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Enhancement of Perfluoropolyether Boundary Lubrication Performance

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SUMMARY

A ball bearing simulator operating under starved conditions was used to perform screening tests to evaluate the boundary lubrication performance of a branched perfluoropolyether (PFPE), K-143 AB. Several approaches to enhance boundary lubrication were studied. These included: (1) soluble boundary additives, (2) bearing surface modifications, (3) "run-in" surface films and (4) ceramic bearing components. In addition, results were compared with two non-perfluorinated liquid lubricant formulations. Based on these tests, the following tentative conclusions can be made: (1) Substantial improvements in boundary lubrication performance were observed with a β -diketone boundary additive and a tricresyl phosphate (TCP) liquid surface pretreatment, (2) the use of rough Si_3N_4 balls ($R_a = 40 \mu\text{-in.}$) also provided increases in test duration, but with concomitant abrasive wear, (3) moderate improvements were seen with two boundary additives (a phosphine and a phosphotriazine) and a neat (100 percent) fluid (a carboxylic acid terminated PFPE); and small improvements with surface pretreatments with synthetic hydrocarbons, a polytetrafluoroethylene (PTFE) coating, and TiC coated 440C and smooth Si_3N_4 balls ($R_a = 1 \mu\text{-in.}$), and (4) two non-PFPE lubricant formulations (a polyalphaolefin (PAO) and a synthetic hydrocarbon) yielded substantial improvements.

INTRODUCTION

Perfluoropolyethers (PFPE) have been used as lubricants for a variety of spacecraft applications for more than two decades (1), (2). In addition, these fluids are candidates for high temperature aeronautical applications (3). Several commercial fluids are available. One is a branched fluid (K fluid) based on the anionic polymerization of hexafluoropropene oxide (HFPO) (4). Another company produces fluids (Z and Y fluids) by photooxidation of perfluoroolefins (5), (6). A third commercial fluid (D fluid) is produced by polymerization of tetrafluoroaxetane followed by direct fluorination (7). Of these fluids, only the K and Z series have been used extensively as liquid lubricants and greases for space applications (8).

Conventional lubricants are always supplied with an additive package that enhances their performance. These additives include: antiwear, EP (extreme pressure), anti-oxidant, anti-degradation, anti-corrosion, etc. In contrast, PFPE's are usually supplied as unformulated (non-additive) basestocks. This is because conventional additives developed for mineral oils, esters, hydrocarbons, etc. are not soluble in PFPE fluids.

A few PFPE soluble additives have been recently developed. The first synthesized additives were to function as degradation inhibitors at high temperatures. These included phosphines (9)-(11) and phosphotriazines (12)-(14). The perfluoroarylphosphines have been reported to extend the upper temperature limits of K fluids to 343 °C and Z fluids to 288 °C (15). However, other data (16) have shown the loss of additive function at 343 °C with K fluids. There is also limited activity for both additive types at 316 °C (12) and limited time of activity (75 to 100 hours) at 288 °C (13). X-Ray photoelectron spectroscopy (XPS) studies (17) of the passivation film formed on M-50 steel surfaces during oxidation-corrosion testing with a PFPE fluid containing a perfluoroaryl phosphine concluded that protective action was afforded by high surface concentrations of some type of phosphorus compound.

Basset et al. (18) reported antiwear activity for a series of fluorinated carboxylic acids and their amine salts. However, only a hydrocarbon basestock was studied. It was concluded that the acids formed a metallic soap that was subsequently converted into surface fluoride. Masuko et al. (19),(20) studied a series of PFPE derivatives (acids,

alcohols, and phosphate esters) in a D fluid basestock using a vacuum four-ball apparatus. These additives yielded antiwear activity with the PFPE acid being the most effective. Sharma et al. (21) reported antiwear activity for an additive (structure not disclosed) in a Z fluid. Later, this was reported (22) to be an alcohol terminated PFPE. Gschwender et al. (22) also reported wear reduction for a PFPE ketone in a linear PFPE basestock. Recently, four-ball wear results (23) have been reported for two other PFPE derivatives: a polar amine salt and a phosphorus containing end group. These additives yielded promising results in Z and Y base fluids to 200 °C. A different class of additives (halogenated aryl esters) has been successfully developed for the lubrication of gold coated slip rings (24).

A unique bearing simulator (25) has been developed for the evaluation of lubricant formulations and surface treatments. This device, known as the WAM 3 apparatus, can also generate a complete performance map showing the transitions from boundary to mixed and finally to elastohydrodynamic (EHL) lubrication. This device has successfully differentiated a series of MIL-L-23699 (std. dev. ± 6 to ± 15 %) and DOD-L-85734 (std. dev. range ± 15 to ± 22 %) aviation oils based on load carrying capacity (26).

Therefore, the objective of this work was to use this apparatus to develop a test protocol for screening tests to determine the enhancement of the boundary lubricating ability of a PFPE (K-143AB) by the use of (1) soluble boundary additives, (2) bearing surface modifications, (3) run-in surface films, and (4) ceramic bearing components. In addition, results are compared with two non-perfluorinated liquid lubricant formulations.

EXPERIMENTAL

Test Fluids

Three different liquid lubricants were used in this study: (1) an unformulated perfluoropolyether (K-143AB), (2) a synthetic hydrocarbon formulated with an antiwear additive and an antioxidant (2001), and (3) a polyalphaolefin formulated with an antiwear additive and an antioxidant (176A). Typical properties and additive contents appear in Table 1.

Lubricant Additives

Three lubricant additives (at one weight percent) were evaluated in the PFPE basestock: (1) a phenyl phosphine, (2) a mono-phosphotriazine, and (3) a PFPE β -diketone. In addition, a fourth material (commercially available), a carboxylic acid terminated PFPE was studied neat (100%). Additive structures and designations appear in Table 2.

Simulator

The simulator is fully described in reference 25. Test configuration consists of a ball-on-disc, as shown in Figure 1. Balls (20.64 or 12.7 mm dia) and discs (10.2 cm dia and 12.7 mm thick) were made of 440C stainless steel. These specimens can be operated over a large range of loads, rolling and sliding velocities, temperatures and environmental conditions. Both ball and disk surface speeds and directions can be controlled. Therefore, a large range of rolling (R) and sliding (S) velocities can be introduced. Independent control of R and S provide a "decoupling" of the entraining velocity in the inlet region from the sliding velocity in the Hertzian region. This provides a method of separating the interaction between the physical and chemical properties of the lubricant. Film thickness is determined by the physical properties of the lubricant in the inlet region. Chemical properties become important in the Hertzian region as sliding conditions are varied.

Procedure

A marginal (starved) lubrication scheme was used. It involves wetting the ball and disc specimens with 0.5 ml of test lubricant, spinning (not in contact) at 2000 rpm (ball) and 1350 rpm (disc) for two minutes prior to testing. Only a thin film of lubricant (not measured) remains on the specimens. Tests are conducted at a normal contact pressure of 1.38 GPa (200 Ksi), a rolling velocity of 1.27 m/sec. and at room temperature (23 °C) in an ambient air environment (RH range, 39 to 63%) The lubricant thickness between the ball and disc is decreased further during testing by introduction of contact slip. Per cent slip is defined as:

$$\% \text{ Slip} = S/R \times 100 \quad \text{where:} \quad (1)$$

$$R = \text{Rolling Velocity} = (V_d + V_b) \quad (2)$$

$$S = \text{Sliding Velocity} = V_d - V_b \quad \text{where:} \quad (3)$$

V_d = disc velocity at contact

V_b = ball velocity at contact

The first 300 sec., after loading, is operated under pure rolling. At 300 sec. and every subsequent 100 sec., contact slip is increased by 2% until 10% slip is attained at 700 sec. At 900 sec. and every subsequent 200 sec., slip is increased by 5% until 1900 sec., when a slip of 40% is attained. This contact slip is maintained to the end of test at 2400 sec. This procedure (designated as "A") was used for all tests using the 12.7 mm dia ball specimens.

Some preliminary tests were conducted with larger balls (20.64 mm dia) and a different test protocol ("B"). Specimens were wetted with 0.5 ml of lubricant and spun at 2000 rpm (ball) and 1200 rpm (disc) for two minutes. As in procedure "A", the first 300 sec. were run under pure rolling. At 300 sec. and every 100 sec., the contact slip is increased by 2% until 10% at 700 sec. At 900 sec., slip is increased to 15% and to 20% at 1500 sec. Twenty percent slip is maintained until test termination at 1800 sec. These tests were run at a rolling velocity of 2.54 m/sec.

All tests were continued until there was a rapid increase in traction coefficient which signified contact failure (as indicated in fig 2(a)). When no failure occurred (i.e. fig 2(b)), tests were suspended at 1800 sec. (for the preliminary test "B") and 2400 seconds (standard test "A"). A post-test analysis of the contact regions on both specimens was performed by optical microscopy. Typically, four tests were run for each set of test conditions.

RESULTS

Preliminary Screening

The K-143 AB base fluid, two additive formulations (1 wt %) and the neat (100%) PFPE carboxylic acid were evaluated using test protocol "B". The additives are designated as TL-1, TL-2 and the carboxylic acid as 157 FSL. These represent the phenylphosphine, mono-phosphatriazine, and PFPE carboxylic acid, respectively (Table 2). Typical traction coefficient as a function of time traces for each appear in Figures 2(a) to 2(d), respectively.

For the K base fluid, Figure 2(a), under pure rolling conditions, the traction coefficient is very low. As the first slip step (2%) is introduced, the traction rises quickly to about 0.15 and remains level until at a 6% slip level, the contact fails and traction rapidly increases and the test is terminated at about 600 seconds. In contrast, the phenylphosphine formulation, Figure 2(b), completed the full 1800 second test with a final traction coefficient of about 0.10. The phosphatriazine, Figure 2(c), and the neat carboxylic acid, figure 2(d), yielded almost identical results. The final traction value for the acid was lower, 0.08. All tests (test duration) are summarized in Figure 3.

As shown in Figure 3, moderate improvements (increase in average test duration of 1.5 to 1.9 times) were observed for the two additive formulations and the neat (100 %) PFPE acid, compared to the unformulated base stock. It is obvious that there is a wide variance in the data. One test with the base stock was suspended (no failure), while some of the formulations failed at low slip levels.

Standard Tests-Alternative Lubricants

Results using the standard test protocol "A" for the two alternative lubricant formulations (2001 and 176A) and the b-diketone additive in 143 AB appear in Figure 4. Baseline data for 143 AB are shown for comparison. As can be seen, the 143 AB base fluid failed in less than 600 seconds at 6% slip. In contrast, the two hydrocarbon based formulations and the β -diketone PFPE formulation yielded substantial improvements (average test durations of two to three times).

Standard Tests-"Run-In" Films

Tricresyl phosphate (TCP), in both liquid and vapor form, were used to generate "run-in" surface films prior to tests with 143 AB. Only two tests were performed and appear in Figure 5. Both TCP vapor and liquid completed the 2400 second test without failure. The specimens were solvent cleaned and relubricated with 143 AB using the standard protocol. The "run-in" film produced with TCP vapor allowed the 143 AB to survive to about 700 seconds and 10% slip. In contrast, the TCP liquid film allowed the 143 AB to complete the 2400 second test.

Standard Tests-Other Surface Pretreatments

Results using other surface pretreatments using hydrocarbon lubricant formulations (176A, 2001, and SHC) and a burnished polytetrafluoroethylene (PTFE) film, appear in Figure 6. Here there was no improvement with 176A and small improvements (20 to 40% increases in average test duration) with the SHC, 2001, and the PTFE film.

Standard Tests-Ceramic Balls

Figure 7 contains results using hybrid systems (TiC coated 440C and Si₃N₄ balls). No improvement was seen with the smooth silicon nitride ball, small improvement with TiC (1.4 times) and substantial improvement with rough silicon nitride (3 times). However, the latter was accompanied by severe abrasive wear which would preclude its use in a real system.

DISCUSSION

Unformulated perfluoropolyethers survive in the boundary lubrication mode by decomposing into reactive species which form surface fluorides, oxides and friction polymers (1), (27), (28). These surface films, although effective in initially reducing friction and wear, usually increase the degradation rate of the lubricant. This, in turn, results in a corrosive wear phenomena (19), (20), (28) that can not be sustained for long durations because of the very high wear rates produced.

Conventional lubricants (i. e. hydrocarbons, esters, etc.) also degrade in boundary contacts, but produce films that are not catalytic (29). In addition, almost all conventional lubricants are fortified with soluble additives which assist in producing boundary films to provide surface protection (30). These additives, which are readily available, are not soluble in PFPE fluids. Methods to render them soluble usually result in loss of additive function.

There are several approaches that can be used to enhance the boundary lubrication performance of PFPE based systems. These include the use of newly synthesized PFPE soluble additives, bearing surface modifications, "run-in" surface films and the use of non-steel based bearing components.

Lubricant Additives

The mechanism of action for PFPE boundary additives is somewhat different than additives for conventional systems. Since PFPE's are already operating in a corrosive wear mode (1), (19), (20), an additive must reduce this wear rate to an acceptable level which is determined by the life requirements of the mechanism. This can be accomplished by incorporating an additive which poisons enough catalytic sites to reduce reaction rates. An additive may also function to provide competition for the lubricant molecules by forming other compounds, such as sulfides, phosphates and carboxylic acid soaps. In addition, these surface films provide friction and wear reduction on their own.

Three of the additives in this study (the phosphine, phosphotriazine, and the carboxylic acid) are considered to be film formers (17),(30). The two phosphorus compounds were actually developed for an anti-corrosion function (12). The fourth additive (the β -diketone) is considered to be a surface site blocker. β -diketones are well known complexing agents for polyvalent metals in their enolate form (31). This compound was most effective in enhancing the performance of the PFPE basestock. However, it should be pointed out that the additives were only studied at an arbitrary one wt. percent level. Therefore, because of molecular weight differences (Table 2), the β -diketone was actually present at a higher molar concentration. This may have contributed to its better performance.

Masuko et al. (20) reported a large reduction in steady state wear rate for a PFPE carboxylic acid (20 wt %) in vacuum using a four-ball apparatus. However, tests in air actually yielded higher wear rates than with the basestock alone. This additive was similar to the 157 FSL studied in this paper.

Surface Pretreatments

Another method of enhancing bearing performance is to pretreat the tribological surfaces, either statically or dynamically, with a neat (100 %) boundary additive or a formulated hydrocarbon based lubricant (32), (33). Using the standard test protocol "A" with neat tricresyl phosphate (TCP) either in the form of a liquid or vapor, resulted in a successful 2400 second test (Figure 5). When relubed with 143 AB and run again, the vapor pretreatment did not improve the test results. However, the liquid pretreatment did result in a successful test. Other pretreatments using three formulated hydrocarbons (176A, SHC and 2001) and a PTFE burnished film yielded only small improvements.

The theory behind the use of pretreatments is that the preformed surface films passivate the metal surface and thus reduce the corrosive wear phenomena to acceptable limits (33),(34). In addition, the phosphate films formed from the additives are excellent boundary lubricants on their own (35). Of course, these films are eventually worn away and are not replenished. Apparently, the durability of the films formed in this study was not sufficient to show any improvements, with the possible exception of liquid TCP.

Ceramic Components

A number of investigators (36) - (38) have proposed the use of ceramic coated or solid ceramic components to extend the life of instruments bearings for use with conventional lubricants. In addition, Carré (39) and Baxter and Hall (40) have shown life extensions for ball bearings with ceramic components using PFPE lubricants. The rationale is that the chemical interactions between the PFPE and iron can be either eliminated or reduced, thus enhancing performance. In our tests, a hybrid system was used (440C discs and either a TiC coated 440C or Si₃N₄ ball). There was small improvement with the TiC ball but none with the smooth (R_a = 1 μin.) Si₃N₄ balls. Only the rough (R_a = 40 μin.) Si₃N₄ balls showed substantial improvement. However, these tests were accompanied by high wear of the 440C disc, at a level which was unacceptable for a real system.

Alternative Lubricants

The two non-PFPE alternative lubricants (2001 and 176A) yielded better results compared to the non-additive PFPE using 440C components. Both of these lubricants contain phosphorus anti-wear additives. However, even with these conventional additive packages, only one test completed the 2400 second protocol.

SUMMARY OF RESULTS

Based on tests with a branched PFPE (143 AB) using a bearing simulator under starved conditions, the following results were obtained:

1. Substantial improvements in test duration were observed with a β-diketone boundary additive and a tricresyl phosphate (TCP) liquid surface pretreatment.
2. The substitution of rough silicon nitride balls for the 440C stainless steel balls also provided substantial improvement in test duration, but with concomitant abrasive wear to the 440C steel disc.
3. Moderate improvements were seen with three boundary additives (a phosphine, a phosphotriazine, and a carboxylic acid); small improvements were seen with surface pretreatments with synthetic hydrocarbons (SHC, 2001); a PTFE coating; and TiC coated 440C; and no improvement with smooth silicon nitride balls.
4. Alternative lubricant formulations (non-PFPE) (176A, 2001) yielded substantial improvements.

CONCLUSION

1. A screening test protocol has been developed which rapidly evaluates boundary additives and surface pretreatments for PFPE based systems.

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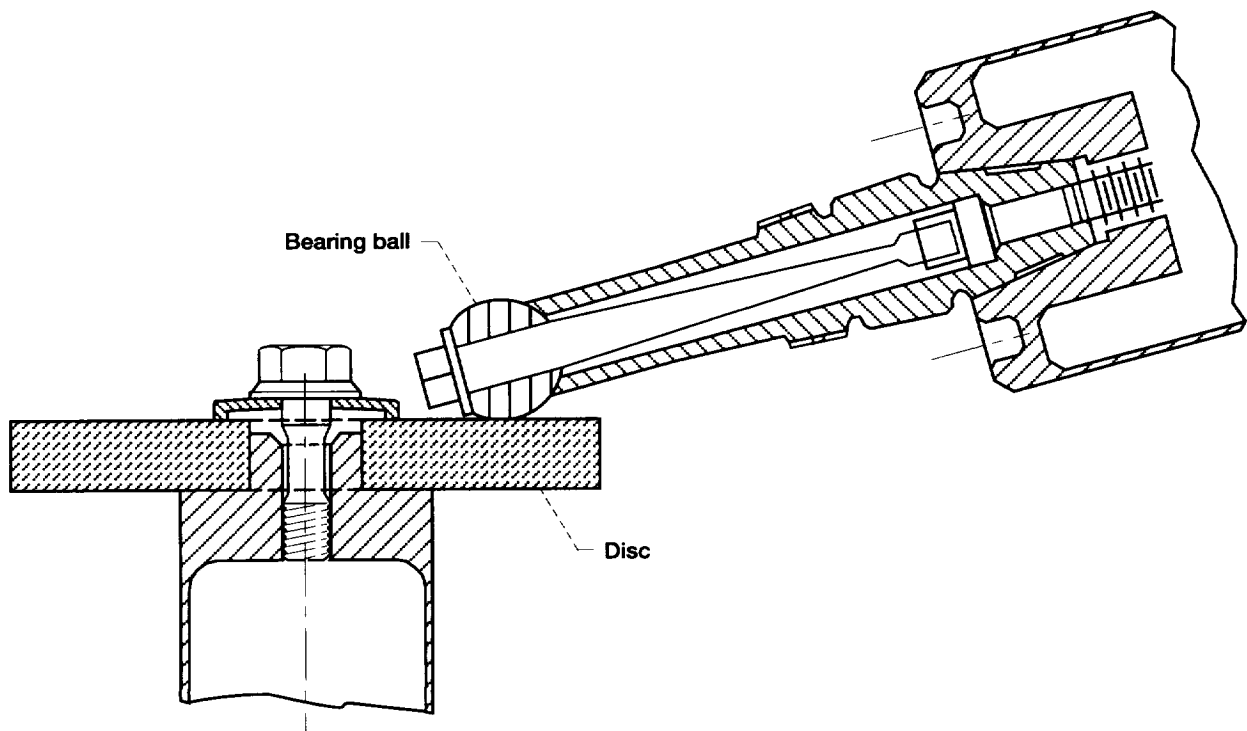


Figure 1.—Test specimen configuration.

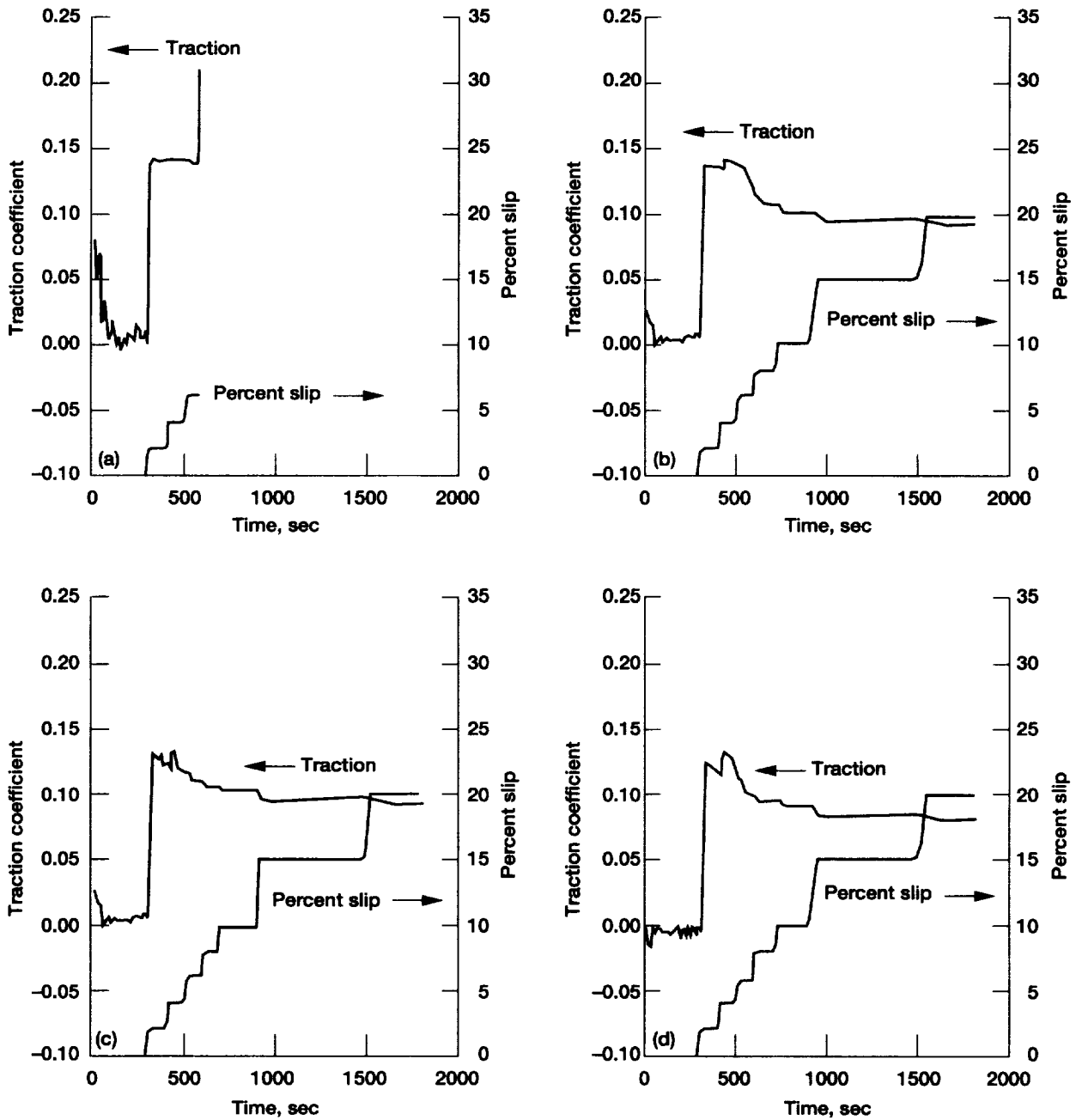


Figure 2.—Traction coefficient and slip as a function of time (test procedure "B"). (a) K-143 AB base fluid. (b) K-143 AB + phenylphosphine (one wt %). (c) K-143 AB + phosphotriazine (one wt %). (d) K-157 FSL carboxylic acid (100%).

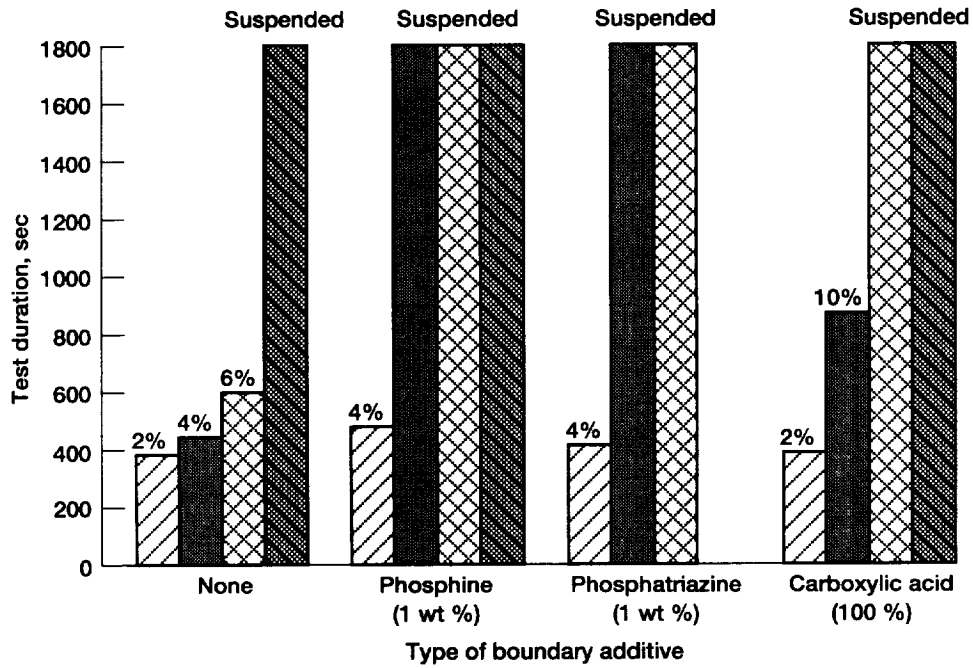


Figure 3.—Test duration for various boundary additives (K-143 AB, 440C steel balls and discs) (test procedure "B").

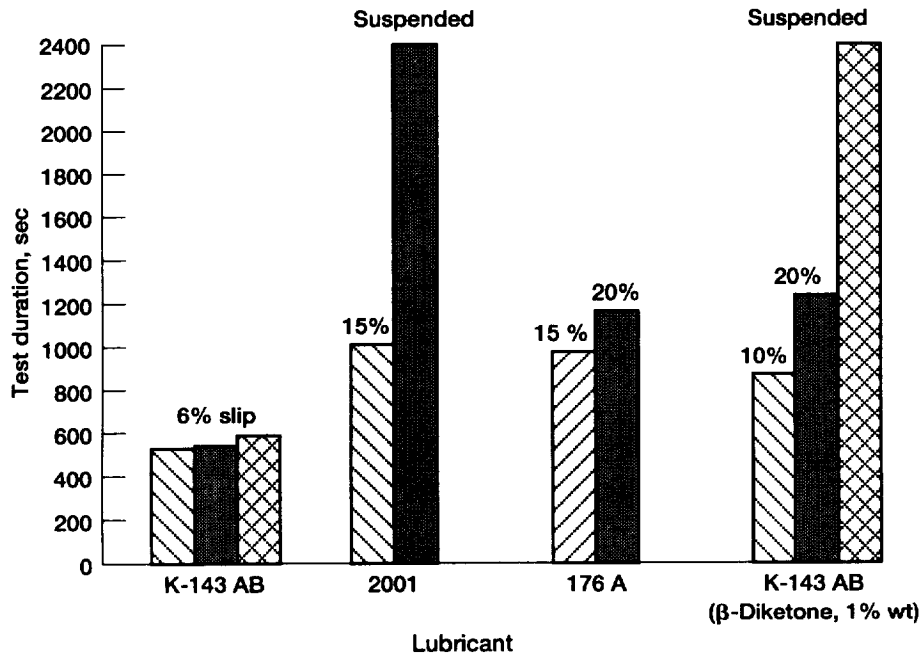


Figure 4.—Test duration for alternative lubricants (440C balls and discs) (test procedure "A").

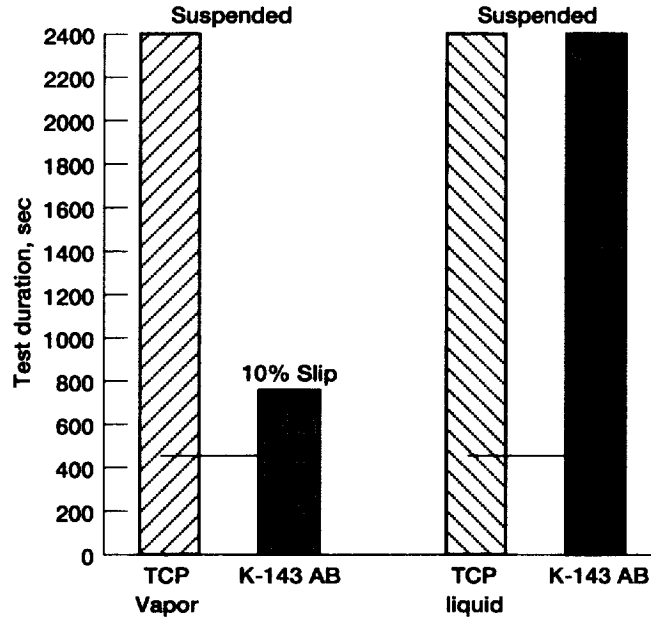


Figure 5.—Test duration for surface run-in with tricresyl phosphate (TCP) vapor and liquid (440C balls and discs) (test procedure "A").

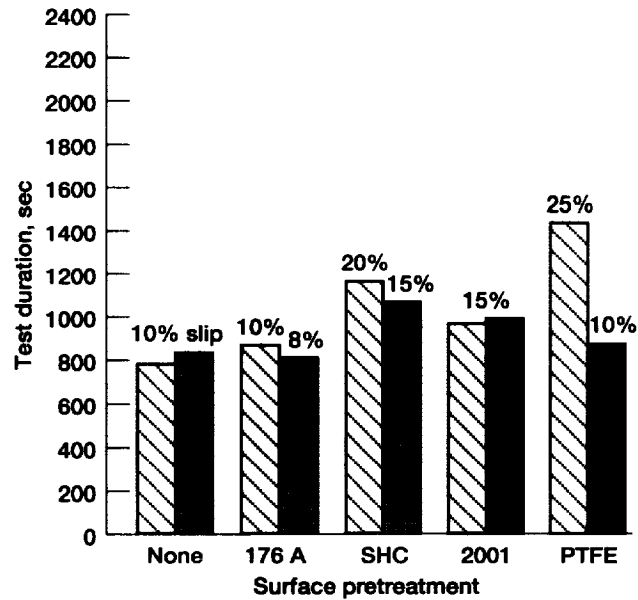


Figure 6.—Test duration for different surface pretreatments (K-143 AB, 440C balls and discs) (test procedure "A").

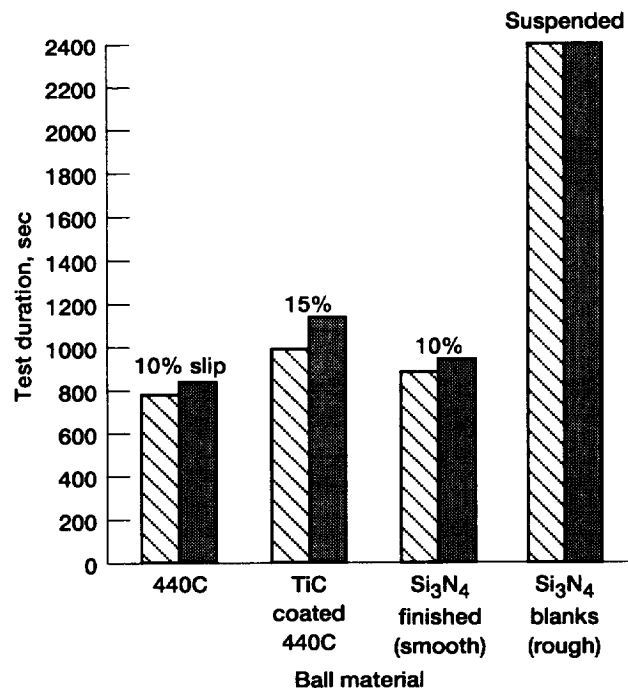


Figure 7.—Test duration for different ball materials (K-143 AB, 440C discs) (test procedure "A").

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13. ABSTRACT (Maximum 200 words) A ball bearing simulator operating under starved conditions was used to perform screening tests to evaluate the boundary lubrication performance of a branched perfluoropolyether (PFPE), K-143 AB. Several approaches to enhance boundary lubrication were studied. These included: (1) soluble boundary additives, (2) bearing surface modifications, (3) "run-in" surface films and (4) ceramic bearing components. In addition, results were compared with two non-perfluorinated liquid lubricant formulations. Based on these tests, the following tentative conclusions can be made: (1) Substantial improvements in boundary lubrication performance were observed with a β -diketone boundary additive and a tricresyl phosphate (TCP) liquid surface pretreatment, (2) the use of rough Si_3N_4 balls ($R_a=40 \mu\text{in}$) also provided increases in test duration, but with concomitant abrasive wear, (3) moderate improvements were seen with two boundary additives (a phosphine and a phosphotriazine) and a neat (100%) fluid (a carboxylic acid terminated PFPE); and small improvements with surface pretreatments with synthetic hydrocarbons, a polytetrafluoroethylene (PTFE) coating, and TiC coated 440C and smooth Si_3N_4 balls ($R_a=1 \mu\text{in}$), and (4) two non-PFPE lubricant formulations (a polyalphaolefin (PAO) and synthetic hydrocarbon) yielded substantial improvements.				
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