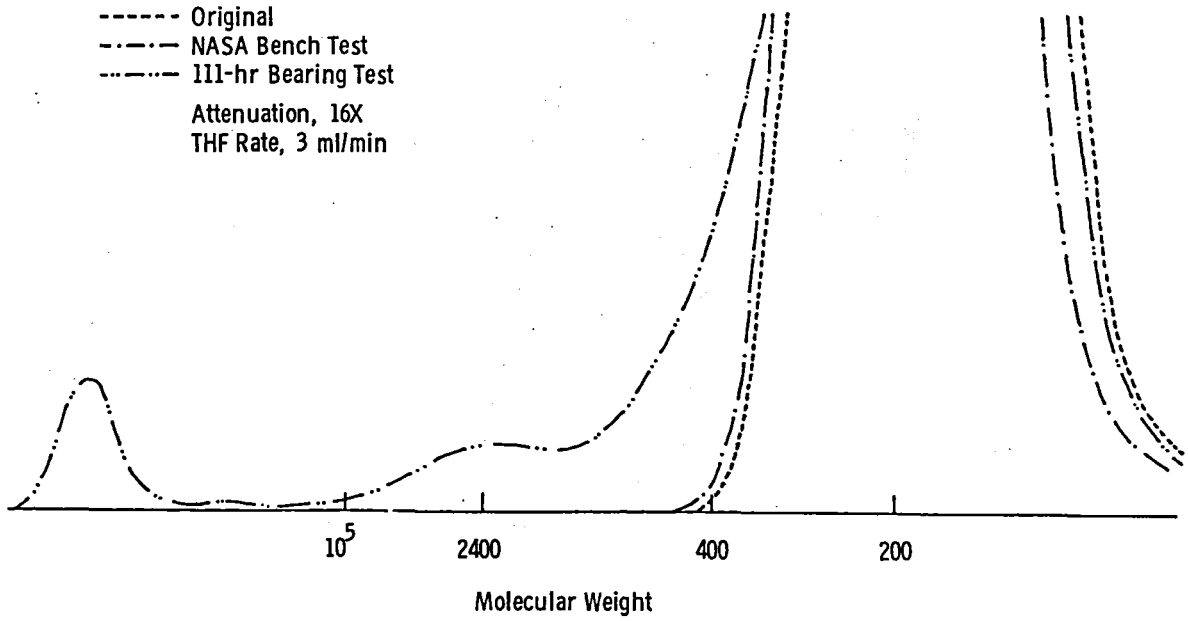


Figure A6. GPC Analysis of MCS 524 + FPPA Before and After Use in Bearing and Bench Pin on Disc Tests

exclusion peak (100,000 MW). This peak could be a reflection of dispersed coke and sludge rather than THF soluble polymeric material.

Micro oxidation tests were then conducted to determine a set of conditions to duplicate the formation of as much as or more high molecular weight oxidation product. A test time of 2 hours at 243°C on steel in the micro oxidation test showed some polymer formation (Figure A7). These conditions are less severe than the actual bearing tests. Based on this result, subsequent tests lasted 1 hour at 353°C. The metals used included a low carbon steel and silver.* The results of the higher temperature tests are shown in Figures A8 through A11. It is apparent that a significant amount of evaporation is encountered in all cases at 353°C. The amount of evaporation was not determined to save the available effort for oxidative evaluations.

*The silver surface was obtained by press fitting a silver specimen in the steel holder. Tool steel in the appropriate form (M50) was not available for these tests. Previous tests have been run on aircraft gas turbine lubricants using low carbon steel, 52-100 bearing steel and 440 C stainless steel. In the case of AGT lubricants, there was little or no difference between low carbon steel and bearing steel. Stainless steel showed the same trends as the bearing steel but to a lesser degree. For the esters and mineral oils all of the steels including the 440 C stainless had a distinct catalytic effect, causing polymerization of the oxidation product.

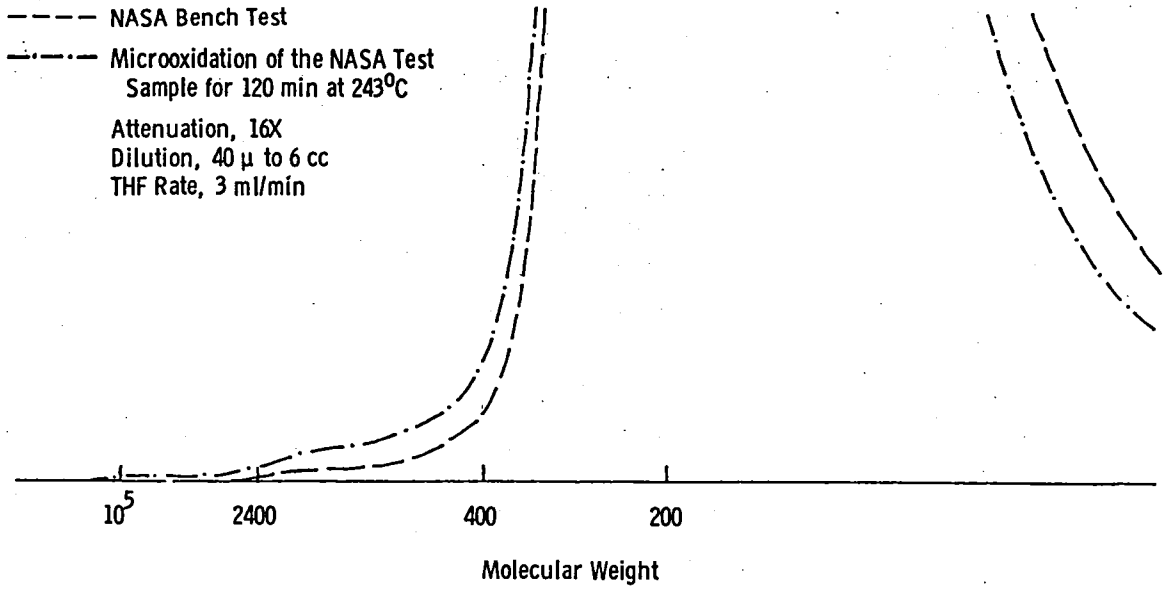


Figure A7. GPC Analysis of MCS 524 + FPPA From a NASA Bench Test Before and After a Microoxidation Test at 243°C

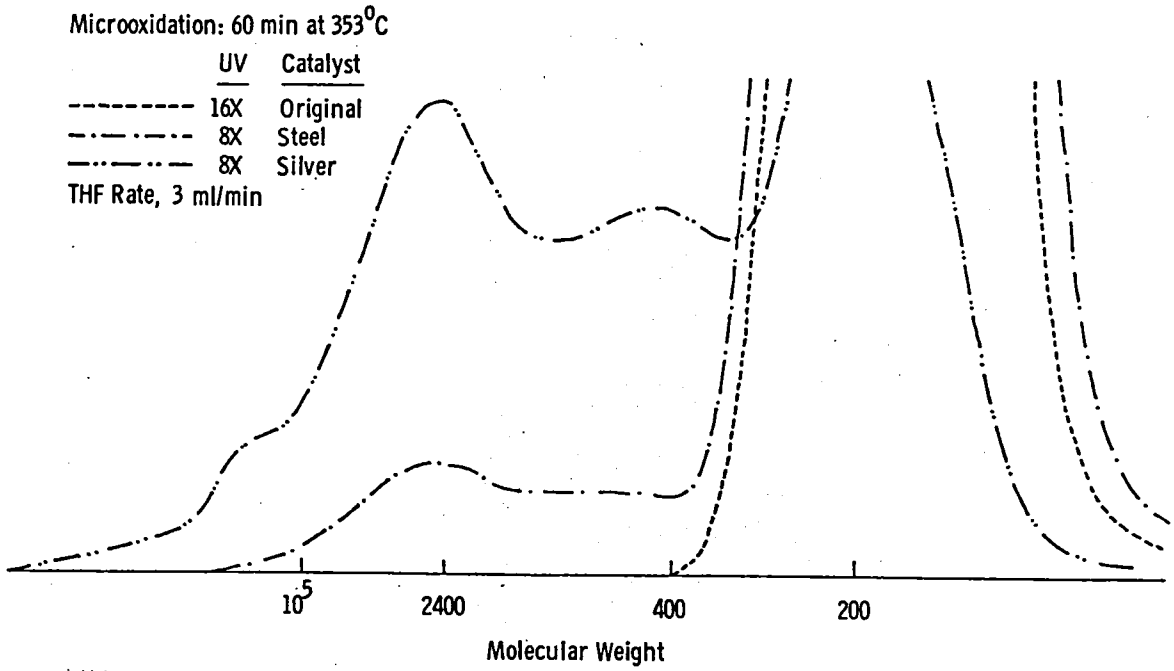


Figure A8. Microoxidation Tests With MCS 524 + PFGA at 353°C Using Steel and Silver Catalysts

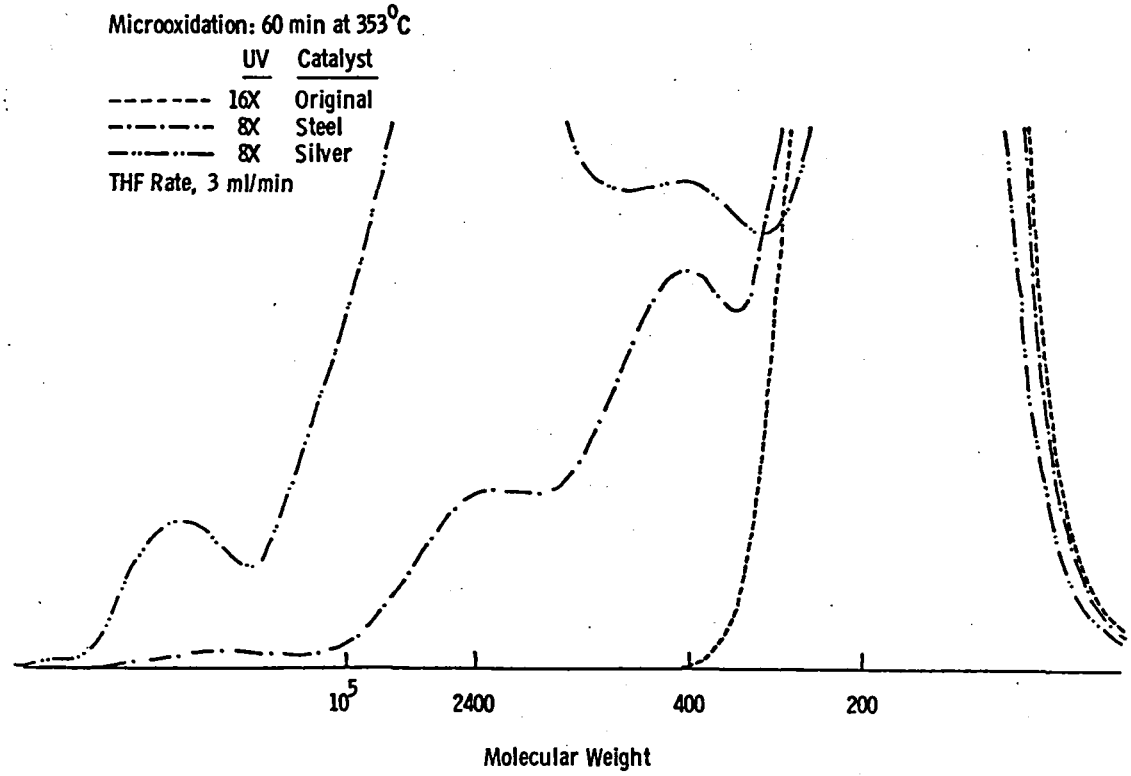


Figure A9. Microoxidation Tests with MCS 524 + PPA at 353°C Using Steel and Silver Catalysts

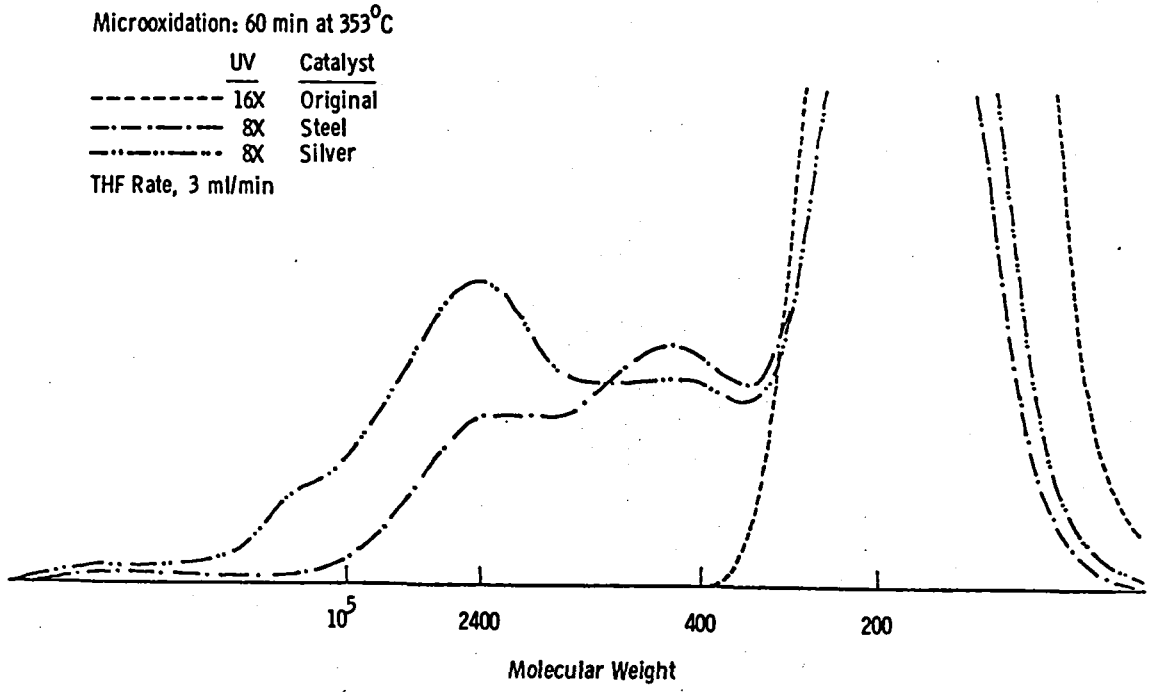


Figure A10. Microoxidation Tests with MCS 524 at 353°C Using Steel and Silver Catalysts

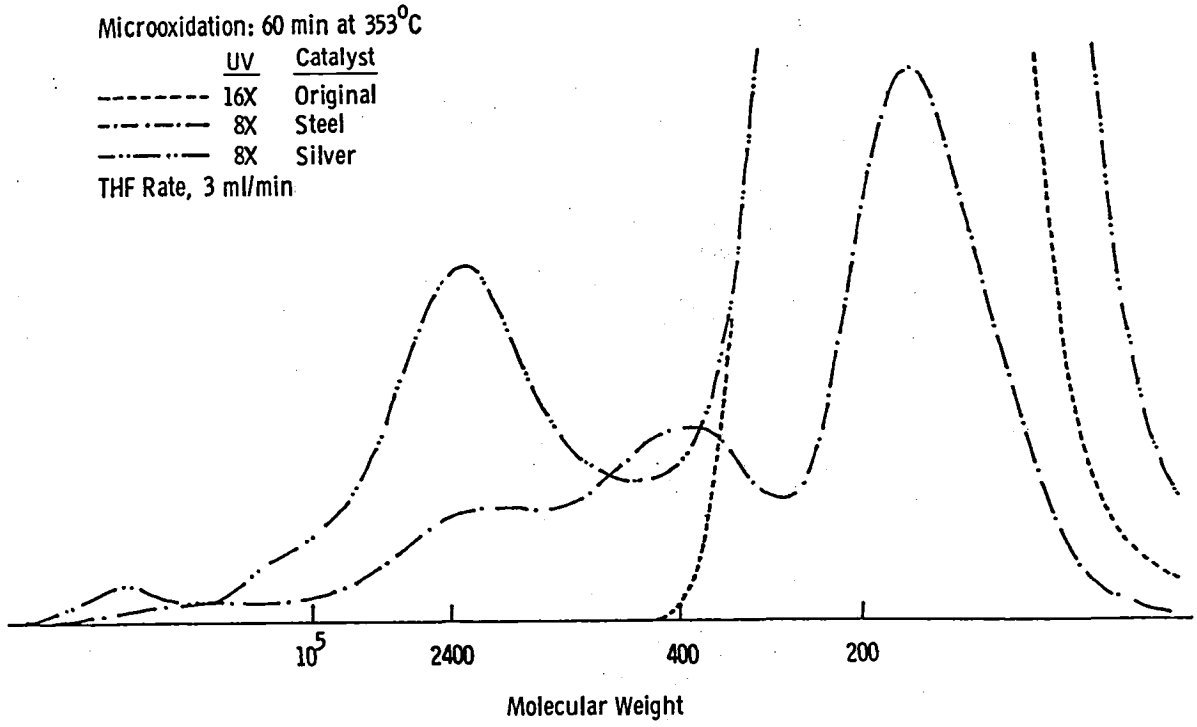


Figure A11. Microoxidation Tests With MCS 524 + FPPA at 353°C Using Steel and Silver Catalysts

Generally, silver generated about two to five times the oxidation product generated by steel. Also, the silver tended to produce more of the higher molecular weight polymeric material than the steel catalyst.

Sample MCS 524 + PPA (Figure A9) showed the largest amount of polymer product with both catalysts. (Note that this fluid also generated the most bearing deposits.) Here, the silver catalyst caused a larger increase in high molecular weight product than the steel.

MCS 524 + FPPA (Figure A11) showed a tendency to form high molecular weight polymeric products with the silver catalyst. It is interesting that the amount of very high molecular weight product (potential sludge and varnish) is relatively high compared with the amount of polymeric product in the intermediate molecular weight range.

The behavior of MCS 524 (Figure A10) is more like that of MCS 524 + PPA in the formation of high molecular products indicative of sludge and varnish. Sample MCS 524 + PFGA (Figure A8) shows a behavior pattern much like that of MCS 524 + PPA.

One problem was noted in the evaluation of the oxidized product from the micro oxidation test. The high temperature with an air flow over the test specimen surface caused evaporation of some of the original fluid which condensed on the walls of the apparatus. Occasionally, some of the condensate inadvertently returned to the test cup during removal of the catalyst specimens from the apparatus. It is believed that all of the oxidized dimers or higher molecular weight oligomers are retained in the test cup as a low volatility product. It is this high molecular weight product that is the precursor of sludge and varnish and therefore the product of interest in these studies.

In conclusion, the micro oxidation tests at 353°C for 1 hour showed substantial rates of polymeric product formation. Metal catalysis influenced the rate of polymer formation. Appropriate procedures can be developed for the collection of all the evaporated and oxidized products from the C-ethers, and analysis of polymeric products from the micro oxidation tests, bearing tests, and macro oxidation-corrosion tests appears feasible.

3. SLOW-SPEED FOUR-BALL TEST (REF. 16)

A. Description of the Rig

This instrument is a reduced-speed version of the familiar Shell four-ball lubrication tester but with disc specimens in place of clamped balls and low thermal inertia specimen holders. The slow speed of rotation (2.2 cm/min) and moderate load ensure metal contact in a near-isothermal environment. Under these conditions wear is negligibly slow, and lubrication is determined by continuously measuring the coefficient of fraction as the test sample is heated from room temperature to 371°C.

Operating conditions used in this contract were:

Speed:	1 rpm (2.2 cm/min)
Load:	4 kg (about 9.65×10^8 N/m² or ∿154,000 psi Hz load)*
Temperature:	room temeprature to 371°C (700°F)
Metallurgy:	M50 ball on M50 discs (R_C 60)** M50 ball on silvered 6415 discs (R_C = 28-32)**

*The loads on the slow four-ball runs of contract NAS3-15333 were also 4 kg though reported as 3 kg. Erroneous readings on the load gauge caused this error.

**These hardnesses matched those of the bearing. The discs used in contract NAS3-15333 were unhardened (∿R_C 20 for 6415).

After each run all parts of the instrument contacted by the fluid were cleaned in benzene in the ultrasonic cleaner.

B. Typical Information

The friction-temperature profile reveals any physical or chemical changes in the surface film which alter the friction coefficient. In effect, the test photographs chemical reactions. The resulting picture can give very precise information about the basic chemistry of particular formulations. For example, one can see and pinpoint:

- the exact temperature of surface reactions
- the presence or absence of additive interferences
- how changes in additive structure effect boundary lubrication
- additive depletion effects
- synergisms

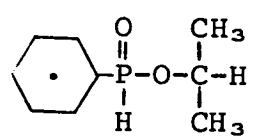
The following figures illustrate some of these points.

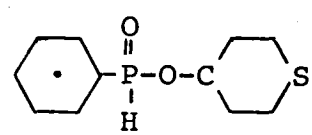
Additive Interferences

Figure A12 contrasts two formulations of MCS 524 - one contains perfluoroglutaric acid and the second contains this acid and an ester of the acid. The curves are virtually identical. This means that the acid is more surface active than the ester, and that the ester does not interfere with the surface reactions of the acid.

Figure A13 shows the large friction spike due to the presence of A-88 in MCS 524. The spike is dramatically reduced by the addition of a disulfide to the A-88. Hence, the disulfide is preventing the A-88 from reaching the surface or is coreacting with it to produce different surface chemistry.

Changes in Additive Structures





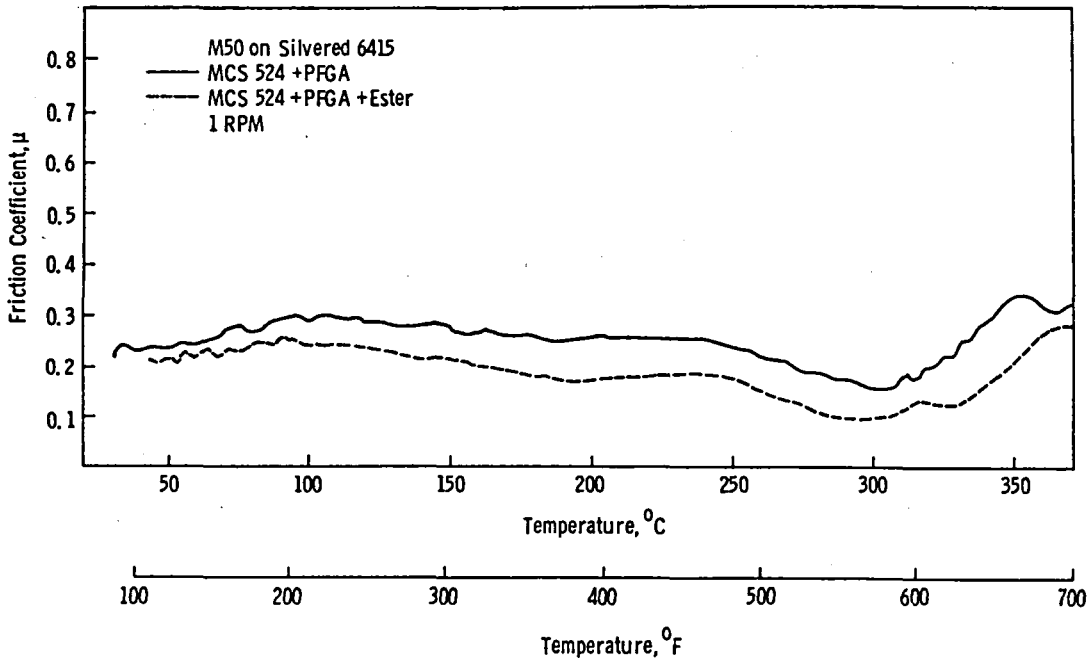


Figure A12. Friction Curves for MCS 524 + ∿0.07% Perfluoroglutaric Acid (PFGA) and MCS 524 + ∿0.07% PFGA + 0.05% Bis(2-ethylhexyl) Perfluoroglutarate

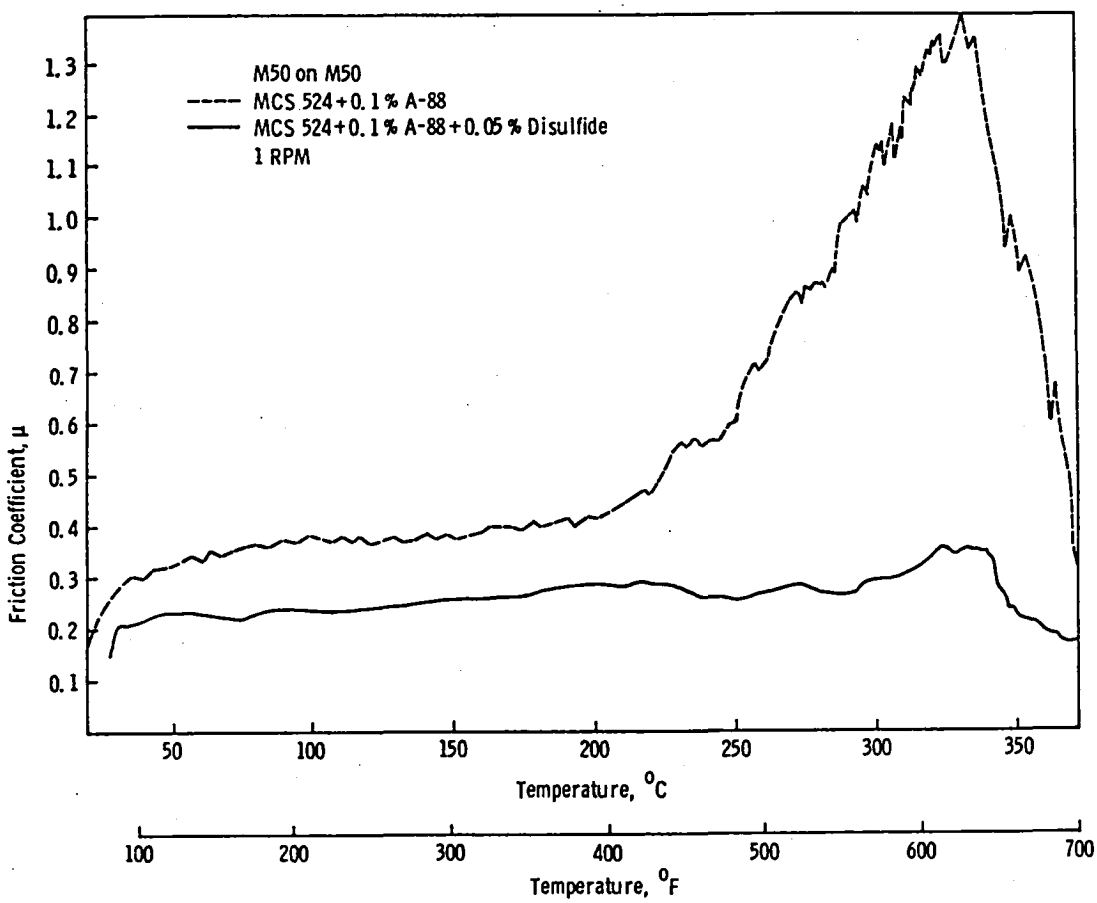


Figure A13. Friction Curves for MCS 524 + 0.1% A-88 and MCS 524 + 0.1% A-88 + 0.05% Bis(3-{[3-(phenylthio)-phenyl]thio}phenyl)disulfide

The curves for these two compounds (Figure A14) are very similar. Thus, there is no advantage in introducing the sulfur atom into the molecule, and the synthetically simpler unsubstituted ester can be considered equivalent to the more complex molecule. (Fast speed tests are needed to confirm this hypothesis.)

The slow four-ball also measures physisorption-desorption. Thus, a typical boundary friction curve for 0.003 molar tetradecanoic acid in tetradecane on stainless steel shows a sharp friction rise at 78°C (ref. 17). This is the temperature of effective desorption of the acid additive from the steel.

C. Test Data: M50 on Silvered 6415 Steel

Many of the additives which lowered the boundary friction had improved bearing life, while those showing little or no friction reduction did not. Consequently, an additive's performance in this test weighed heavily in its selection for a bearing test (section 6), and this test became a quick initial screen to discard ineffective additives.

The following compounds lowered the boundary coefficient of friction. Their curves are Figures A15 through A22 respectively.

∿0.07% perfluoroglutaric acid (PFGA) + 0.06% phenylphosphinic acid (PPA)

∿0.07% PFGA + 0.06% PPA + 0.1% bis(trimethylsilyl) perfluoroglutarate (SPFGA)

∿0.07% PFGA + 0.05% bis(2-ethylhexyl) perfluoroglutarate

∿0.07% PFGA + 0.3% SPFGA

0.1% 1-methylethyl phenylphosphinate + 0.05% trichloroacetic acid (TCA)

0.075% [3-(trifluoromethyl)phenyl]phosphinic acid (FPPA)

0.1% 1-methylethyl phenylphosphinate

0.1% Emcol PS-236 + 0.05% dibenzyl disulfide

Modest lowering of μ occurred with

0.1% phenylboric acid (Figure 23)

0.1% A-88 + 0.05% [3-(phenylthio)phenyl]phosphinic acid (FPPA) (Figure A24)

0.1% bis(trimethylsilyl) phosphonate (Figure A25)

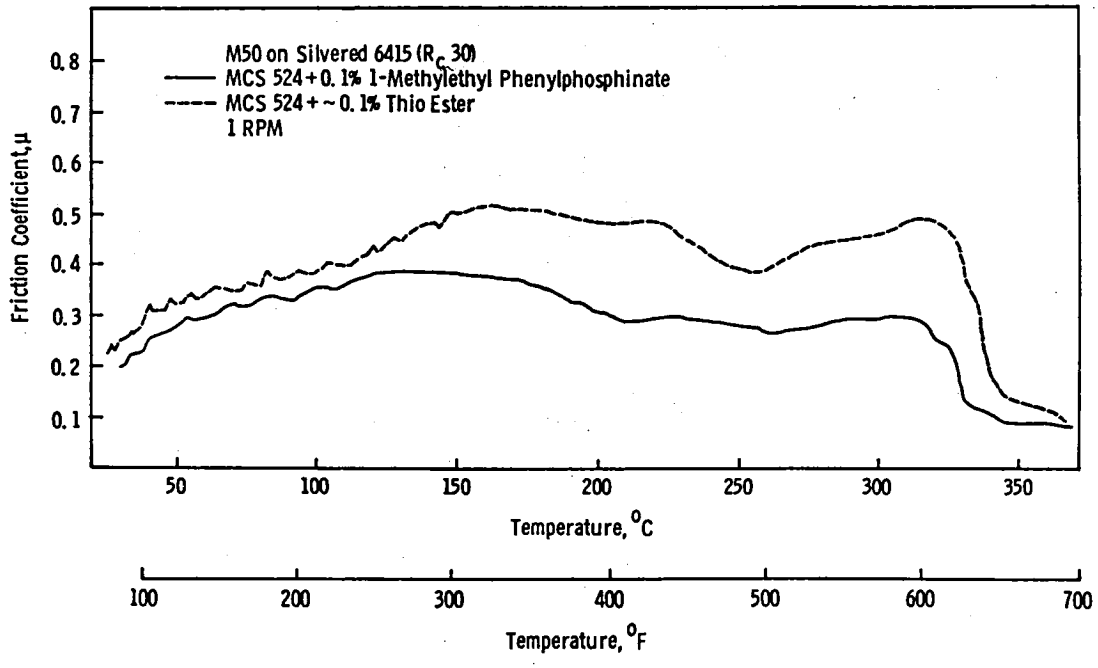


Figure A14. Friction Curves for MCS 524 + 0.1% 1-Methylethyl Phenylphosphinate and MCS 524 + ∿0.1% Tetrahydro-2H-thiopyran-4-yl Phenylphosphinate

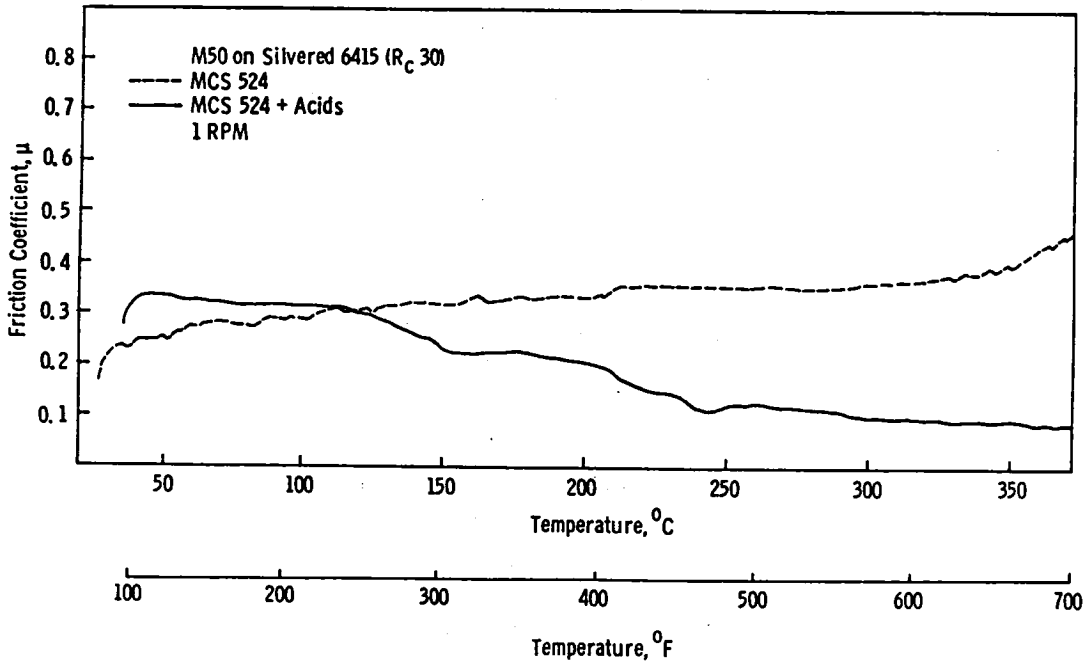


Figure A15. Friction Curves for MCS 524 and MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.06% Phenylphosphinic Acid

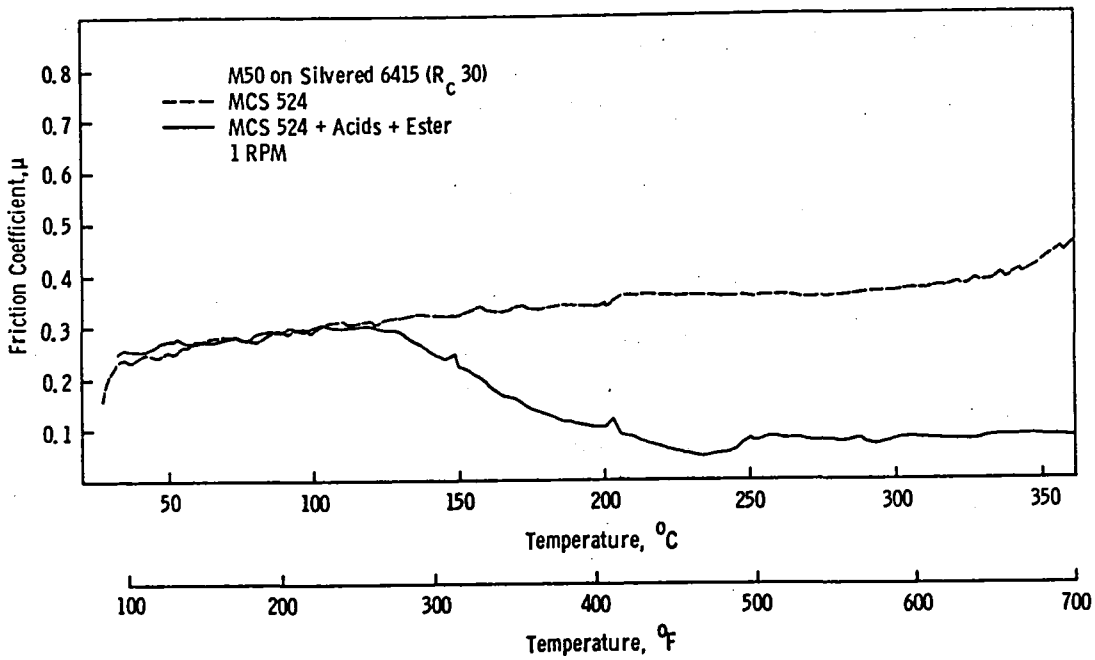


Figure A16. Friction Curves for MCS 524 and MCS 524 + ∿0.07% PFGA + 0.06% PPA + 0.1% SPFGA

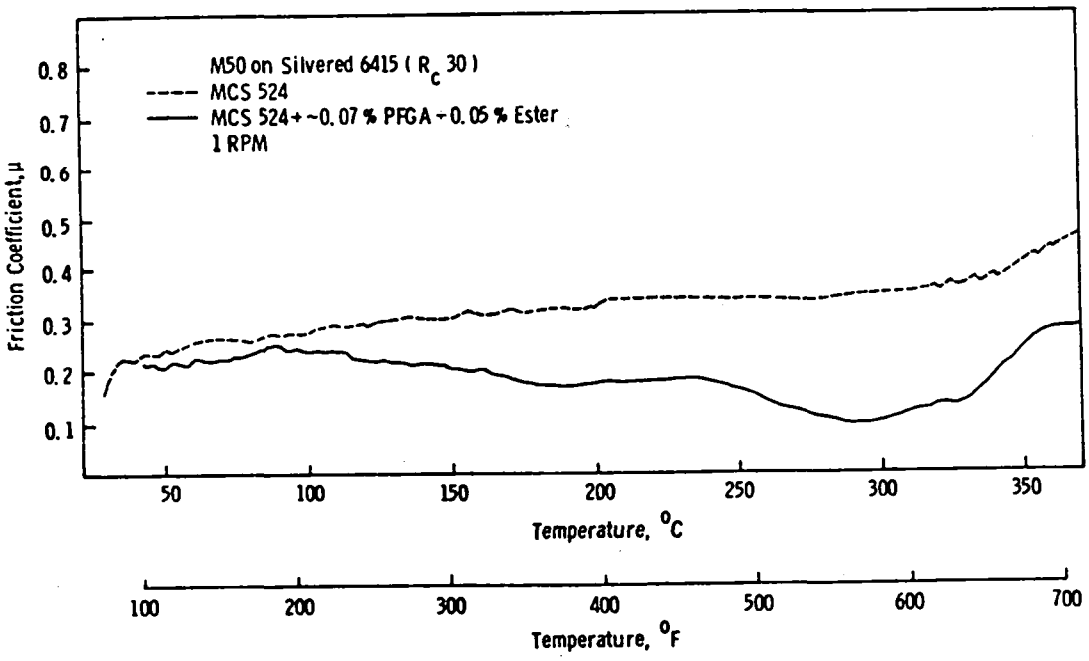


Figure A17. Friction Curves for MCS 524 and MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.05% Bis(2-ethylhexyl) Perfluoroglutarate

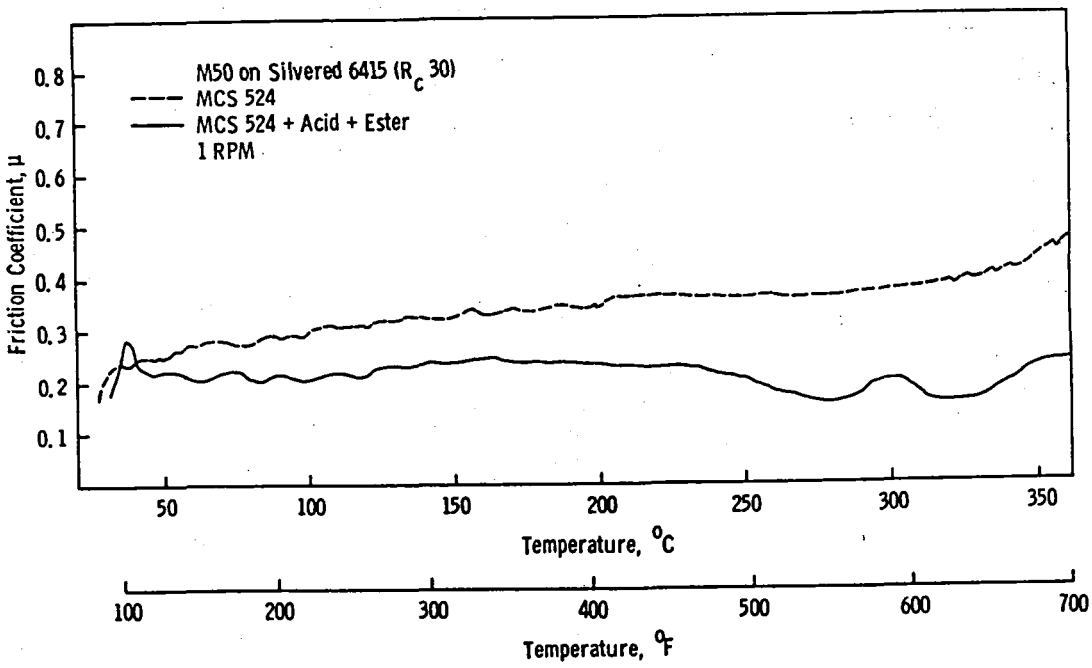


Figure A18. Friction Curves for MCS 524 and MCS 524 + ∿0.07% PFGA + 0.3% SPFGA

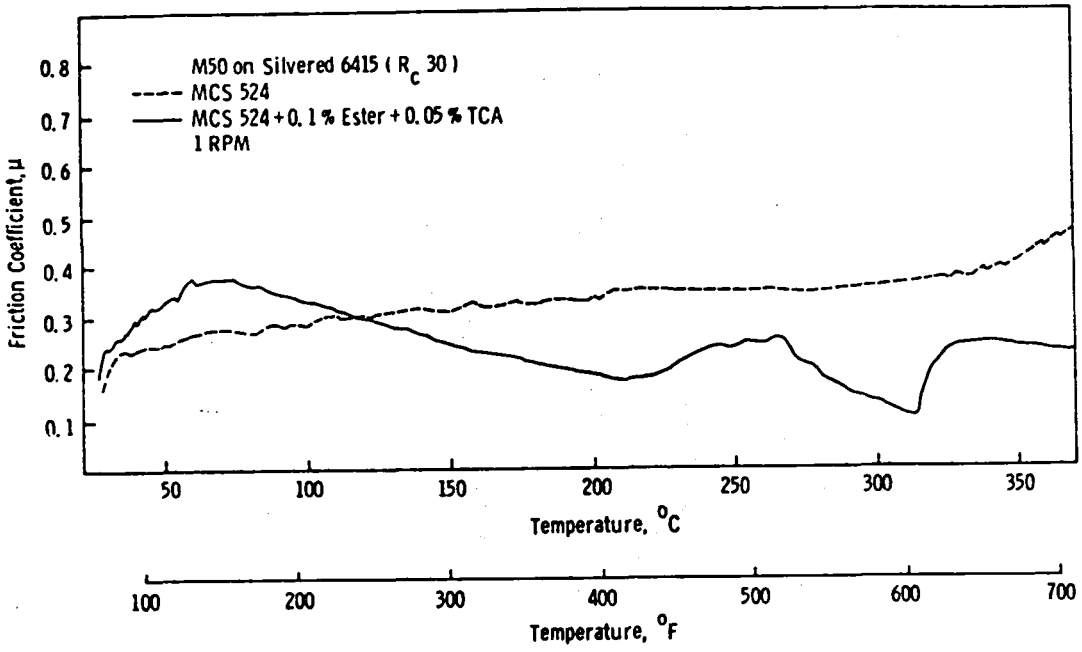


Figure A19. Friction Curves for MCS 524 and MCS 524 + 0.1% 1-Methylethyl Phenylphosphinate + 0.05% Trichloroacetic Acid

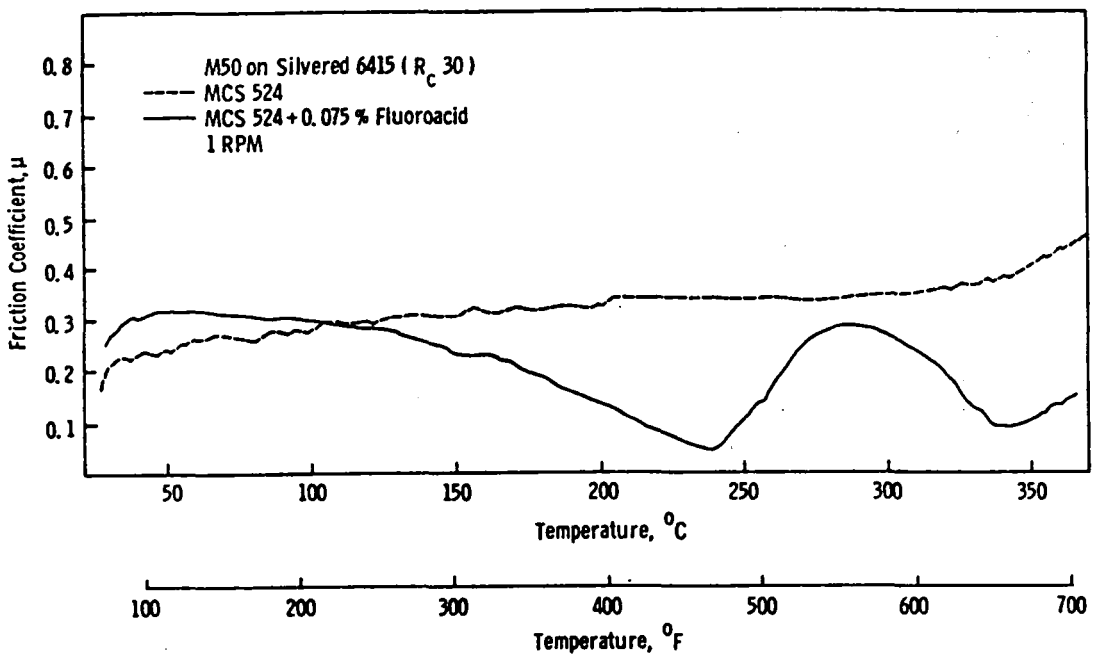


Figure A20. Friction Curves for MCS 524 and MCS 524 + 0.075% [3-(Trifluoromethyl)phenyl]phosphinic Acid

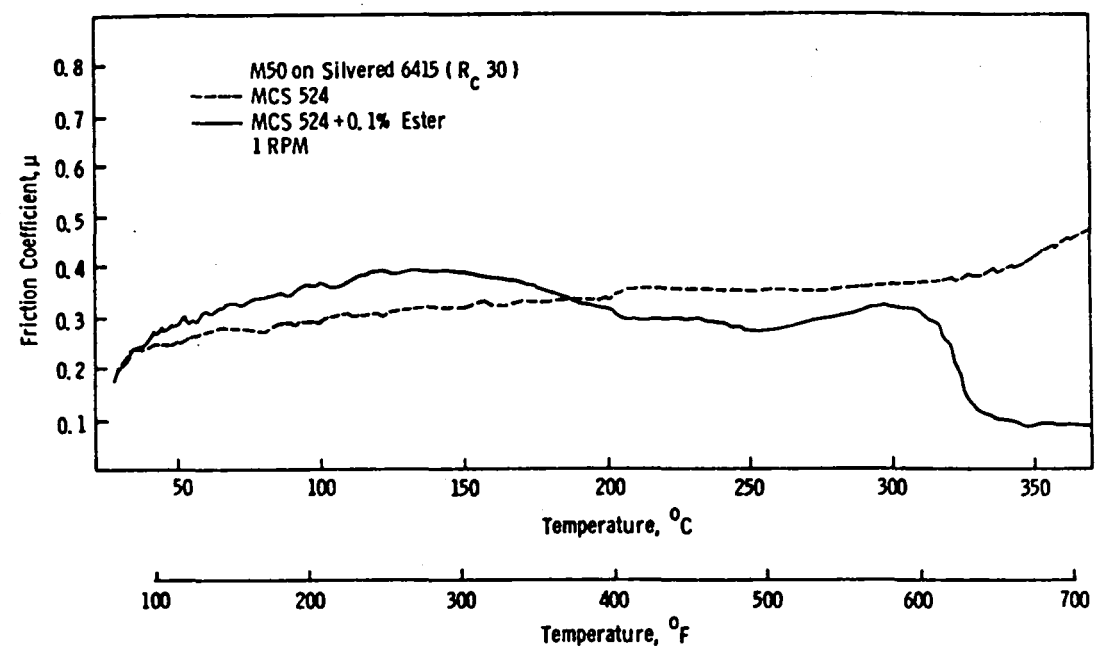


Figure A21. Friction Curves for MCS 524 and MCS 524 + 0.1% 1-Methylethyl Phenylphosphinate

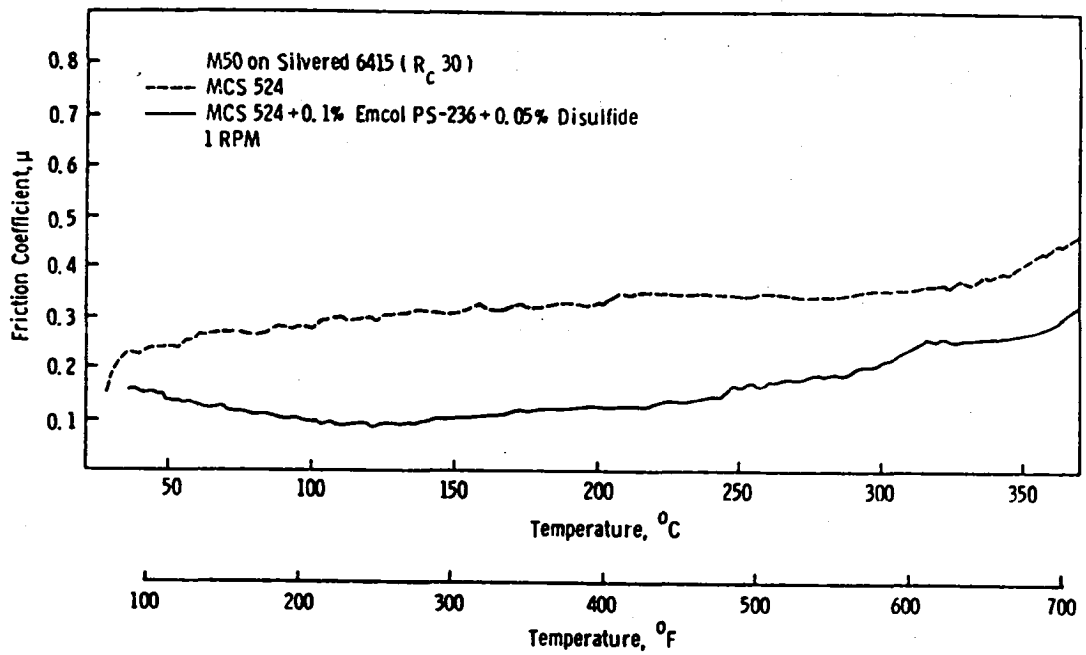


Figure A22. Friction Curves for MCS 524 and MCS 524 + 0.1% Emcol PS-236 + 0.05% Dibenzyl Disulfide

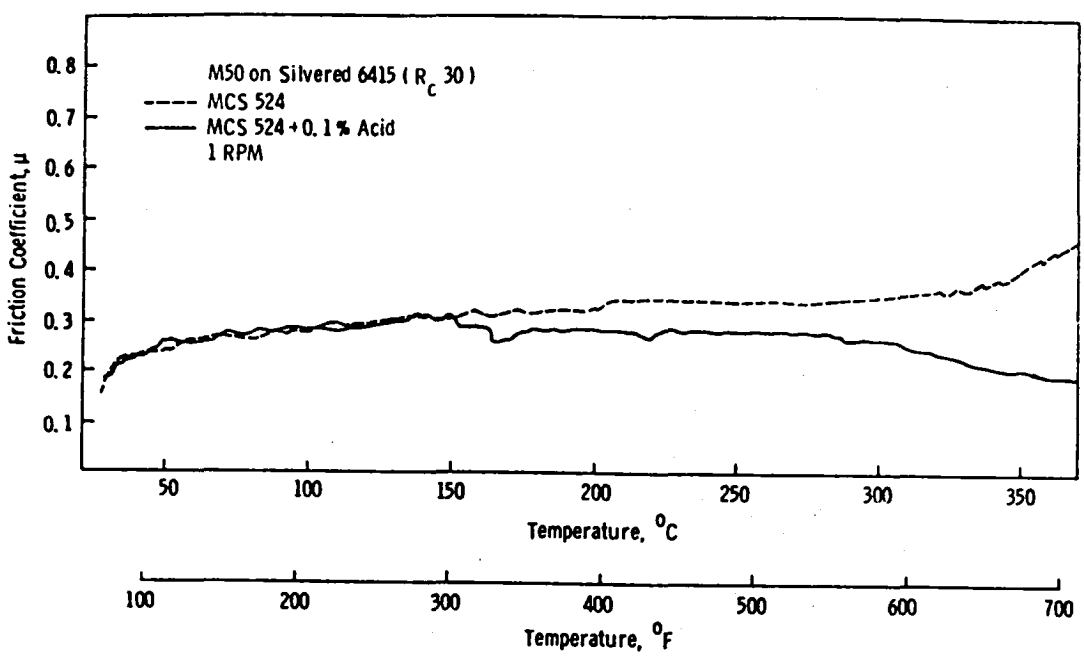


Figure A23. Friction Curves for MCS 524 and MCS 524 + 0.1% Phenylboric Acid

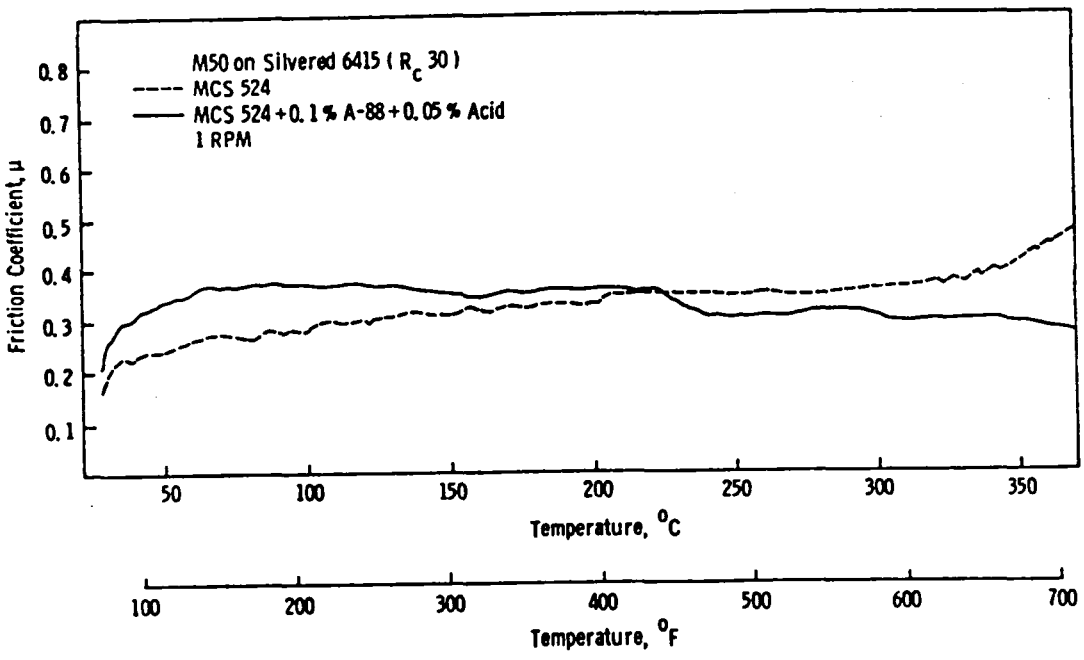


Figure A24. Friction Curves for MCS 524 and MCS 524 + 0.1% A-88 + 0.05% [3-(Phenylthio)phenyl]phosphinic Acid

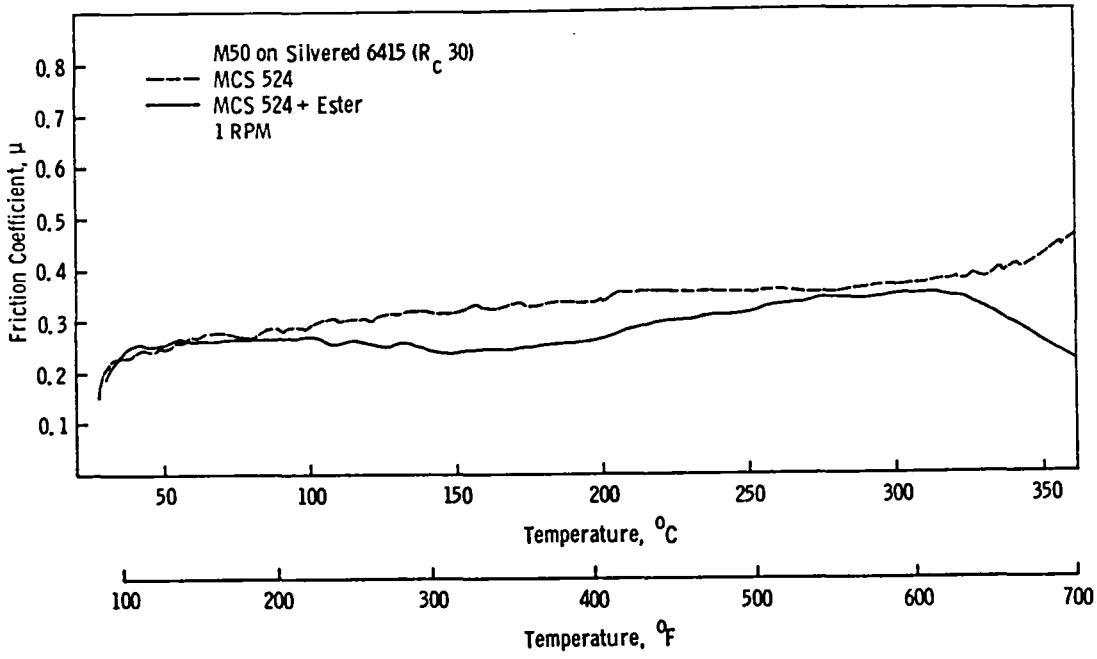


Figure A25. Friction Curves for MCS 524 and MCS 524 + 0.1% Bis(trimethylsilyl) Phosphonate

Ineffective additives included those listed below. Their curves are not shown.

∿0.1% potassium 3-(3-phenoxyphenoxy) phenate

∿0.1% potassium 3-(3-phenoxyphenoxy) phenate + 0.05% bis(trimethylsilyl) phosphite

0.2% tetraphenyltin

0.1% Olin polysilicate cluster

0.1% 3-{[3-(phenylthio)phenyl]thio}benzoic acid

0.1% bis(3-{[3-(phenylthio)phenyl]thio}phenyl)-disulfide

combination of the last disulfide and acid each at 0.1%

Figure A26 shows the curve for MCS 1892.

D. Test Data: M50 on M50

The μ-temperature curves for C-ether blends did not correlate whatsoever with bearing life, and so the data were not used in ranking the additives. This test did occasionally elucidate additive mechanisms. Also, it predicted good lubrication by esters, i.e., by MCS 1892. Surprisingly, the slow-speed test, M50 on silvered steel, did not show much lowering of the friction coefficient for MCS 1892.

Figures A27 through A38 are the curves for eleven C-ether candidate fluids and for MCS 1892.

4. FAST FOUR-BALL: M50 ON SILVERED 6415 BALL

We wanted to use the fast four-ball test primarily as a deposition test. The need for a deposition test arose when one test fluid that had a reasonably good oxidation-corrosion test gave, surprisingly, excessive sludge deposits during a 94-hour bearing test. This was rationalized by assuming the dynamic wear process led to the sludge formation. To screen for this, deposits were looked for in a fast-speed four-ball tester run under a constant air flow. This would provide both a wear and an oxidative environment.

Under mild conditions (i.e., no load applied during the warmup to 316°C), virtually all fluids tested gave no bulk deposits. Under harsh conditions (application of a 10-kg load during the warmup), 10 of 13 fluids gave heavy bulk deposits. Thus, the test was generally indiscriminate and insensitive. Moreover, two of the three relatively clean blends had heavy bearing deposits.

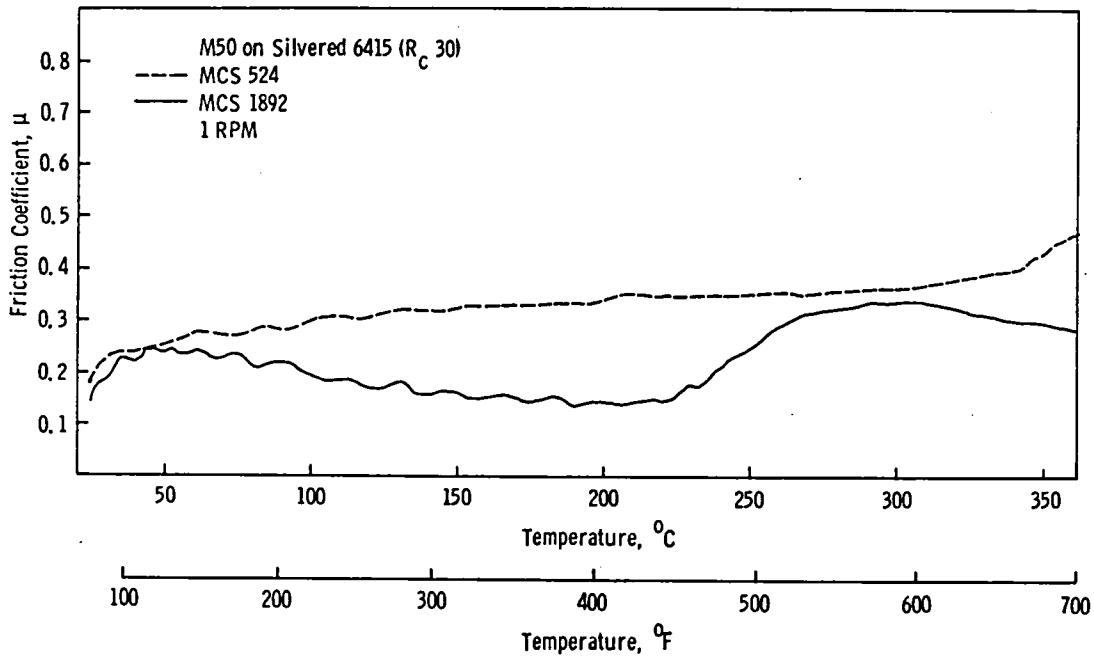


Figure A26. Friction Curve for MCS 1892

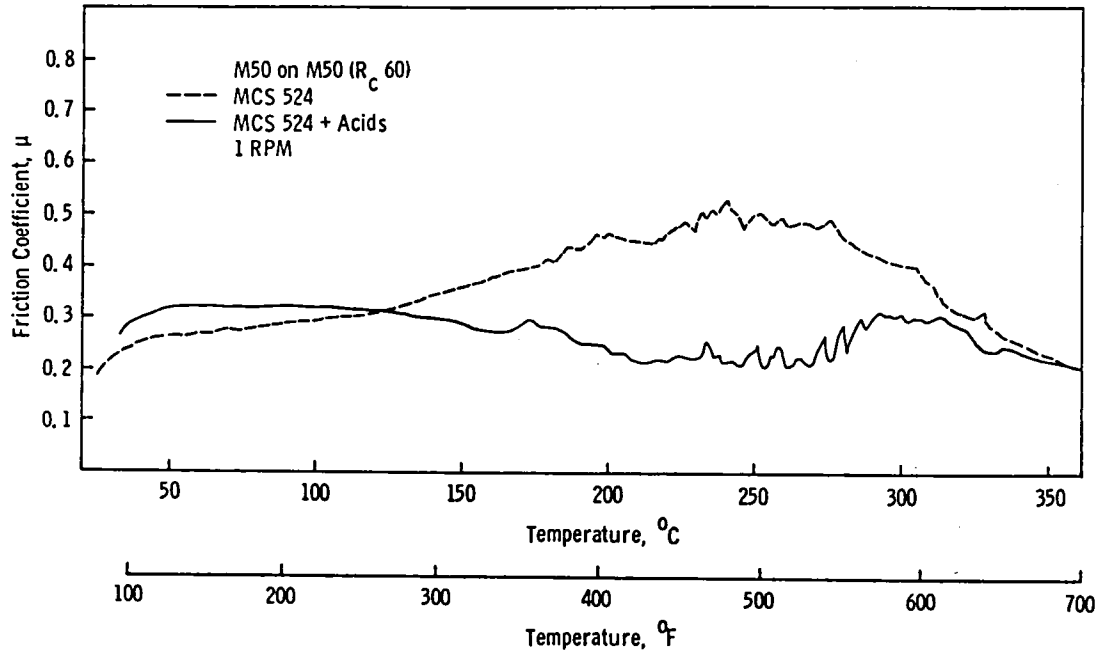


Figure A27. Friction Curves for MCS 524 and MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.06% Phenylphosphinic Acid

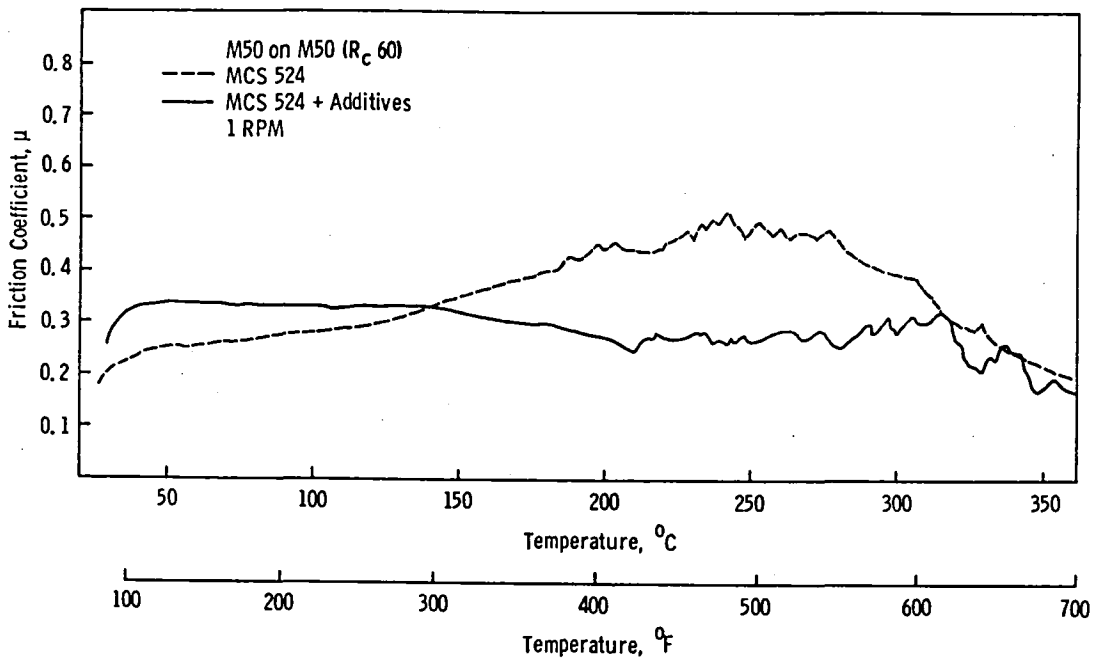


Figure A28. Friction Curves for MCS 524 and MCS 524 + ∿0.07% PFGA + 0.06% PPA + 0.1% SPFGA

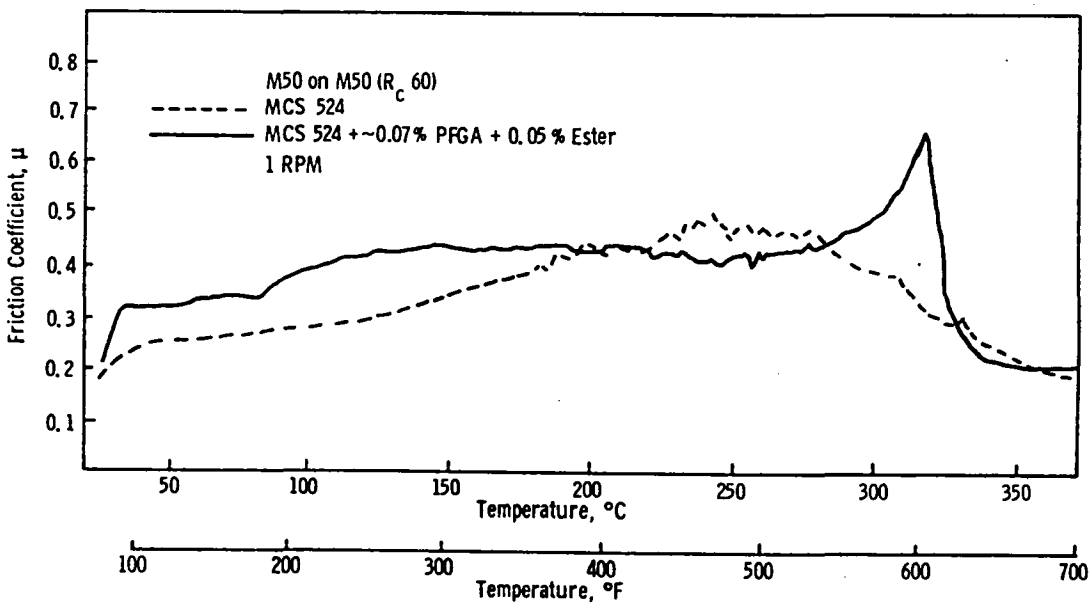


Figure A29. Friction Curves for MCS 524 and MCS 524 + ∿0.07% Perfluoroglutaric Acid + 0.05% Bis(2-ethylhexyl) Perfluoroglutarate

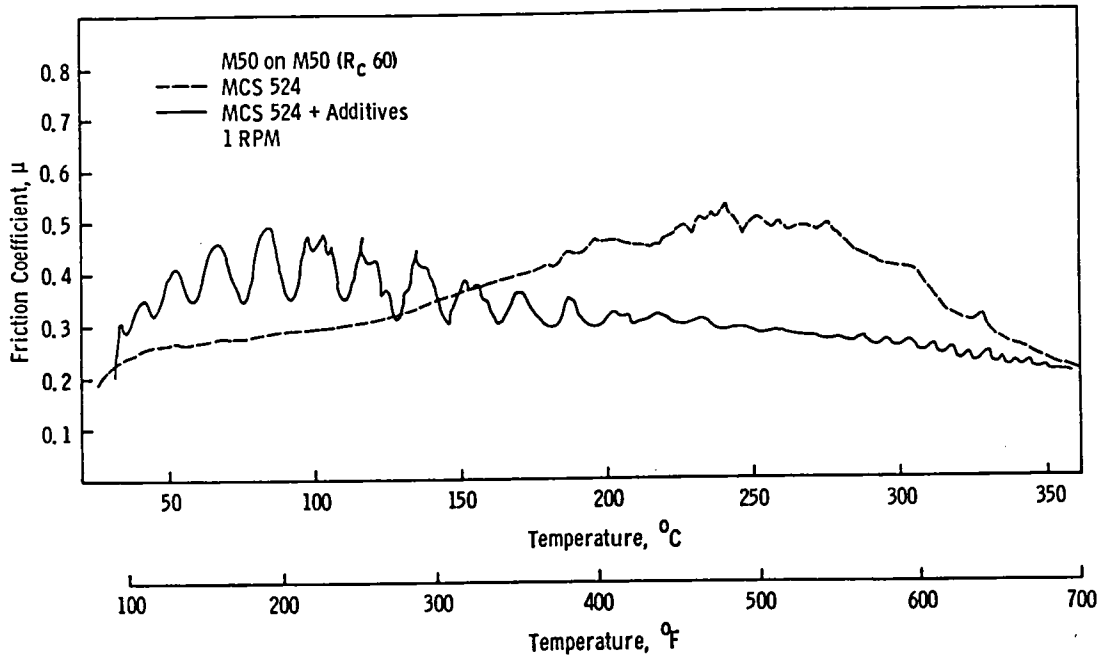


Figure A30. Friction Curves for MCS 524 and MCS 524 + ∿0.07% PFGA + 0.3% SPFGA. Oscillations in the curve may be due to misalignment of a disc.

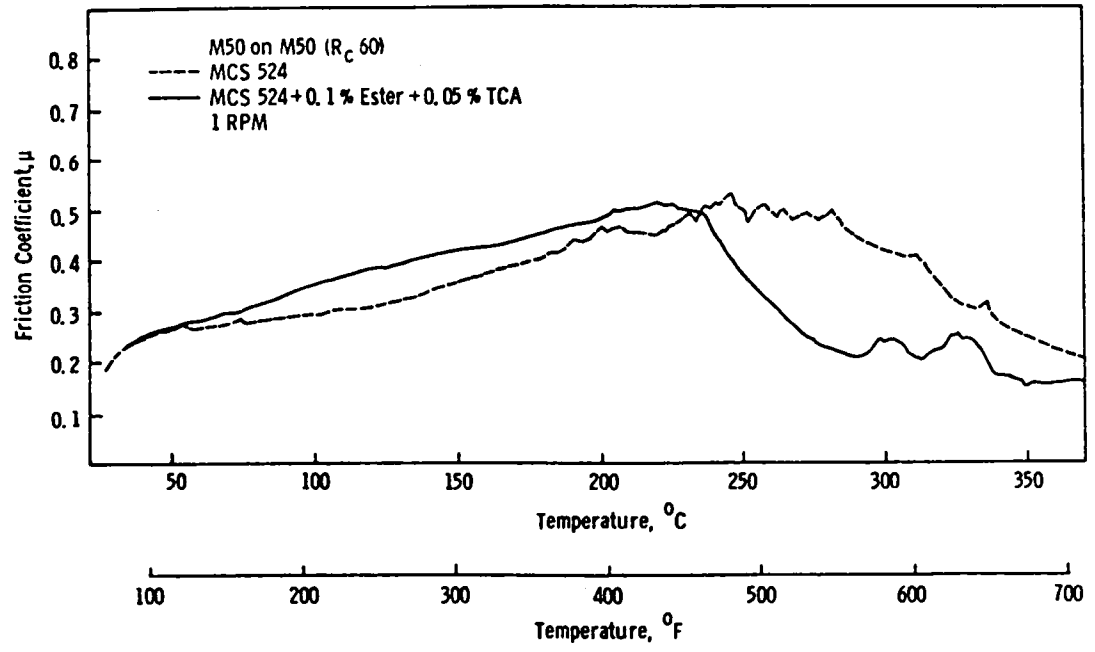


Figure A31. Friction Curves for MCS 524 and MCS 524 + 0.1% 1-Methylethyl Phenylphosphinate + 0.05% Trichloroacetic Acid

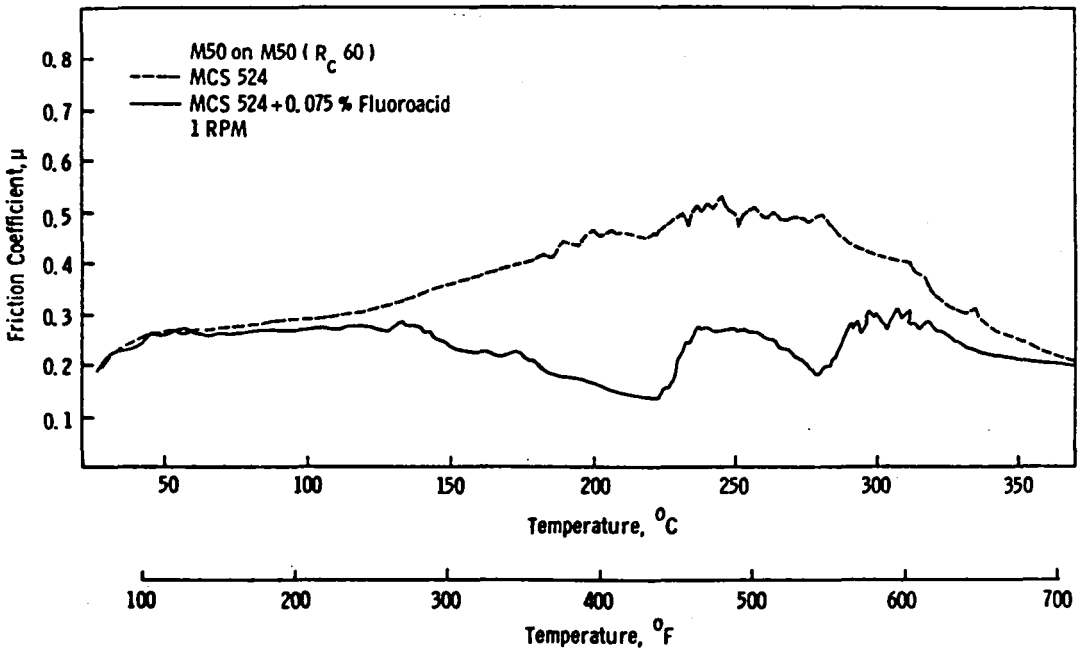


Figure A32. Friction Curves for MCS 524 and MCS 524 + 0.075% [3-(Trifluoromethyl)phenyl]phosphinic Acid

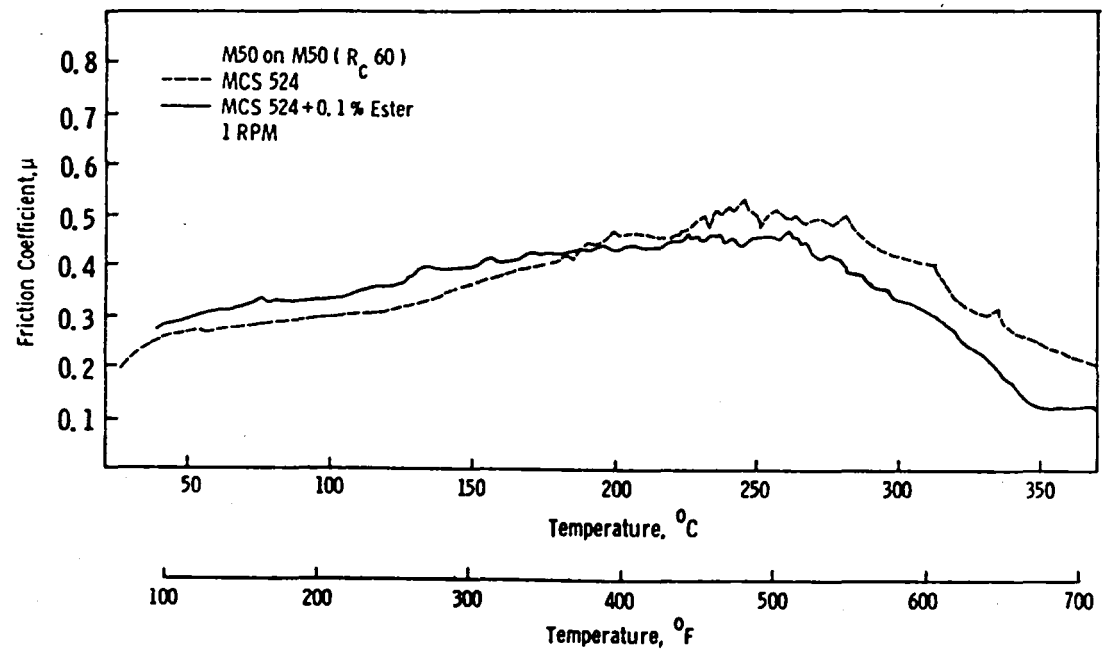


Figure A33. Friction Curves for MCS 524 and MCS 524 + 0.1% 1-Methylethyl Phenylphosphinate

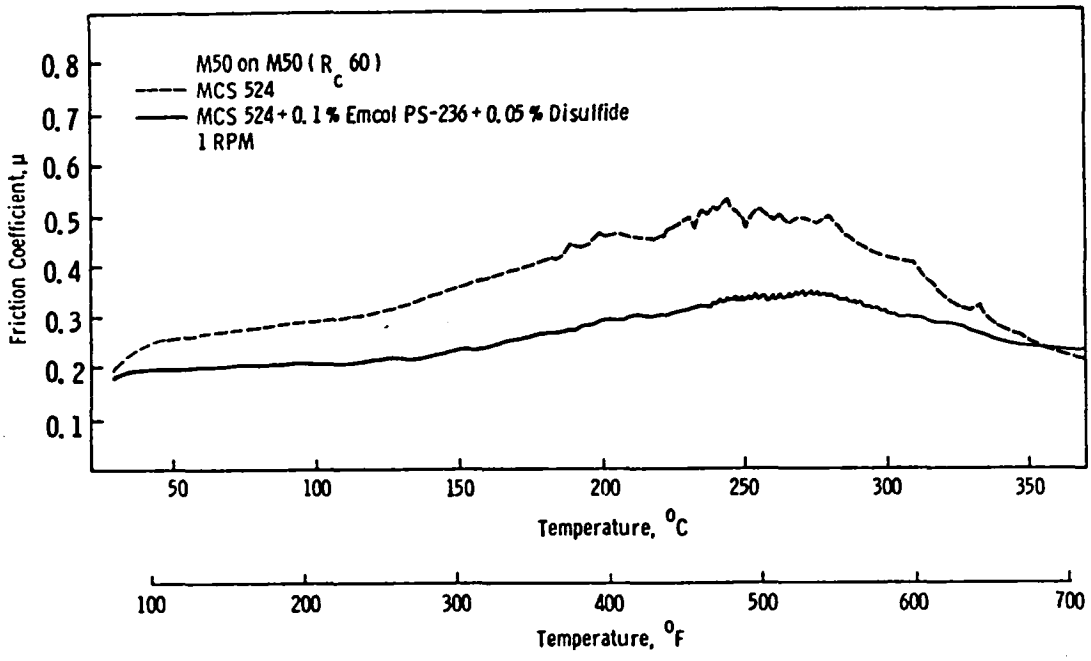


Figure A34. Friction Curves for MCS 524 and MCS 524 + 0.1% Emcol PS-236 + 0.05% Dibenzyl Disulfide

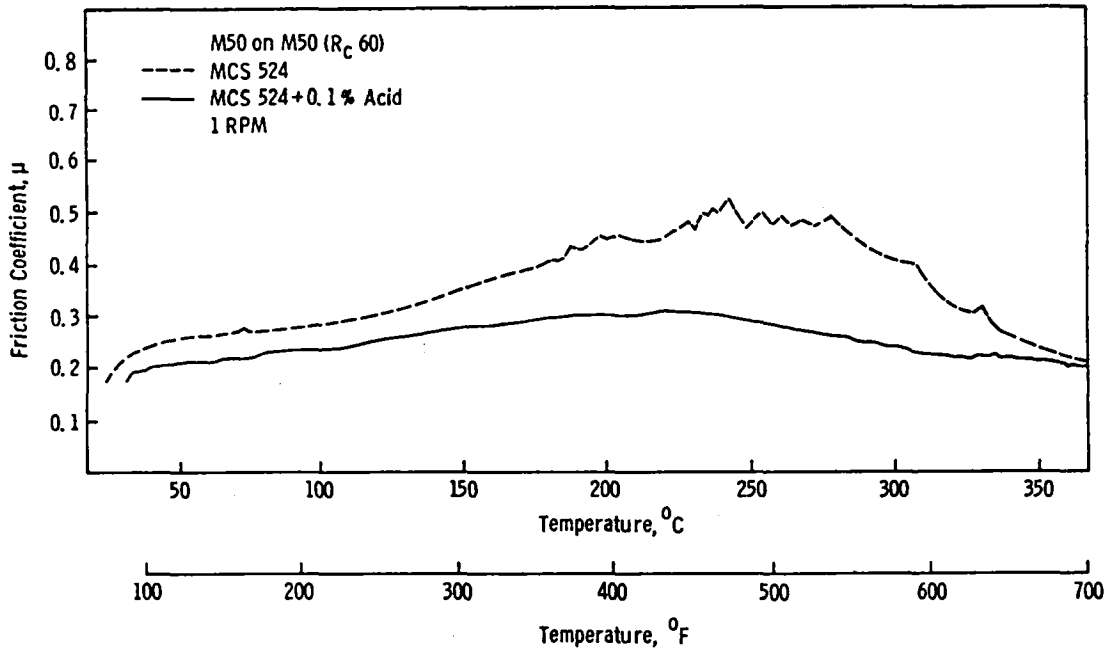


Figure A35. Friction Curves for MCS 524 and MCS 524 + 0.1% Phenylboric Acid

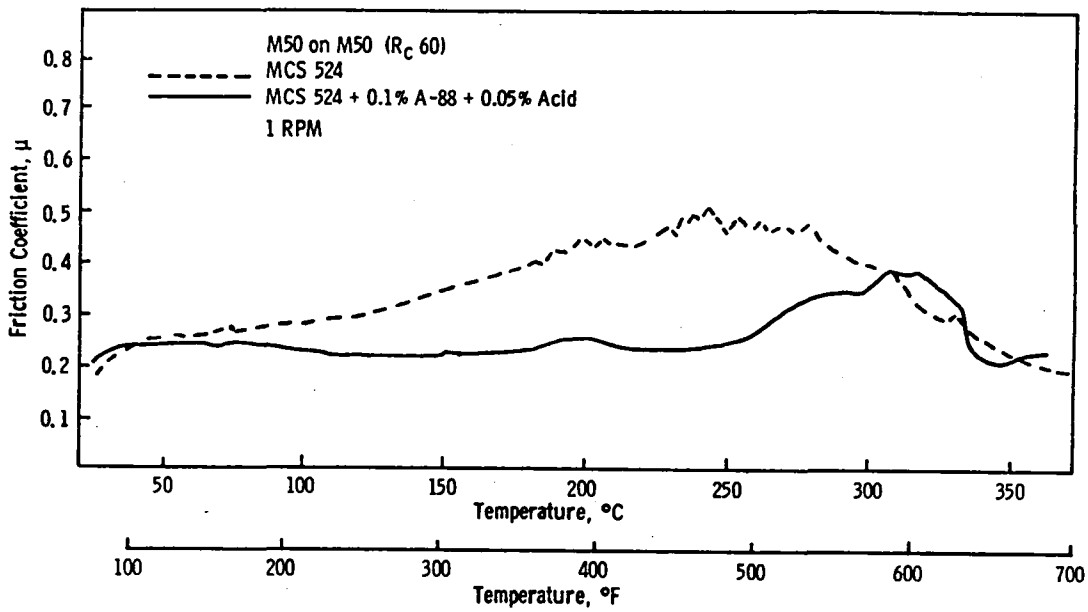


Figure A36. Friction Curves for MCS 524 and MCS 524 + 0.1% A-88 + 0.05% [3-(Phenylthio)phenyl]phosphinic Acid

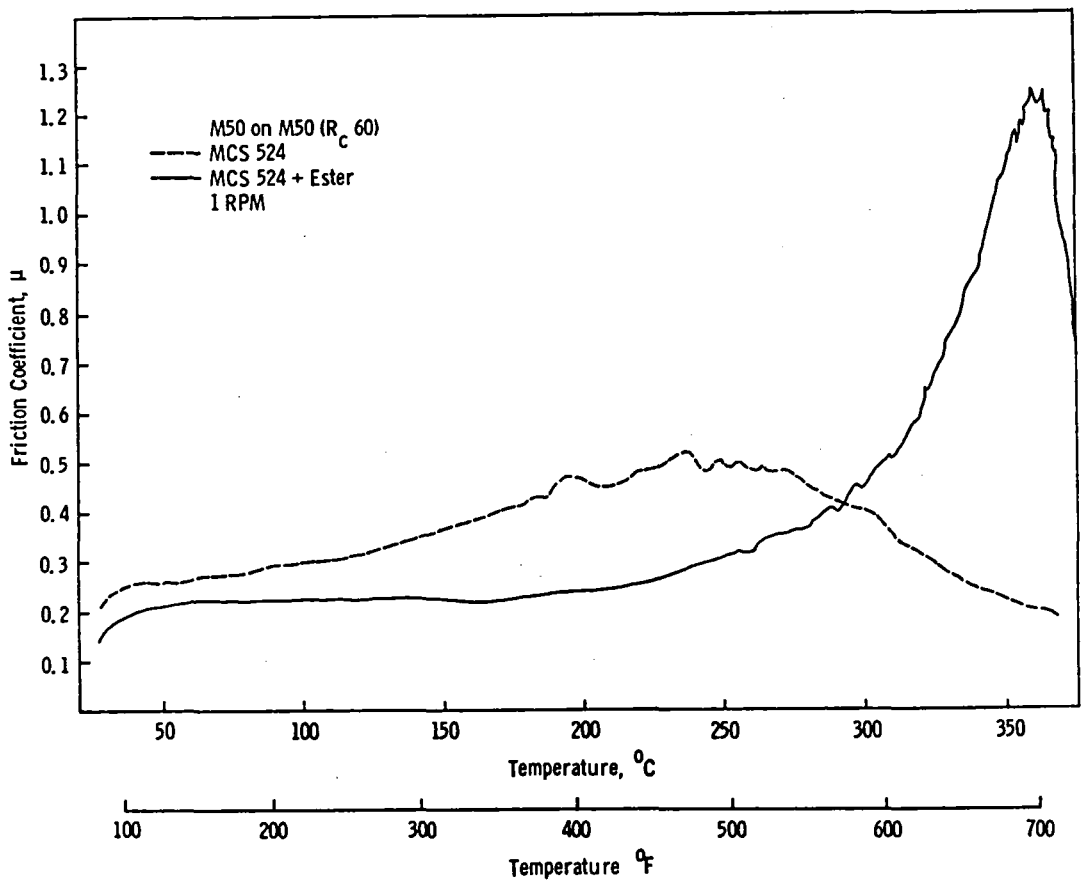


Figure A37. Friction Curves for MCS 524 and MCS 524 + 0.1% Bis(trimethylsilyl) Phosphonate

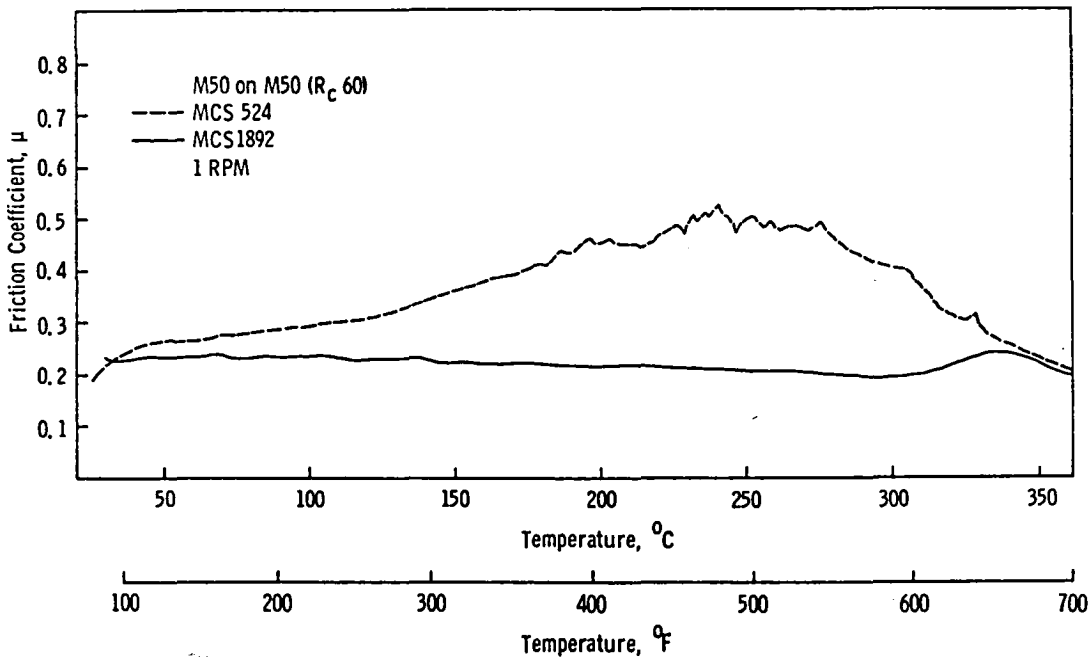


Figure A38. Friction Curves for MCS 1892 and MCS 524

Wear scars also resulted from the bench test, and these data (Table A5) were used in the additive selection analysis. The desirability factor of Table A5 is a rating system for the additives with 10 representing the smallest wear scar (the most desirable additive) and 0 representing the largest wear scar. These factors are used in statistical analyses of the data.

TABLE A5. - WEAR SCARS OF ADDITIVES IN MCS 524 ON THE FAST FOUR-BALL TEST AFTER 1 HOUR AT 316°C

(M50 on silvered 6415, 10-kg load, 1260 rpm, 3.5 liters air/hr, load applied during warmup)

Additives[a]	Average Scar Diameter, mm	Desirability Factor	Bearing Life, hr
H	1.12 (1.11, 1.12)	10	111
∿0.07% PFGA	1.32 (1.43, 1.21)	8	100[b]
0.1% A-88 + 0.05% TCA	1.37 (1.40, 1.33)	8	47[b]
C	1.39	8	
G	1.42 (1.63, 1.21)	7	13
D	1.49	7	
0.1% PPA	1.52 (1.64, 1.41)	6	94[b]
B	1.53	6	
A	1.63	5	
F	1.67	5	
0.1% Emcol PS-236 + 0.05% tetrasulfide	1.96	3	0.3[b]
E	2.09	3	
None	2.6 (3.8, 1.4)	0	0.6[b]

[a]See Tables 2 and 3 for additive codes.

[b]Data from contract NAS3-15333.

5. HIGH FREQUENCY RIG (HFR) TESTS

A. Summary

This instrument modifies the slow four-ball to obtain better simulation of fast speed lubrication. For C-ether formulations, many of the reactions seen in the slow four-ball also took place in the high frequency test, but the temperatures of some reactions did not match.

B. Description of the Rig

This recently designed apparatus alters the slow four-ball test to obtain frequent asperity contacts at slow speed. The rationale for this change is explained below:

Satisfactory screening for lubrication failure requires simultaneous simulation of both surface temperature and the repetition rate of asperity contacts. High speed tests such as the fast four-ball achieve the correct repetition rate, but the surface temperature remains unknown because of the flash rise at the contacts. Slow speed tests eliminate surface frictional heating and so the surface temperature equals the bulk temperature. However, for the rotating member, long time periods pass between asperity contacts. This may allow time for additive reactions on the surface which would not occur in fast-moving equipment.

The high frequency rig resolves this dilemma by attaining frequent contacts at slow speeds. This is done by oscillating a peg against a stationary flat back and forth at high frequency but over a small distance. Because the amplitude is small, the velocity is low and causes only a 5-10°C temperature rise. The high frequency ensures continual contact. Placing the entire assembly in an oven allows temperature control while a force gauge measures the coefficient of friction. A more detailed description of the rig and its use in studying diesel engine piston scuffing is in print.*

In the present studies, an M50 steel peg oscillated against a silvered 6415 surface. Initial experiments using a 0.64-cm (1/4-in.) diameter ball resulted in quick penetration of the silver layer. Use of the lowest possible load and an arm rounded to the curvature of a 2.54-cm (1-in.) radius minimized this problem. Specific test temperatures followed those of the bearing tests.

C-ether blends: Contact began at 150°C. It continued as the temperature rose to 316°C over 15 minutes and held at 316°C for 30-40 minutes.

Ester (MCS 1892): The test started at 150°C with a friction trace obtained up to 232°C. Other parameters included:

Frequency: 50 Hz
Load: 200 g
Contact pressure: 6.9×10^7 N/m^2 (10^4 psi)
Stroke: 1 mm

*See ASLE preprint No. 80-AM-4D-1 by Dr. A. Cameron and T. N. Mills.

Prior to use, test pieces were cleaned ultrasonically in toluene, then acetone, and air dried. Because of the duration of the test and high temperatures, it was occasionally necessary to add small amounts of fresh oil to the rig.

C. Test Results

The ester fluid's friction dropped from an initial 0.18 to 0.07 at 232°C, a value lower than any displayed by a C-ether.

Some of the C-ether curves are outlined in Table A6 and in a different way in Table A7. Highlights of these traces include:

- Above 200°C, the friction for PFGA additive dropped steadily from 0.29 to 0.14. This acid performed well in the bearing test.
- The general shape of the curves for the arylphosphinic acids resembled that of the corresponding slow four-ball curves. That is, two reactions (friction lowerings) took place, one at very high temperature. However, the first reaction took place at a higher temperature in the high frequency rig.
- Curves for combinations of PFGA plus arylphosphinic acids looked like those of the arylphosphinic acids. In the slow four-ball, such combinations showed synergistic friction lowering.

Generally the HFR recorded the high temperature reactions observed in the slow four-ball. Sometimes the friction rose after addition of fresh oil. In some of the bearing tests, filter pluggings (wear?) resulted after charging make-up fluids.

6. RUB-BLOCK TESTS

The final report of contract NAS3-15333 (ref. 3) describes the test rig in detail. Essentially, it uses a ring rotating against two stationary blocks to measure friction and/or wear. Wear tests using an M50 ring on silvered 6415 blocks were not reproducible. All subsequent tests used M50 on M50, with each test consisting of two parts - a slow speed friction test and a fast speed wear test.

In the friction test, the speed was idled from 1,000 rpm to 0 rpm at constant loads with recording of the resulting torque. Six loads were used per test. Pounds-force on the specimens at each successive load were as follows: 0, 5.9, 14.7, 26.5, 44.2, and 61.8. The initial load produced contact between the blocks and the ring; application of the higher loads followed sequentially with load release after each idle to 0 rpm.

TABLE A6. - COEFFICIENT OF FRICTION AT DIFFERENT TEMPERATURES DURING HFR TESTS ON C-ETHERS

Additive[a]	μ, 150°C	μ, 250°C	μ, 316°C (start)	μ, 316°C (finish)	Remarks
None	0.16	0.17	0.18	0.18	
PFGA	0.23	0.24	0.18	0.15	Peak μ = 0.29 at 180°C
PPA	0.23	0.3	0.37	0.11	Small μ lowering, 220-285°C
FPPA	0.2	0.26	0.2	0.11	Sharp μ drop, 250-290°C
PFGA + PPA	0.18	0.32	0.15	0.08	Fresh oil added at end of run; sharp μ drop at 280°C
PFGA + FPPA	0.2	0.1	0.28	0.18	μ drop at 200-260°C; μ rise after adding fresh oil
PFGA + PPA + SPFGA	0.25	0.3	0.16	0.11	Sharp μ drop at 190-220°C; μ peaks at 250°C; small μ rise after adding fresh oil

[a]See Table 2 for abbreviations.

TABLE A7. - TEMPERATURE OF REACTIONS OF C-ETHERS IN THE SLOW FOUR-BALL AND HFR TESTS

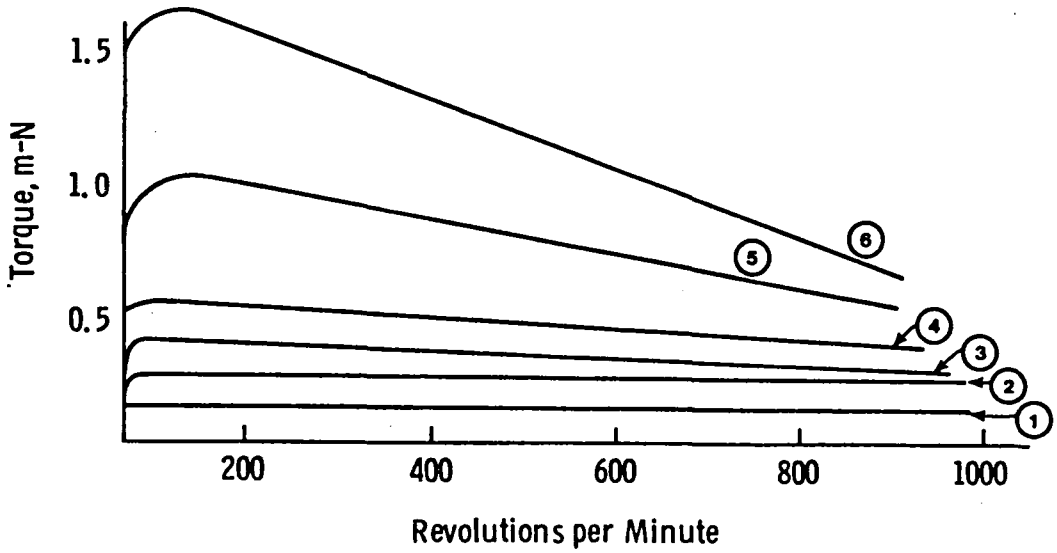
Additive[a]	Slow Four-Ball		HFR
	M50/M50	M50/Silvered 6415	
PPA	100-200°C; above 316°C	120-215°C; above 270°C	220-285°C (small); above 316°C
FPPA	125-225°C; above 316°C (?)	125-240°C; above 300°C	250-290°C; above 300°C
PFGA		100-300°C	Above 200°C
PFGA + PPA	150-280°C	100-370°C	210-250°C (small); above 280°C

[a]See Table 2 for abbreviations.

The instrument was then run for 1/2 hour at 10,000 rpm and 10.6 lb-force, giving a high-speed, steel-on-steel wear test.

A. Slow Speed Friction Test Data

Figure A39 presents an idealized form of typical torque-speed curves for the MCS 524 base stock. As the speed decreases and the load increases, the torque increases. Most formulations in MCS 524 gave lower torques than the base stock. Table A8 summarizes these experiments. Some of the data were taken from contract NAS3-15333. Again, the desirability factor is a rating system ranking the performance of the various additives.



(1) 0 lb-force (4) 26.5 lb-force
(2) 5.9 lb-force (5) 44.2 lb-force
(3) 14.7 lb-force (6) 61.8 lb-force

Figure A39. Rub-Block Torque-Speed Curve for MCS 524: M50 on M50, 316°C

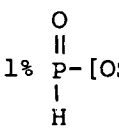
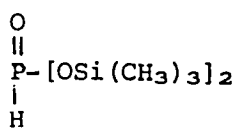
B. Test Data From The Fast Speed Wear Test

After 30 minutes at 10,000 rpm, the base stock produced a wear scar of 0.51 cm. High, oscillatory friction accompanied this wear. In contrast, five of the candidate formulations gave noticeable wear reductions and smooth friction. The data are presented in Table A9.

The standardization of the wear test with the A-88/TCA blend resulted in one good performance and one poor performance. This emphasized the desirability of duplicate or triplicate runs.

The attempt to improve the wear of potassium salt blends by adding a sterically hindered phosphonate proved unsuccessful.

TABLE A8. QUALITATIVE DESCRIPTION OF THE TORQUE-SPEED CURVES OF MCS 524 FORMULATIONS: SLOW-SPEED RUB-BLOCK TEST AT 316°C, M50 ON M50

Additives[a]	Description of the Curve	Desirability Factor
H	Lower torque	10
∿0.07% PFGA + 0.06% PPA	Lower torque	9
C	Lower torque	9
G	Lower torque	9
A	Lower torque	8
B	Like MCS 524	4
D	Like MCS 524	4
None	Standard (see Figure A39)	4
F	Higher torque	3
E	Higher torque	2
A-88 + TCA	a) Higher torque	3
	b) Lower torque	8
0.1% 	Like MCS 524	4
0.1% ØOØOØOK	Higher torque	2
0.1% ØOØOØOK + 0.05% 	Higher torque	2
∿0.07% PFGA + 0.06% + 0.1% SPFGA	Higher torque	2

[a]See Tables 2 and 3 for additive codes.

TABLE A9. - RUB-BLOCK WEAR OF MCS 524 FORMULATIONS

(M50 on M50, 316°C, 10,000 rpm, 30 min)

Additives[a]	Wear Scar		Friction	Desirability Factor
	cm	inch x 0.01		
B	0.03	1	Smooth	10
A	0.04	1-1/2	Smooth	10
H	0.08	3	Smooth	9-1/2
PFGA + PPA	0.08	3	Smooth	9-1/2
G	0.11	4-1/2	Smooth	9
C	0.13	5	Smooth (initial spike)	9
E	0.18	7	Fairly rough	6
F	0.51	20	Rough	0
D	0.53	21	Rough	0
None	0.51	20	Rough	0
A-88 + TCA	0.05	2	Smooth	9-1/2
	0.51	20	Rough	0
0.1% $\begin{matrix} O \\ \| \\ P\text{-}[OSi(CH_3)_3]_2 \\ \| \\ H \end{matrix}$	0.06	2-1/2	Smooth	9-1/2
0.1% ØOØOØOK	0.46	18	Rough	0
0.1% ØOØOØOK + 0.05% $\begin{matrix} O \\ \| \\ P\text{-}[OSi(CH_3)_3]_2 \\ \| \\ H \end{matrix}$	0.36	14	Rough	0
∿0.07% PFGA + 0.06% PPA + 0.1% SPFGA	0.11	4-1/2	Smooth	9

[a]See Tables 2 and 3 for additive codes.

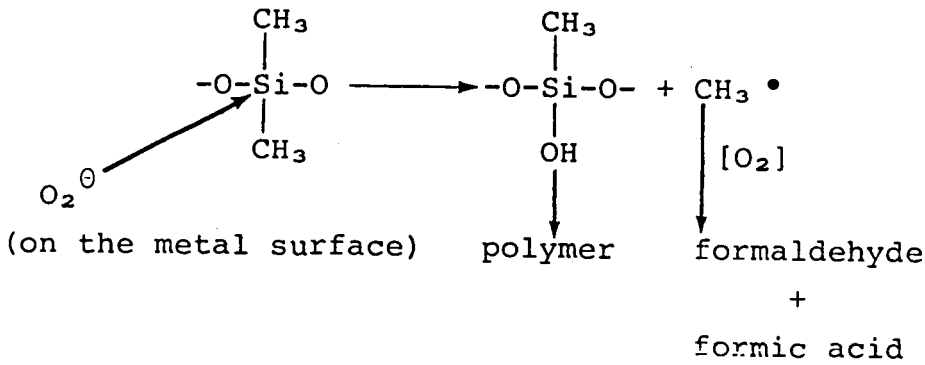
APPENDIX B

SCREENING TESTS: MCS 1305 FORMULATIONS

Eight of ten blends survived the initial oxidation-corrosion tests. Usually, these tests were run without copper since the unformulated base stock can give deposits when copper is present. Two compounds screened as copper inhibitors proved ineffective. The data are in Table B1.

Phenylboric acid inhibits copper corrosion by C-ethers but failed to protect copper in the C-ether/disiloxane fluid. Moreover, the boric acid blends had higher viscosity increases than the unformulated MCS 1305. The question arises: Why is the additive effective in one base stock but not in the other? Studies of the polymerization of methyl silicones suggest an explanation.

This polymerization is catalyzed by metal oxides such as copper or iron oxides which are thought to react via an oxidative attack of oxide anion on the silicon atom (ref. 18). This splits off a methyl radical and forms an oxy-silicone which can cross-link or polymerize:



The methyl fragment is oxidized to formic acid which can attack copper as long as the acid is present in the system. The disiloxane components of MCS 1305 have silicon atoms similar to the silicon in silicones. Therefore, there is a pathway for oxidation of these molecules which is not available for C-ethers.

In the fast-speed four-ball tests, the MCS 1305 base stock and blends gave more deposits than the corresponding C-ether fluids. This may be related to the tendency of silicones to gel under boundary lubrication conditions. Some additives (e.g., A-88)

TABLE B1. - OXIDATION-CORROSION TESTS ON MCS 1305 BLENDS

(48 hours, 5 liters air/hour)

Additives[a]	Viscosity Increase, %		Copper Weight Loss,[b] mg/cm²		Silver Weight Loss,[b] mg/cm²		Deposits	
	260°C	278°C	260°C	278°C	260°C	278°C	260°C	278°C
None	87	128	-3.6	-7.6	-3.3	-1.9	none	medium sludge
	4	6	(c)	(c)	-0.2	-0.8	none	none
0.1% A-88	8	9	(c)	(c)	-0.2	-0.4	none	none
0.1% A-88 + 0.05% TCA	8	10	(c)	(c)	-0.3	-0.4	none	none
A	7	8	(c)	(b)	-0.2	-0.4	none	none
B	8	5	(c)	(c)	-0.3	-0.5	none	none
C	6	15	(c)	(c)	-0.6	-0.9	none	none
D	193		-4.3		-3.7		none	none
	5	7	(c)	(c)	-0.5	-0.5	none	light coke
I	7	11	(c)	(c)	-0.2	-0.3	light sludge	light coke
0.1% A-88 + 0.05% dibenzyl disulfide	6	8	(c)	(c)	-0.4	-0.5	none	none
			FAILURES					
E	121		-3.9		-3.8		none	none
0.2% phenylboric acid	112	285	-4.3	-7.5	-3.8	-4.4	none	none
K	115		-7.2		-2.9		none	none

[a] See Table 3 for coding of the additives.

[b] Negligible weight loss for magnesium, aluminum, titanium and iron.

[c] No copper coupon present.

sharply reduced the bulk deposits but none eliminated them. The test results are listed according to wear scar in Table B2.

TABLE B2. - WEAR SCARS OF MCS 1305 BLENDS ON THE FAST FOUR-BALL TEST AFTER 1 HOUR AT 316°C

(M50 on silvered 6415, 10-kg load, 1260 rpm, 3.5 liters air/hr, load applied during warmup)

Additives[a]	Average Scar Diameter, mm
C	1.41
I	1.61
D	1.87
A	2.46
A-88 + trichloroacetic acid	2.70
J	2.99
B	3.03
A-88	2.69, 1.41 (shortened tests due to noise)
None	3.29

[a]See Table 3 for coding of the additives.

Some of the additive surface reactions shown by the slow four-ball test (Figures B1 through B17) paralleled those in C-ethers. Occasionally, however, we see signal differences. The most noticeable, that for A-88, M50 on M50, results in elimination of the large μ rise observed in C-ethers (Figure B17).

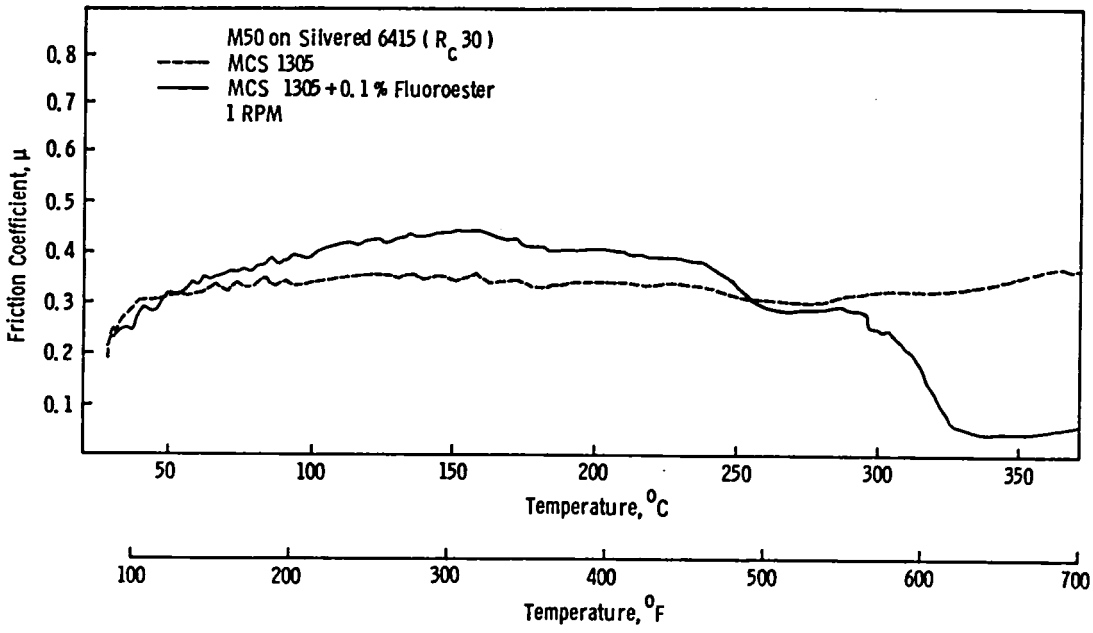


Figure B1. Friction Curves for MCS 1305 and MCS 1305 + 0.1% 2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-ethyl Phenylphosphinate

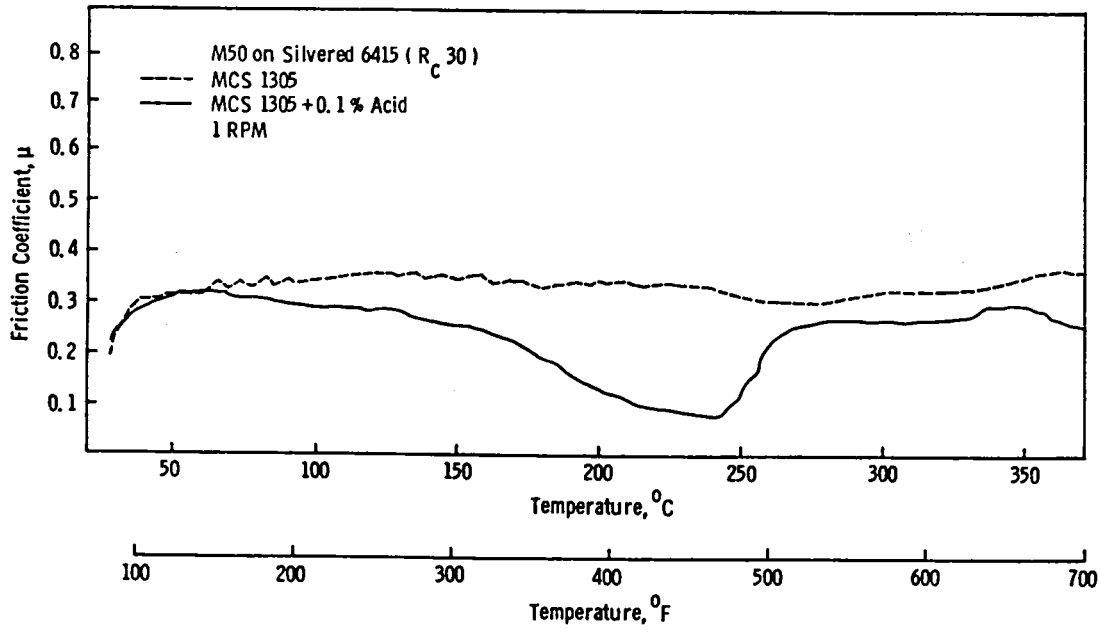


Figure B2. Friction Curves for MCS 1305 and MCS 1305 + 0.1% [3-(Trifluoromethyl)phenyl]phosphinic Acid

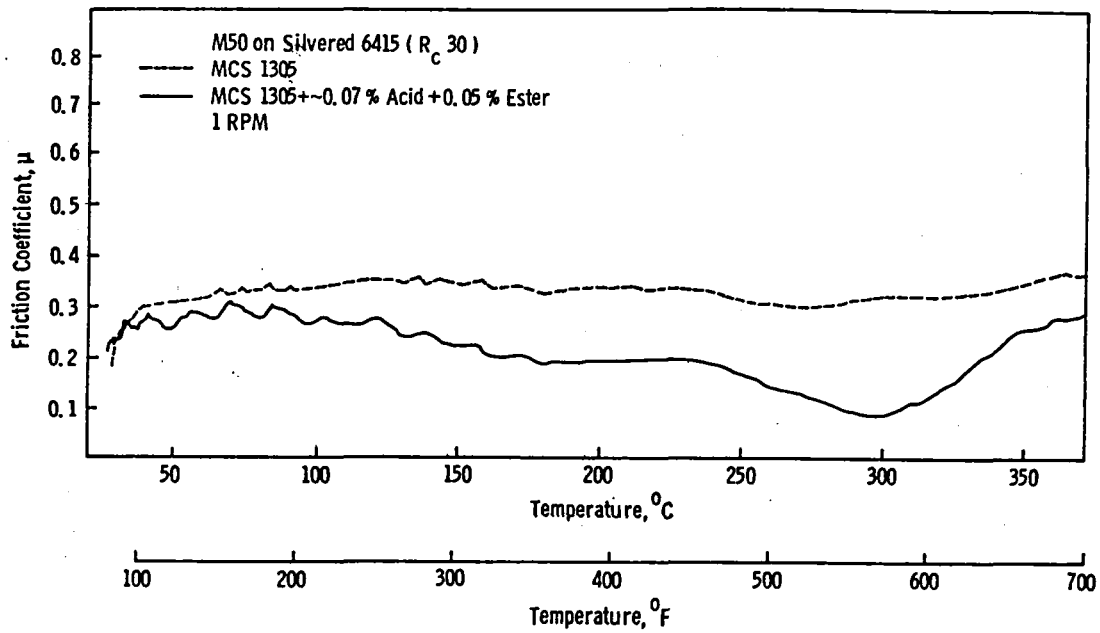


Figure B3. Friction Curves for MCS 1305 and MCS 1305 + ∿0.07% Perfluoroglutaric Acid + 0.05% Bis(2-ethylhexyl) Perfluoroglutarate

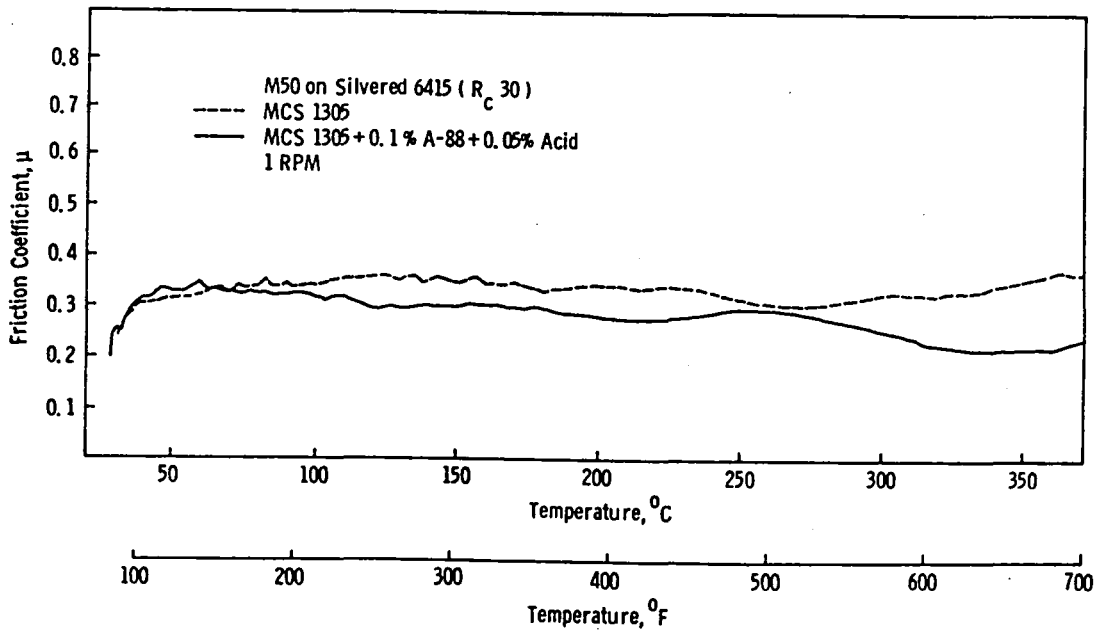


Figure B4. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88 + 0.05% [3-(Phenylthio)phenyl]phosphinic Acid

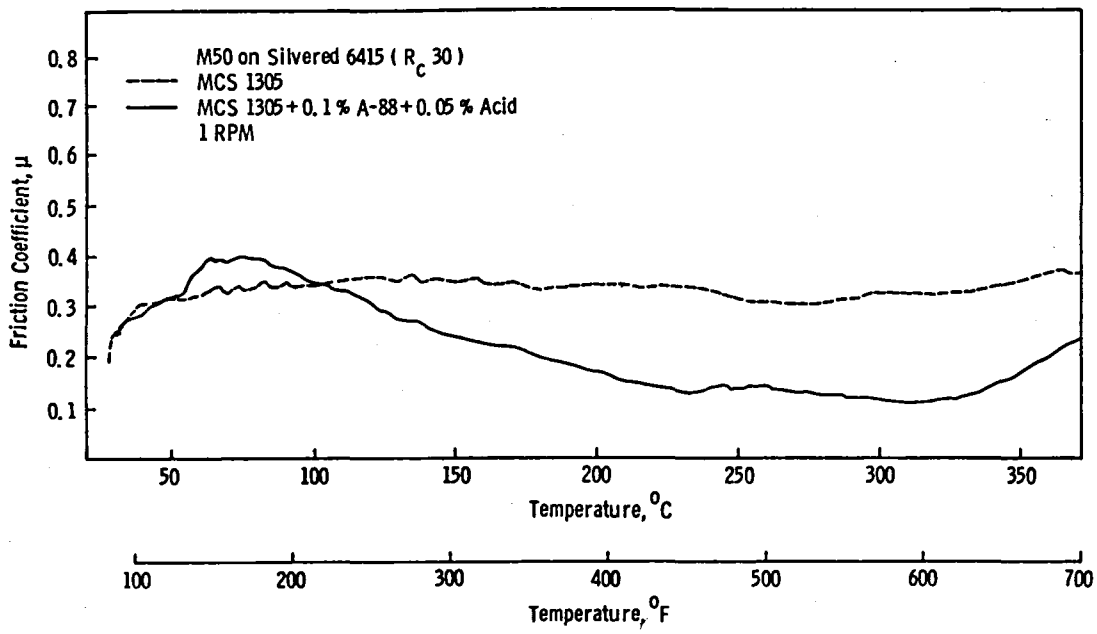


Figure B5. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88 + 0.05% Trichloroacetic Acid

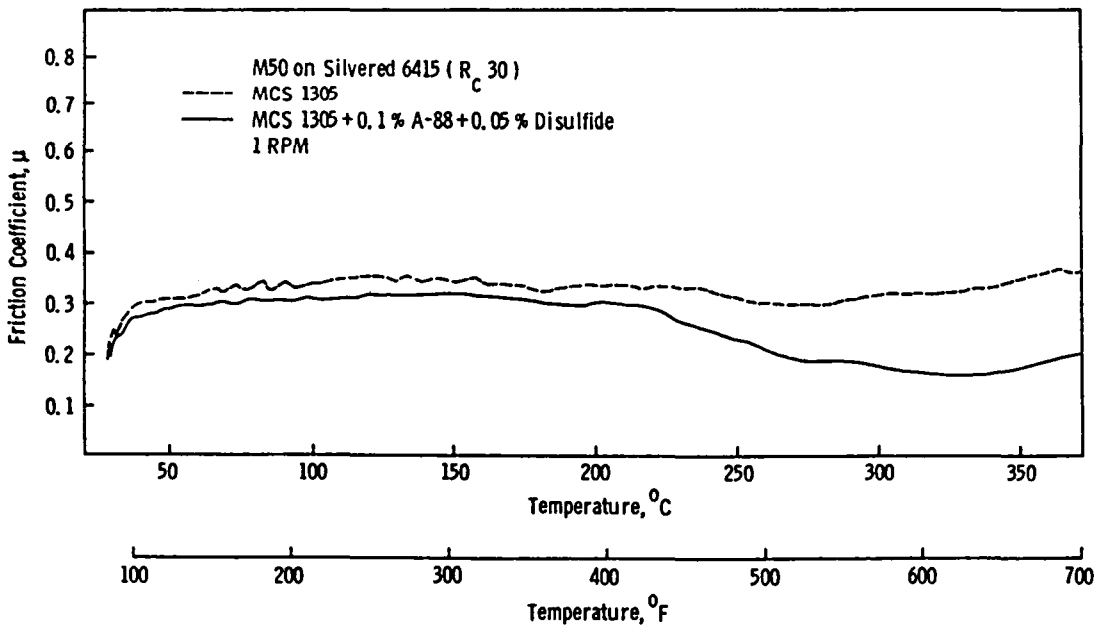


Figure B6. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88 + 0.05% Dibenzyl Disulfide

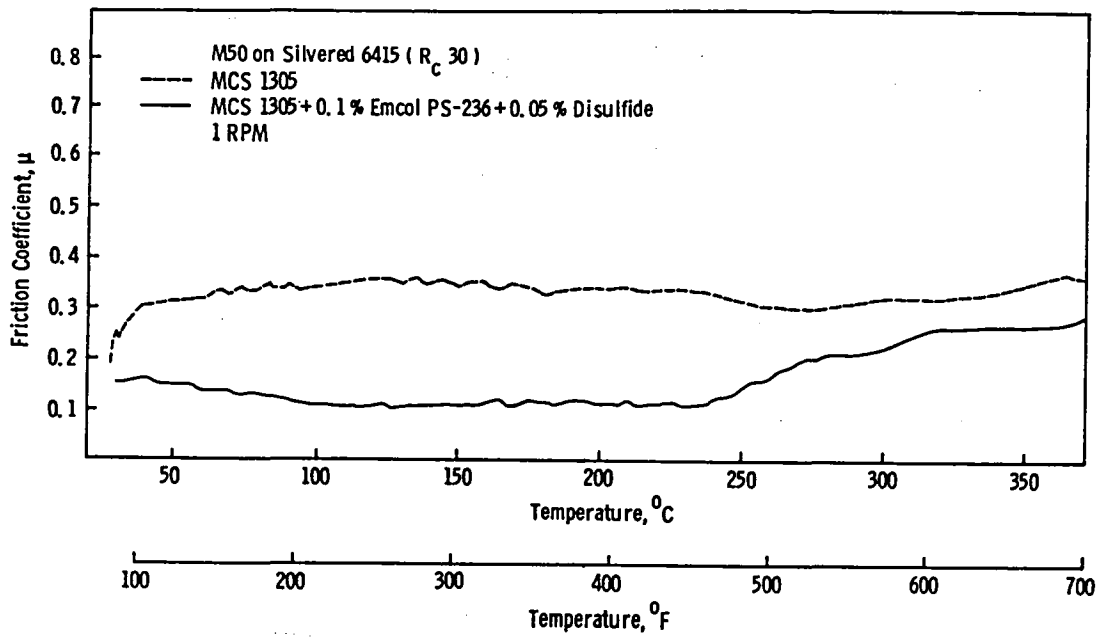


Figure B7. Friction Curves for MCS 1305 and MCS 1305 + 0.1% Emcol PS-236 + 0.05% Dibenzyl Disulfide

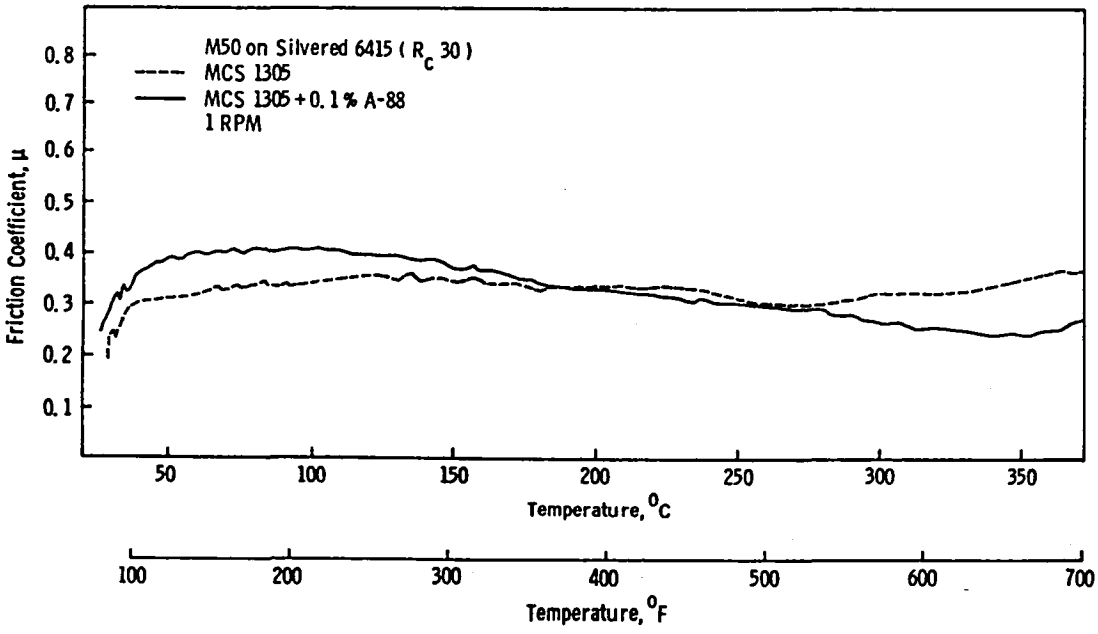


Figure B8. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88

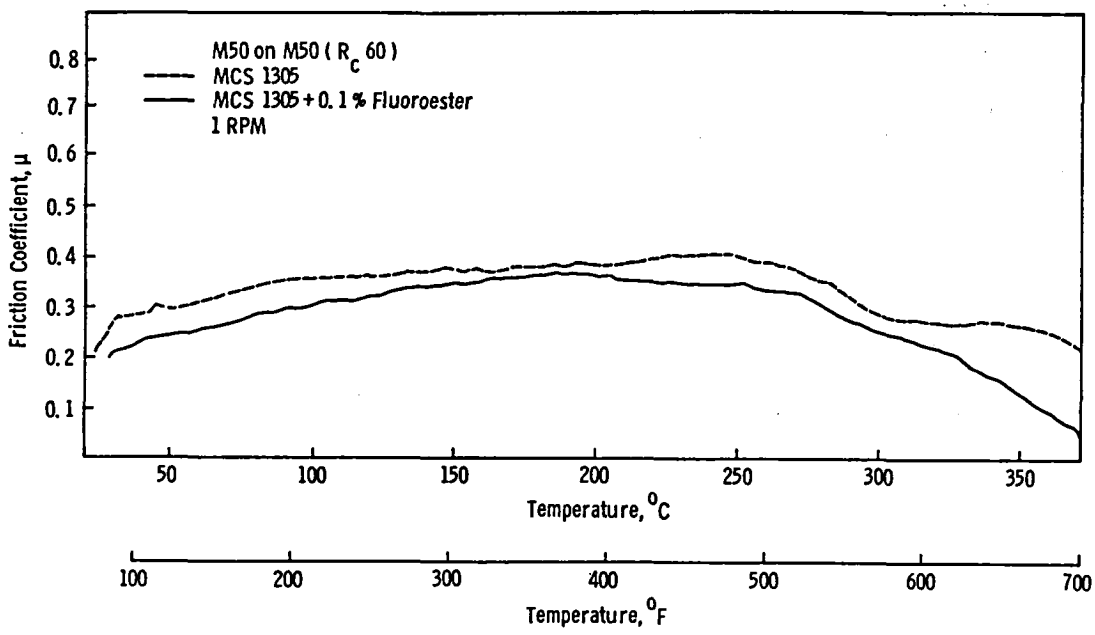


Figure B9. Friction Curves for MCS 1305 and MCS 1305 + 0.1% 2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]-ethyl Phenylphosphinate

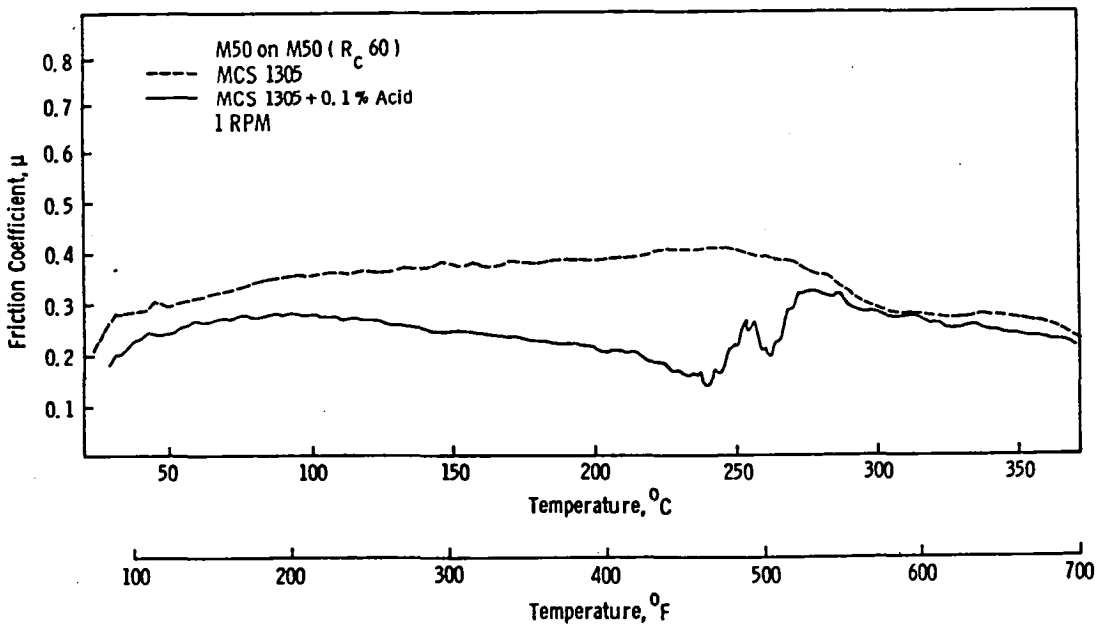


Figure B10. Friction Curves for MCS 1305 and MCS 1305 + 0.1% [3-(Trifluoromethyl)phenyl]phosphinic Acid

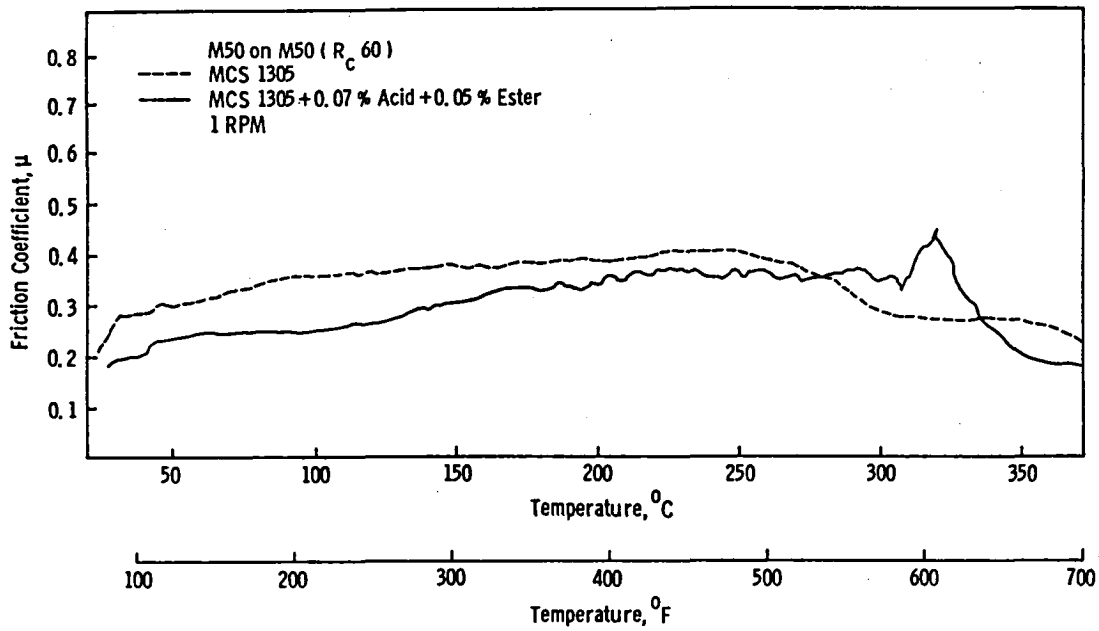


Figure B11. Friction Curves for MCS 1305 and MCS 1305 + ∿0.07% Perfluoroglutaric Acid + 0.05% Bis(2-ethylhexyl) Perfluoroglutarate

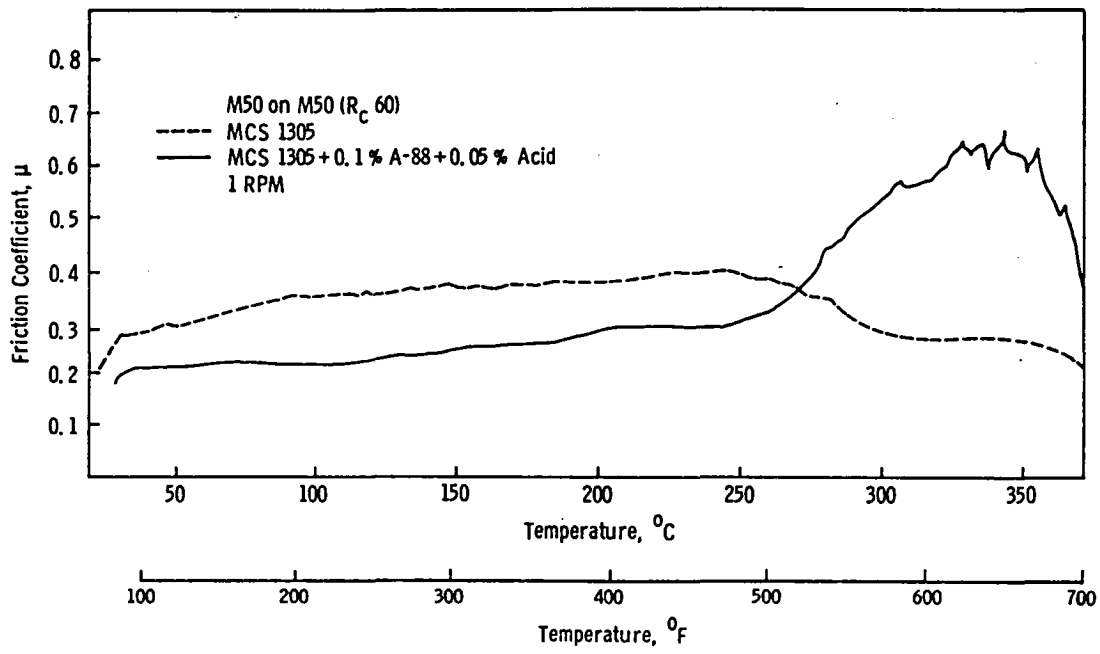


Figure B12. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88 + 0.05% [3-(Phenylthio)phenyl]phosphinic Acid

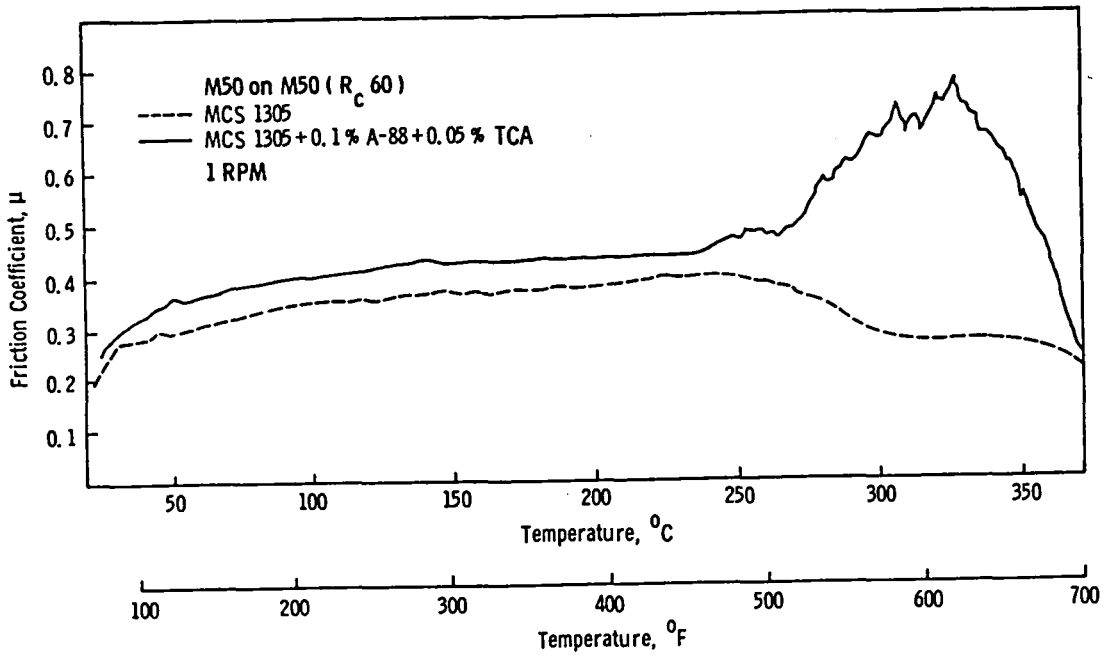


Figure B13. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88 + 0.05% Trichloroacetic Acid

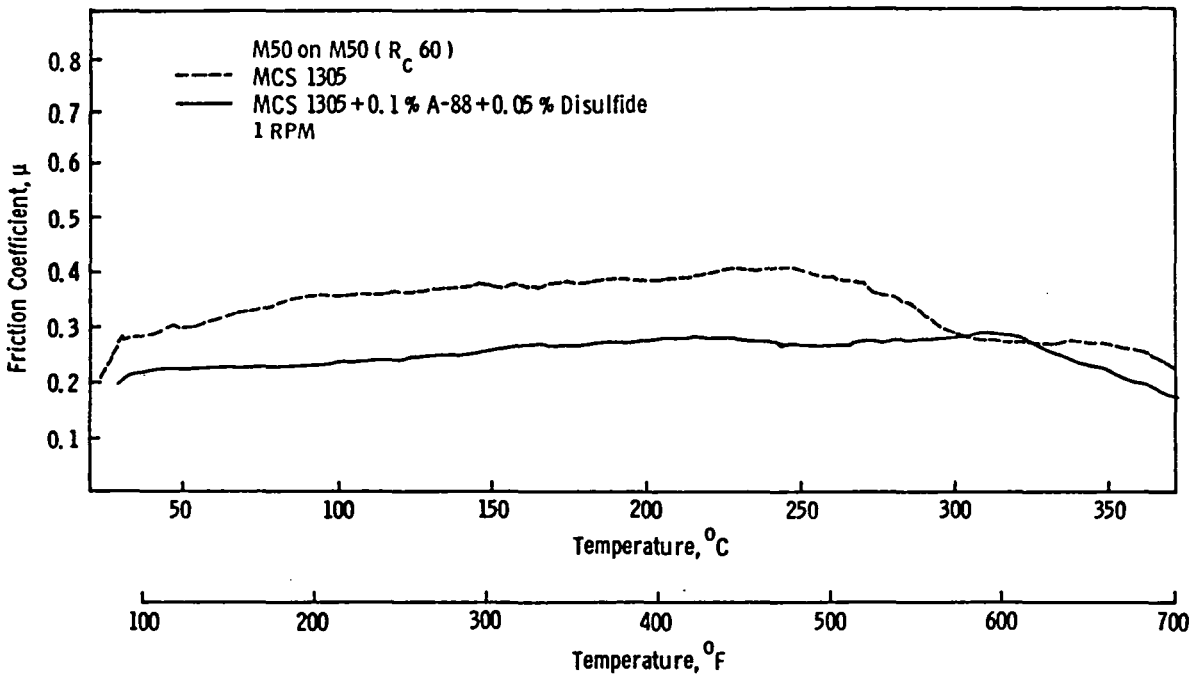


Figure B14. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88 + 0.05% Dibenzyl Disulfide

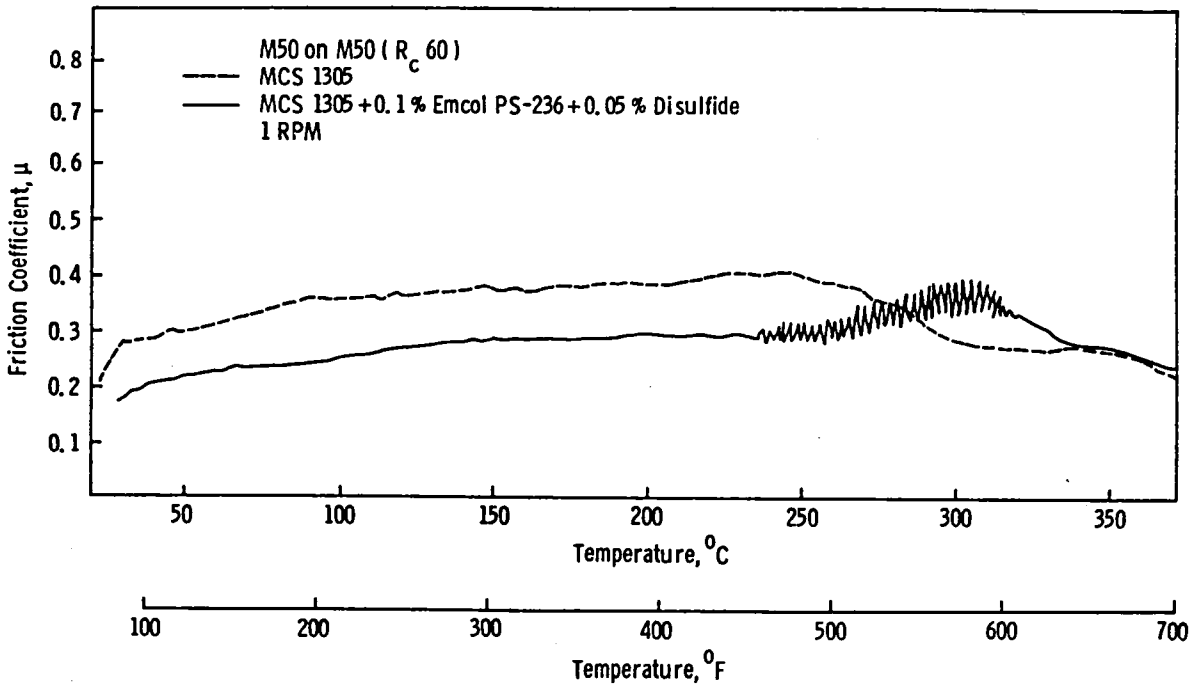


Figure B15. Friction Curves for MCS 1305 and MCS 1305 + 0.1% Emcol PS-236 + 0.05% Dibenzyl Disulfide

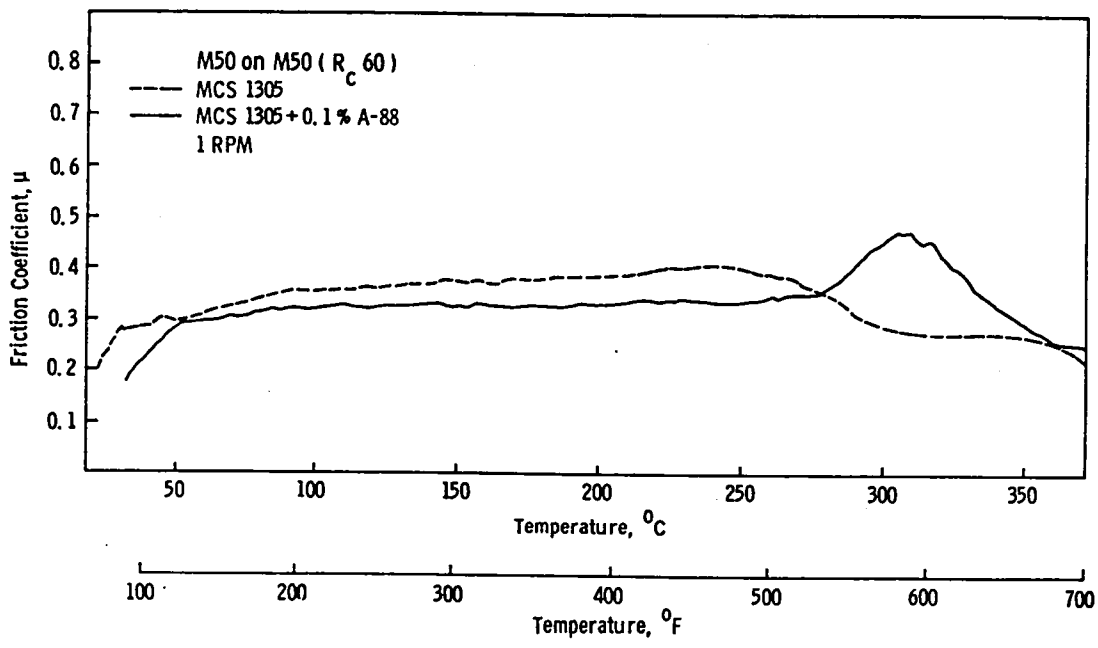


Figure B16. Friction Curves for MCS 1305 and MCS 1305 + 0.1% A-88

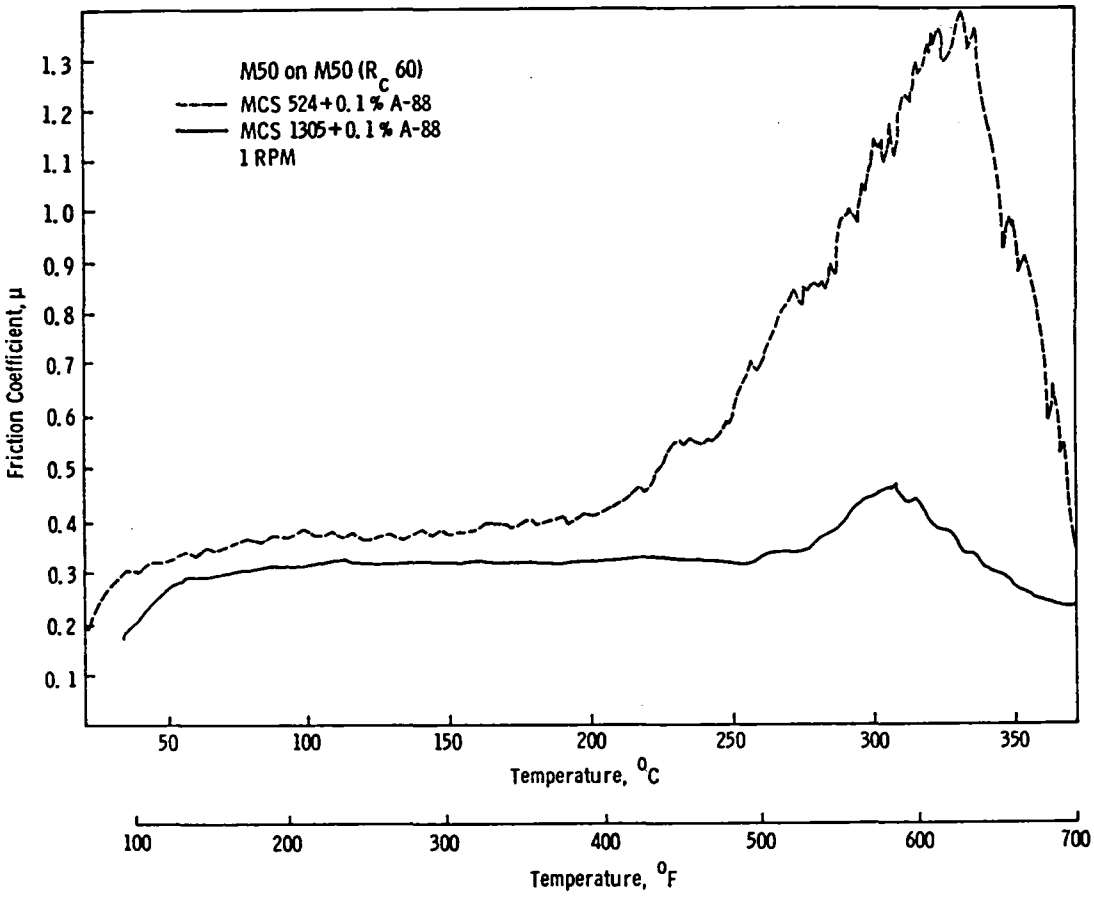
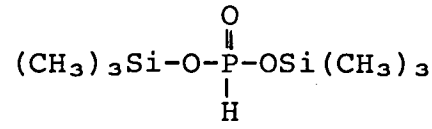


Figure B17. Friction Curves for MCS 524 + 0.1% A-88 and MCS 1305 + 0.1% A-88

APPENDIX C

SURFACE ANALYSIS OF TEST PARTS FROM TESTS ON MCS 524 + 0.1% BIS(TRIMETHYLSILYL) PHOSPHONATE: INCORPORATION OF SILICON ONTO STEEL SURFACES



Bis(trimethylsilyl) phosphonate

We conducted electron probe analyses of different areas of wear test specimens run on MCS 524 + 0.1% of the above silyl phosphonate. The purpose: to gain insight into the additive mechanisms and specifically to determine whether this compound reacts by incorporating silicon onto metal surfaces. The specimens examined included blocks from rub-block tests and slow four-ball test discs.

The data in Table C1 clearly show an uptake of silicon in the matrix (noncontact) area of the M50 block. The silicon content is double that for a run on MCS 524 without an additive. No increase in silicon occurred in the contact.

TABLE C1. - PERCENT SILICON IN WEAR TEST SPECIMENS

	MCS 524	MCS 524 + 0.1% Bis(trimethylsilyl) Phosphonate
M50 block scar	0.11	0.15
M50 block matrix	0.17	0.31
M50 slow four-ball disc: scar		0.33
matrix		0.34
Silvered 6415 slow four-ball disc: scar		0.02
matrix		0.04

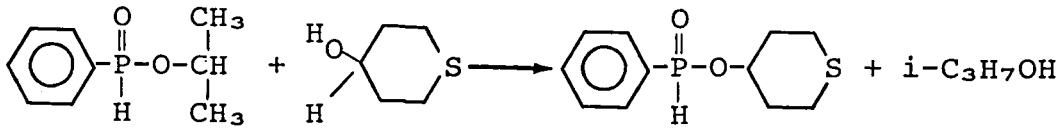
M50 slow four-ball discs showed an increase in silicon both in the contact and in the matrix. In surprising contrast, silvered 6415 steel discs showed very little silicon in either the contact or the matrix. Thus, the reaction or adsorption which transfers silicon onto the surface takes place preferentially on the steel.

The analyses covered 20 individual areas of each block's matrix and wear scar. Two discs of each slow four-ball metallurgy were examined with 10 analyses run per contact area. Table C1 averages the sets of data.

APPENDIX D

SYNTHESES OF ADDITIVES

1. TETRAHYDRO-2H-THIOPYRAN-4-YL PHENYLPHOSPHINATE (III)



(I) (II) (III)

1-Methylethyl phenylphosphinate (compound I, 11.6 g, 0.0625 mole) and tetrahydrothiopyran-4-ol (compound II, 8.0 g, 0.0624 mole) were charged to a 100-ml round-bottomed flask under nitrogen. This mixture was heated at various temperatures and pressures with each heating cycle being broken at room temperature for withdrawal of an aliquot. Table D1 contains details of the reaction conditions. When the product ester reached 39%, a buildup of byproducts (probably including phenylphosphinic acid) occurred, and so the crude product was vacuum distilled. A vacuum of 0.05 mm obtained from an oil pump was not low enough for effective distillation, so the mixture was distilled from a molecular still using a mercury diffusion pump.

Fraction	Skin Temperature, °C	Weight, g
1	82-100/8 x 10^{-4} mm	1.5
2	100-120-110/8 x 10^{-4} mm	6.8
3	110/8 x 10^{-4} to 10^{-3} mm	2.1
4	below 110/9 x 10^{-4} mm	0.7

TABLE D1. - REACTION CONDITIONS AND GLC ANALYSES FOR PREPARATION OF COMPOUND III

			GLC Area, %			
Cycle	Time	Temp, °C	Product	Starting Alcohol	Starting Ester	Acid
1	25 min	95-110	2	40	51	
2	1 to 1.5 hr	115/35 mm	5	39	47	
3	6 hr	115/∿30 mm	26		33	3
4	22.5 hr	119/∿30 mm	39	19	10	∿10

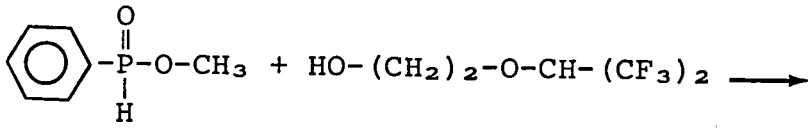
Fraction 1: GLC showed mostly starting materials and only 6% product.

Fraction 2: GLC analyses were not reproducible and showed a purity varying from 71% to 32%. NMR showed much greater purity. The area ratio of aromatic to aliphatic hydrogens almost matched that of the desired ester. There was no acid present; there was a small (5-10%) aliphatic impurity which had little if any 1-methylethyl group present. Elemental analysis for carbon was slightly outside the limit of ± 0.3% carbon.

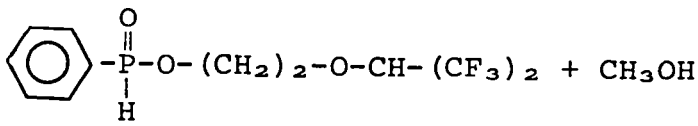
	% C	% H
Calculated for $C_{11}H_{15}O_2PS$:	54.5	6.2
Found:	53.7, 53.5	6.4, 6.8

Fractions 3 and 4: These cuts contained fairly large amounts of acid impurities.

2. 2-[2,2,2-TRIFLUORO-1-(TRIFLUOROMETHYL)ETHOXY]ETHYL PHENYLPHOSPHINATE (III)



(I) (II)

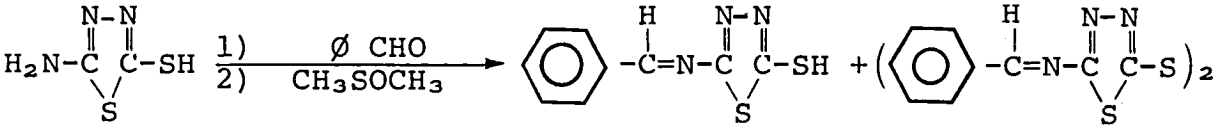


(III)

After heating 0.08 moles of compounds I and II with a trace of sodium at 160°C for 3.5 hours, application of a modest vacuum (∿450 mm) for 2 more hours produced crude product. Topping through a 2-inch Vigreux column removed 4.2 g of low boilers. Subsequent distillation of the residue in a molecular still yielded 9.3 g (34% conversion) of a center cut which contained 97.6% product. Elemental analysis, mass spectrum, and NMR confirmed the structure. The NMR areas were:

PH = 0.96 (1.0 theoretical)
alkyl H = 5.06 (5.0 theoretical)
aryl H = 4.97 (5.0 theoretical)

3. 2-MERCAPTO-5-BENZILIDENEIMINO-1,3,4-THIADIAZOLE
(done like ref. 19)



(I) (II) (III)

Compound I (6.65 g, 0.05 mole) was refluxed with benzaldehyde (5.3 g, 0.05 mole) and benzene (200 ml) in a 500-ml round-bottomed flask joined to a Dean-Stark trap. Very little water evolution occurred until 50 ml of dimethylformamide was added as a cosolvent. Then overnight reflux produced 2 ml of an insoluble phase in the trap. This is more than the theoretical amount of water. Dimethyl sulfoxide (50 ml) was then charged and another 0.6 ml of insolubles collected. Stripping under vacuum (to 0.1 mm) gave organge crystals which, after drying on a porous clay plate, contained 39.5% carbon. Trituration with acetone raised the percent carbon to 44%, still 5% below the theoretical 49.1% of the initially desired disulfide (compound III).

Retreatment of this crude product (7 g) with benzaldehyde (2 g), benzene (170 ml) and dimethylformamide (40 ml) and subsequent direct filtration gave an off-white crystalline product. A mass spectrum indicated this was the thiol compound (II) rather than the corresponding disulfide, III. When run under chemical ionization conditions, the base peak occurred at 222 with a very small peak at 441. Structure II would give this pattern (M+1 and 2M+1 peaks respectively) whereas compound III should give a larger peak at 441. No parent ion for structure III was observed under electrical ionization conditions.

After two triturations with acetone, the elemental analysis agreed reasonably with that of the thiol:

	% C	% H	% N
Calculated for $C_{18}H_{12}N_6S_4$: (compound III)	49.1	2.7	19.1
Calculated for $C_9H_7N_3S_2$: (compound II)	48.9	3.2	19.0
Found:	48.8, 48.8	3.5, 3.4	18.4, 18.6

4. BIS(3-{[3-(PHENYLTHIO)PHENYL]THIO}PHENYL)DISULFIDE

This material was made by a proprietary method.

	% C	% H	% S
Calculated for $C_{36}H_{26}S_6$:	66.4	4.0	29.6
Found:	66.3, 66.6	4.0, 4.1	29.2, 29.2

After its preparation, the sample was taken up in benzene and filtered to remove a few particles of foreign matter. Stripping the solvent in a vacuum oven left a small amount (∿3%) of benzene contamination.

5. BIS(2-ETHYLHEXYL) PERFLUOROGLUTARATE

$$(CF_2)_3(CO_2H)_2 + 2HOCH_2\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}(CH_2)_3\text{-}CH_3 \longrightarrow$$

$$C_4H_9\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}CH_2\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}(CF_2)_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}\underset{\displaystyle C_2H_5}{\underset{|}{CH}}\text{-}C_4H_9 + 2H_2O$$

Azetroping a commercial sample (50.3 g) of perfluoroglutaric acid with 220 ml of toluene in a flask equipped with a Dean-Stark trap removed 1.9 g of water and left 98.4 g (0.2 mole) in the pot. 2-Ethylhexanol (52.4 g, 0.4 mole) was then charged along with 1 g of p-toluenesulfonic acid. After 3.75 hours of refluxing, the residue was washed twice with 100 ml of water and dried over sodium sulfate. Vacuum distillation stripped the solvent. The residue (78 g, 87% conversion) had a GLC purity of 99.0%.

	% C	% H
Calculated for $C_{21}H_{34}F_6O_4$:	54.3	7.4
Found:	54.3, 54.5	7.1, 7.3

6. BIS(TRIMETHYLSILYL) PHOSPHONATE

A preparation described in the literature (ref. 20) gave product of satisfactory purity (98.7%).

7. BIS(TRIMETHYLSILYL) PERFLUOROGLUTARATE

$$(CF_2)_3\text{-}(CO_2H)_2 + (CH_3)_3SiNHSi(CH_3)_3 \longrightarrow$$

$$(CH_3)_3Si\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}(CF_2)_3\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}O\text{-}Si(CH_3)_3 + NH_3$$

The literature describes a convenient method for making silylated di-acids (ref. 21). The product, obtained in 96% conversion, boiled at 63°C at 0.5 mm. GLC purity exceeded 99.7%.

	% C	% H
Calculated for $C_{11}H_{18}F_6O_4Si_2$:	34.4	4.7
Found:	34.5, 34.3	4.0, 4.0

8. a) [3-(PHENYLTHIO)PHENYL]PHOSPHINIC ACID
   b) 3-{[3-(PHENYLTHIO)PHENYL]THIO}BENZOIC ACID
   c) POTASSIUM 3-(3-PHENOXYPHENOXY) PHENATE
   d) [3-(TRIFLUOROMETHYL)PHENYL]PHOSPHINIC ACID

The preparation of all of these compounds involved proprietary methods. All elemental analyses agreed with the desired structure. Compound b melted at 117-8°C and d at 70-71.5°C.

APPENDIX E

SYNTHESES OF INTERMEDIATES

The references cited below describe the syntheses:

Methyl phenylphosphinate: reference 22

1-Methylethyl phenylphosphinate: references 22 and 23

Tetrahydro-2H-thiopyran-4-ol: reference 24

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy ethanol: reference 25

The latter alcohol boiled at 69°C at 36 mm.

APPENDIX F

FAILURE ANALYSIS OF C-ETHER LUBRICATED BEARINGS BY SKF INDUSTRIES, INC.

(SKF Report No. AL79T046)

SKF examined 6 split-inner ring angular-contact 80 mm bore ball bearings made of M50 steel with inner-ring-riding silver-plated AMS6415 steel cages from 600°F bearing tests. These tests were run for 100 hours or to prior failure at 25,000 rpm (2×10^6 DN) under a thrust load computed to produce a maximum Hertz stress of 200,000 psi on the inner race. Different lubricants were used in each test, consisting of C-ether base stock as well as the same base stock plus various experimental additives tested in turn, circulated at 0.82 gpm from a system containing an initial charge of 7000 cc, with an oil-inlet temperature of 500°F and a bearing outer ring temperature of 600°F. Results of this examination are described below.

S/N 7 BEARING FROM TEST NO. 8 (REF. 3) (MCS 524)

Bearing S/N 7 ran only 14 hours before failure with the base stock containing no additives other than antifoam. The cage bore land-riding surface was worn heavily at one spot with 1 to 2 mm depth of steel removed. The rolling tracks on the balls and races contained what appeared to be wear debris from the cage mashed into these contact surfaces. No further analysis was made of this base-line bearing.

S/N 23 BEARING FROM TEST NO. 21 (MCS 524 + PFGA + PPA)

This bearing was tested with an experimental antiwear additive and ran 23 hours before the test was stopped by filter plugging and excessive bearing heat generation. The cage bore again was worn very severely with 3 to 4 mm wear depth at one point, enough to cause unintentioanl contact of the cage OD on the outer ring lands and ball groove. Again the ball and race contact tracts were severely debris dented, but otherwise were in remarkably good condition for a bearing having suffered cage seizure. No further effort was devoted to this bearing.

S/N 22 BEARING FROM TEST NO. 20 (MCS 524 + FPPA)

Using another antiwear additive with this bearing, the test ran 111 hours without gross failure, despite recurrent filter pluggings. Much less wear had occurred on the cage bore, 0.1-0.2 mm at the maximum point, which is still much more wear than normally occurs at cage guide surfaces. The track surfaces in this bearing were heavily coked and debris laden, with some glazing and frosting type lubrication distress.

The inner ring track was documented by scanning electron microscopy (SEM) as shown in Figures F1 and F2. The lacquer buildup from lubricant decomposition at the shoulder edge of the track is shown in Figure F1-a, and wear debris and denting, presumably from cage wear, is shown in Figures F1-b and F1-c. Figure F2 also shows a higher magnification view of a lubrication distress band just inside the groove bottom edge of the track where all traces of the surface finishing marks have been obliterated and the surface metal has been plastically deformed or smeared on a microscale.

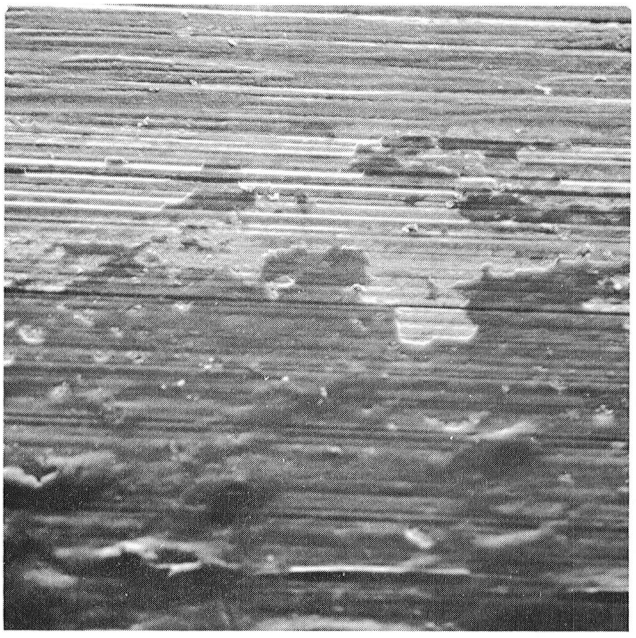
S/N 12 BEARING FROM TEST NO. 11 (REF. 3) (MCS 524 + PFGA)

This bearing successfully ran 100 hours on another formulated C-ether. It suffered the least cage wear of all bearings examined, with only the silver plate completely removed at the contact arc on the cage bore and no significant wear of the underlying steel. The silver plate was also completely stripped off of one face of the cage. The wear tracks were glazed and debris dented with some slight frosting and heavy staining and coking deposits of lubricant decomposition products.

SEM documentation of the inner ring track contact surface damage on this bearing is given in Figures F3 and F4. Lubricant coking at the track edge is shown in Figure F3-a. Glazing and micropitting, which has a frosty visual appearance, is shown in Figures F3-b and F3-c. Figure F4-c shows the original groove surface outside the wear track, the features of which are almost but not completely obliterated in the track, indicating that there is no gross wear of the surface, only microplastic surface damage. Experience has shown that micropitting resulting from this glazing damage can act eventually as stress risers and initiation points for surface originated contact fatigue spalling at much shorter bearing lives than are obtained without such lubrication distress.

The stripping of the silver plate off the cage, of course, is another undesirable result of this test. There are two cage silver plating types now in common use in aircraft engine bearings: AMS 2410 which uses a nickel strike under the silver, and AMS 2412 which uses a copper strike. The nickel variation requires a higher bake temperature (900°F, compared to 500°F for the copper strike silver plate) and is normally preferred for extremely high temperature applications. The copper variation produces a more consistently tight bond of the silver plate to the underlying steel and is preferred at present aircraft engine bearing operating temperatures.

Figures F5 and F6 show SEM photos of a rough saw-cut section of an undamaged portion of the silver plated cage from bearing S/N 12, together with wavelength dispersive x-ray maps of this section indicating that a copper strike was used in plating this

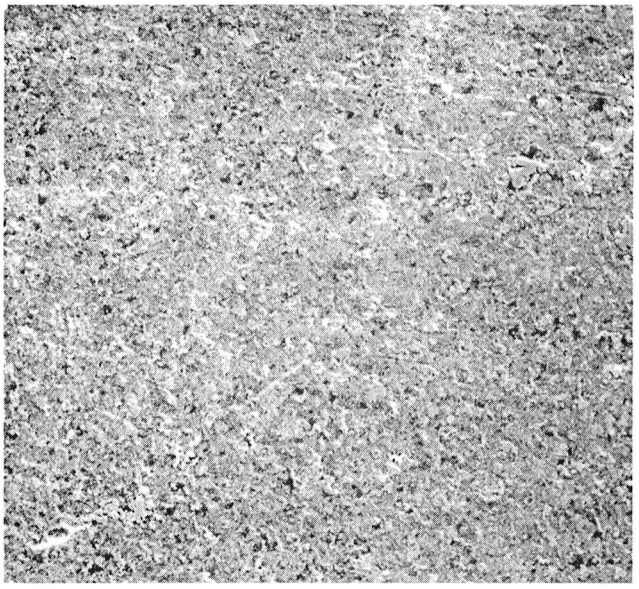


a. Edge of track near shoulder (500X)

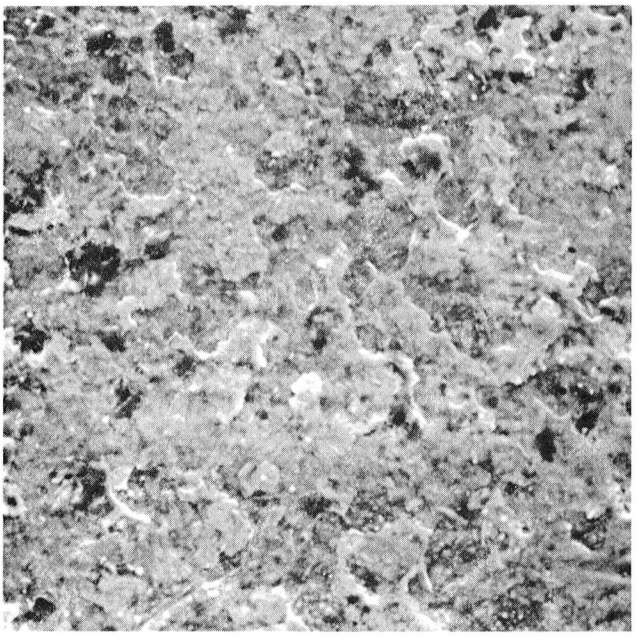
b. Inside track near shoulder edge (500X)

c. Near track center at groove bottom (500X)

Figure F1. SEM Photographs of S/N 22 Bearing Inner Ring Track After 111-Hour Test No. 20

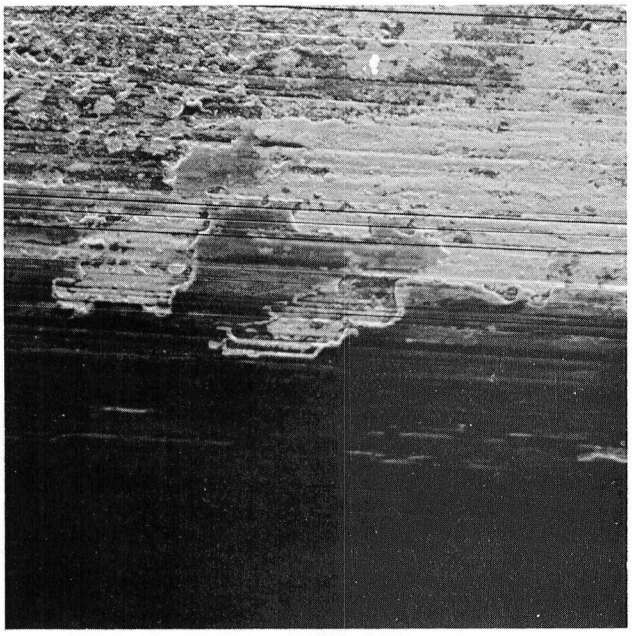


a. Near track edge at groove bottom (500X)



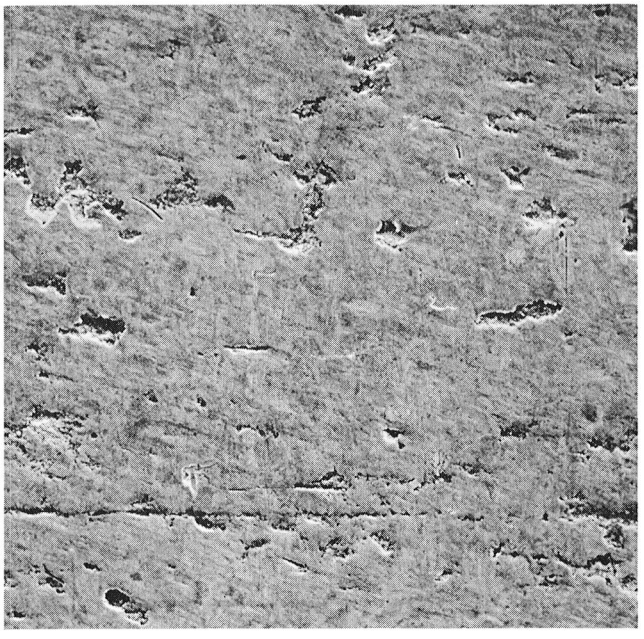
b. Higher magnification of view a (2500X)

Figure F2. SEM Photographs of S/N 22 Bearing Inner Ring Track After Test No. 20 Showing Metal Surface Microsmearing Damage



a. Edge of track near shoulder (500X)

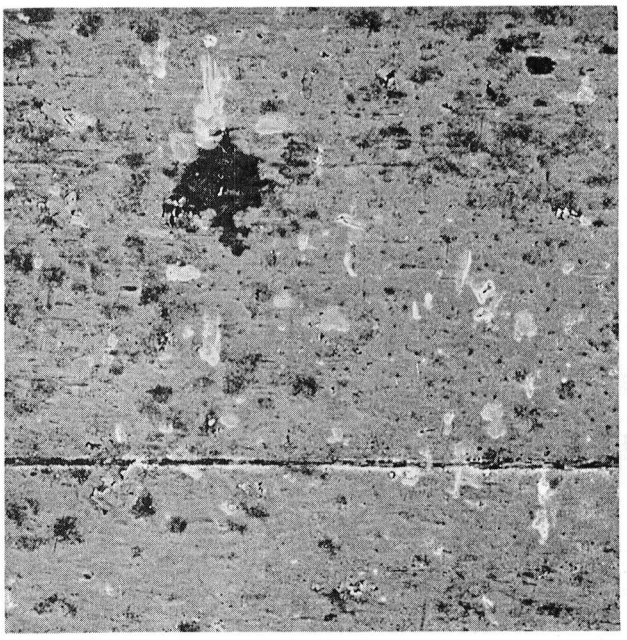
b. Inside track near shoulder edge (500X)



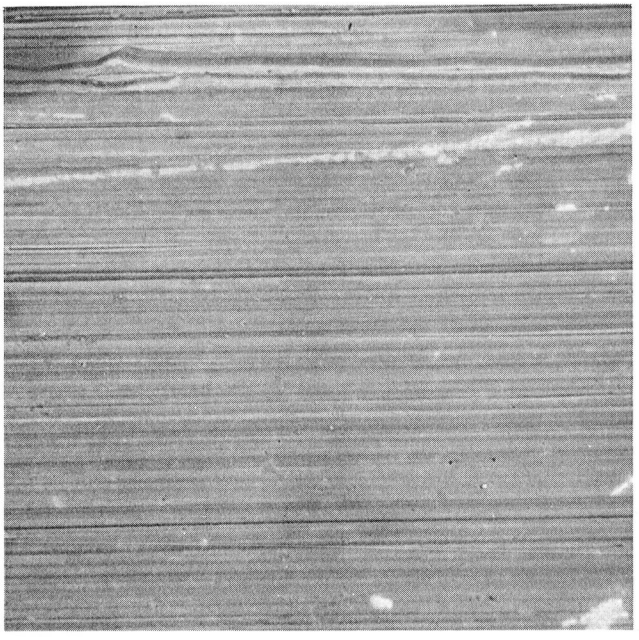
c. In center of track (500X)

Figure F3. SEM Photographs of S/N 12 Bearing Inner Ring Track After 100-Hour Test No. 11

a. Near track center at groove bottom (500X)

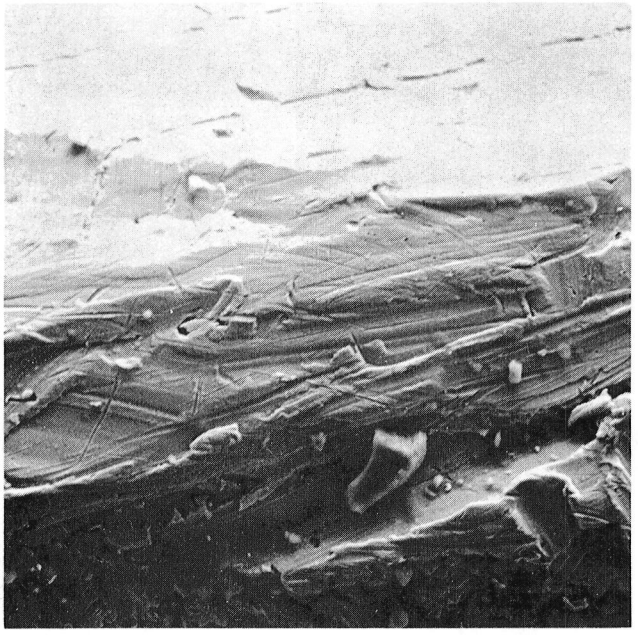


b. Near track edge at groove bottom (500X)

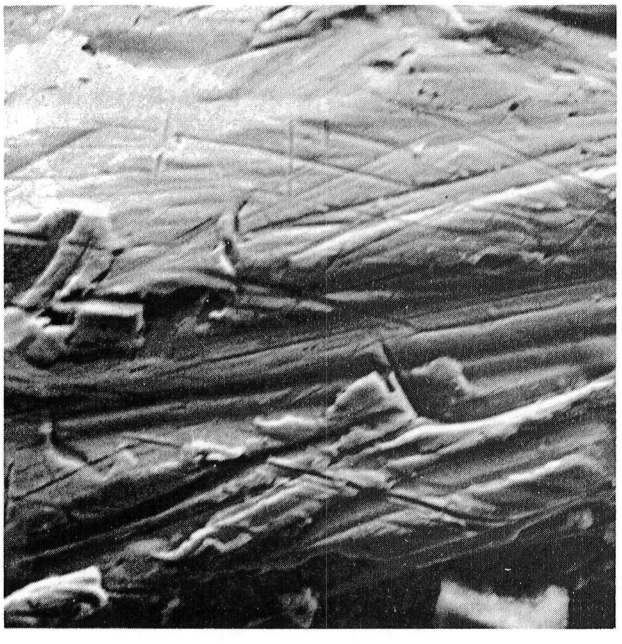


c. Typical groove surface outside track (500X)

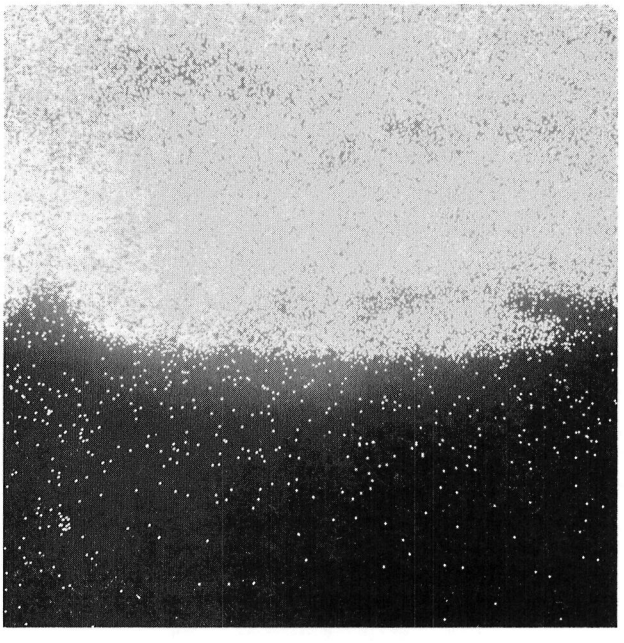
Figure F4. SEM Photographs of S/N 12 Bearing Inner Ring Groove After Test No. 11



a. Edge view of plated cage surface (760X)

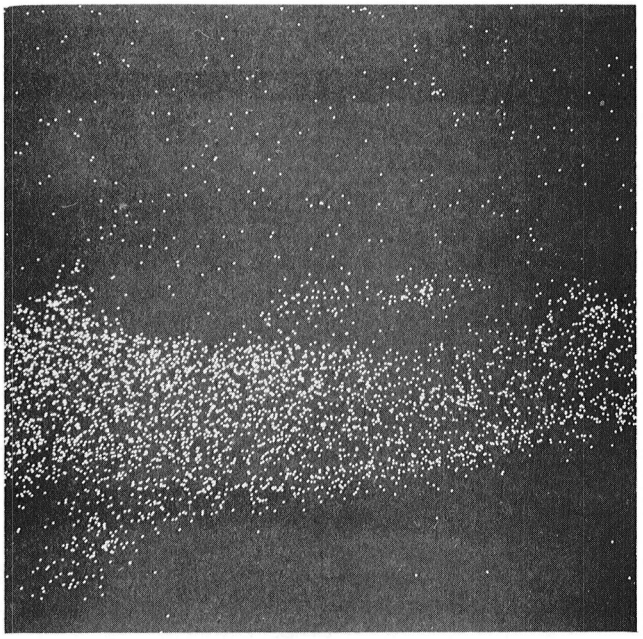


b. Higher magnification of view a (1900X)



c. Iron x-ray map of view b (1900X)

Figure F5. SEM Photographs of Saw Cut Cage Section from S/N 12 Bearing After Test No. 11



a. Silver x-ray map of view in Figure F5-b (1900X)

b. Copper x-ray map of view in Figure F5-b (1900X)

Figure F6. SEM Wavelength Dispersive X-Ray Maps of Saw Cut Cage Section from S/N 12 Bearing Showing Evidence of Copper Strike Used with Silver Plate

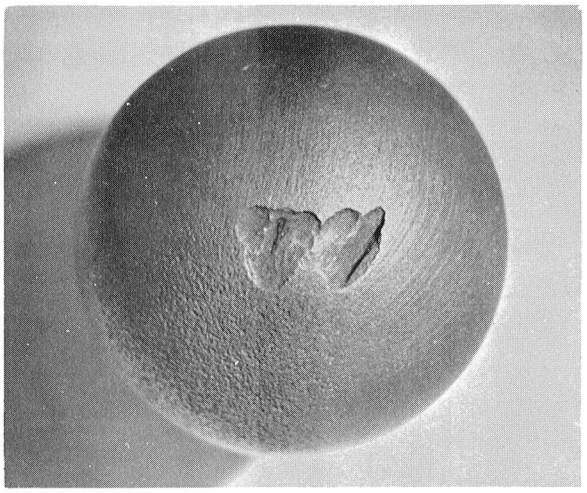
cage. (Note that the intensity of the light dotted regions in the x-ray maps indicate relative content of the element analyzed.) The silver plate in another undamaged portion of this cage was tested for bond strength according to AMS 2412 with a razor blade and was found to peel off in ribbons typical of poor bonded plate instead of crumbling into particles as is found regularly with silver plated cages having a good bond to the underlying steel. (The silver plate on the cage from S/N 22 bearing was also tested for bond strength with similar results.)

In previous successful M50 bearing testing of C-either lubricant MCS 293 at SKF (ref. 5, 6 and 7), silver plated cages having the nickel strike variation were used with no problem of silver peeling at 600°F temperatures. Early testing at this temperature with low viscosity synthetic lubricants, however, resulted in excessive cage bore wear similar to that observed on the present 80 mm bore bearing cages. Since hydrodynamic short bearing theory predicts increased load capacity with the cube of the bearing width, the cage lands (actually a type of short bearing) were increased by about a factor of 1.6, and no further problems of cage bore wear were experienced after that (ref. 5).

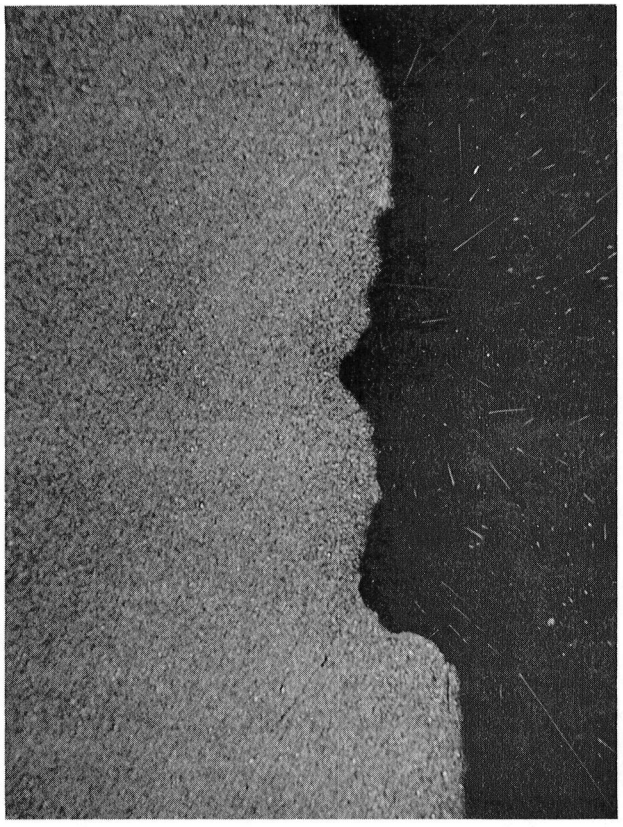
S/N 25 BEARING FROM TEST NO. 23 (MCS 524 + PFGA + SPFGA)

In a repeat test with a similar additive as in Test No. 11 with S/N 12 bearing, this bearing ran 81 hours before being stopped by excessive bearing steel chips found in the lubricant. Spalling had occurred on the outer race and on five balls, and the cage bore was worn in one spot about 0.2 mm through the silver plate and into the steel. Although the cage silver plate was peeled off the steel at the edge of the cage bore wear area, the plate was intact everywhere else on the cage. Severe denting from the ball spall edges and spall debris prevented meaningful analysis of the wear tracks. A gummy film of lubricant was found on most surfaces and very little coking as in the other bearings, although there was some staining.

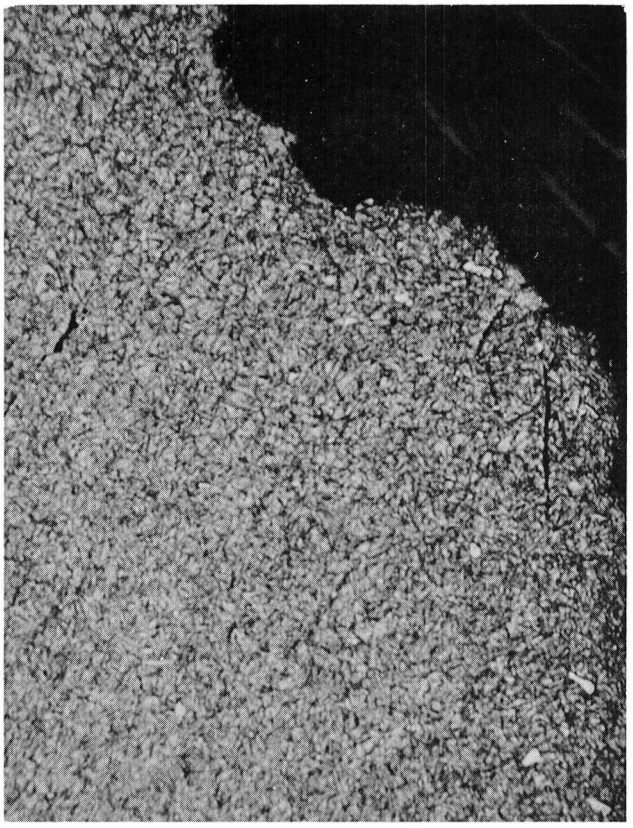
Some of the fatigue spalls were unusually deep, especially on the balls, so the structure and heat treatment of the steel was analyzed. The hardness measured 62-63 R_c, and metallographic examination showed a fine martensitic structure with less than 1% retained austenite and no soft constituents, all within expected proper M50 steel bearing specifications. Nital etch and hot acid etch analysis also checked out satisfactorily, with no evidence of nonmetallic inclusions found at any spall initiation sites. As shown in Figure F7, however, hot acid etching of the spalls on the balls (see Figure F7-a) revealed that the spall initiation area followed the steel grain flow lines, as confirmed by metallographic sectioning (see Figures F7-b and F7-c).



a. Overall view of spall on a ball (4X)



b. Section through spall with original ball surface at lower right (100X)



c. High magnification of view b showing spall cracks following steel grain flow lines (300X)

Figure F7. Photomicrographs of Spalled Balls from S/N 25 Bearing After 81-Hour Test No. 23

S/N 26 BEARING FROM TEST NO. 24 (MCS 524 + PFGA + SPFGA)

In this repeat test of No. 23 with identical lubricant and test conditions, cage failure occurred in 1 hour. About 1 mm depth was worn into the cage bore and the silver plate was blistered and peeling off the steel in several places. The bearing was coked but not as severely as S/N 12 in Test No. 11.

The general impression of all the bearings examined is that the low viscosity-high temperature operation in these tests results in very marginal lubrication conditions for the bearing design and materials used. Improved bonding of the silver plate on the cages can be obtained by close control of electroplating conditions, using high-temperature nickel flash and baking treatments, although the cage design probably also should be modified to provide less stress on the lubricant at the viscosity level in these tests. These improvements in the cage will result in improved lubrication distress conditions at the primary load-carrying ball-race contacts by reducing surface-damaging traction forces. However, some contact slip in high-speed bearings is inevitable (spinning, for example) and it is essential to long life operation that the lubricant additive system be matched to the bearing raceway surface finish, as well as perhaps special coating systems, to provide an easily sheared surface layer on a damage-resistant undercoat. The SKF test bearings run successfully with Monsanto MCS 293 lubricant some years ago were special black oxide coated for this purpose. A number of improved rolling contact resistant coatings have become available since then, and are now under evaluation at SKF.

APPENDIX G

NEW TECHNOLOGY

Novel chemicals which showed activity as lubrication additives in bench tests included:

Bis(trimethylsilyl) perfluoroglutarate

[3-(Trifluoromethyl)phenyl]phosphinic acid

2-[2,2,2-Trifluoro-1-(trifluoromethyl)ethoxy]ethyl phenylphosphinate

APPENDIX H

MCS NUMBERS FOR MCS 524 BLENDS

(See Table 2 for Additive Abbreviations)

MCS 1890 = MCS 524 + ∿0.07% PFGA + 0.05% PFGE
MCS 1891 = MCS 524 + 0.1% A-88 + 0.05% [3-(phenylthio)phenyl]-phosphinic acid
MCS 1954 = MCS 524 + 0.1% phenylboric acid
MCS 1964 = MCS 524 + 0.1% Emcol PS-236 + 0.05% dibenzyl disulfide
MCS 1965 = MCS 524 + 0.075% FPPA
MCS 1966 = MCS 524 + 0.1% 2-[2,2,2-trifluoro-1-(trifluoromethyl)-ethoxy]ethyl phenylphosphinate
MCS 1967 = MCS 524 + 0.1% MEP + 0.05% TCA
MCS 2032 = MCS 524 + 0.1% MEP
MCS 2051 = MCS 524 + ∿0.07% PFGA + 0.06% PPA
MCS 2064 = MCS 524 + ∿0.07% PFGA + 0.06% PPA + 0.1% SPFGA
MCS 2068 = MCS 524 + ∿0.07% PFGA + 0.3% SPFGA

APPENDIX I

MCS NUMBERS FOR MCS 1305 BLENDS

(See Table 2 for Additive Abbreviations)

MCS 1892 = MCS 1305 + 0.1% A-88
MCS 1894 = MCS 1305 + 0.1% A-88 + 0.05% TCA
MCS 1895 = mCS 1305 + 0.1% A-88 + 0.05% [3-(phenylthio)phenyl]-phosphinic acid
MCS 1968 = MCS 1305 + ∿0.07% PFGA + 0.05% PFGE
MCS 1969 = MCS 1305 + 0.1% Emcol PS-236 + 0.05% dibenzyl disulfide
MCS 1970 = MCS 1305 + 0.1% A-88 + 0.05% dibenzyl disulfide
MCS 1971 = MCS 1305 + 0.1% 2-[2,2,2-trifluoro-1-(trifluoromethyl)-ethoxyl]ethyl phenylphosphinate
MCS 2031 = MCS 1305 + 0.1% FPPA

APPENDIX J

SYMBOLS AND ABBREVIATIONS

Symbol	Meaning
A-88	Proprietary additive
BOT	Bulk operating temperature
FPPA	[3-(Trifluoromethyl)phenyl]phosphinic acid
GLC	Gas liquid chromatography
HFR	High frequency rig
MCS	Monsanto Company sample
MEP	1-Methylethyl phenylphosphinate
NMR	Nuclear magnetic resonance
PFGA	Perfluoroglutaric acid
PFGE	Bis(2-ethylhexyl) perfluoroglutarate
PPA	Phenylphosphinic acid
RI	Refractive index
SEM	Scanning electron microscope
SPFGA	Silylated perfluoroglutaric acid
TAN	Total acid number
TCA	Trichloroacetic acid
THF	Tetrahydrofuran
UV	Ultraviolet
Visc.	Viscosity
μ	Coefficient of friction

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