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Development and Preliminary Evaluation of Aryl Ester Boundary Additives for Perfluoropolyethers

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Abstract

A series of additives were developed for evaluation as boundary lubrication enhancers for perfluoropolyethers. They are composed of a hydrocarbon aryl component (for lubrication improvement) and a fluorinated side chain (for solubility enhancement). The two moieties are joined by an ester linkage. Five boundary additives were evaluated in a perfluoropolyether basestock (Fomblin Z25) using a specially designed four-ball apparatus. Additives were evaluated at a one wt% concentration. Conditions included: an atmosphere of dry air at atmospheric pressure, a 200N load, a speed of 100 rpm, room temperature, and 440C stainless steel specimens. Two monoesters, 2,4,6-trimethyl E_2 and H_5PDFO yielded wear rate reductions of approximately 60 and 35%, respectively. One diester, $H_4[E_2]_2$, had no activity, while two other diesters (a diester of bisphenol A and $H_4[E_4]_2$ were pro-wear.

Introduction

Perfluoropolyethers (PFPE) are widely employed as lubricants for space applications because of their excellent thermal (ref. 1) and chemical stability (ref. 2) and are particularly effective in the elastohydrodynamic regime (ref. 3). However, when employed as a boundary lubricant, PFPE performance is more variable and less predictable (refs. 4 and 5). The most significant problem encountered when using PFPE's in the boundary lubrication mode is the unavailability of soluble additives. This results from the fact that the vast additive technology developed for hydrocarbon and ester based lubricants cannot be applied to PFPE's because of their inherent insolubility. Soluble phosphorus based additives have been developed for anti-corrosion and anti-degradation (refs. 6 and 7) but these have little or no boundary lubrication activity (refs. 8 and 9).

Masuko et al (ref.10) studied a series of PFPE derivatives (acids, alcohols, and phosphate esters) in a Demnum basestock using a vacuum four-ball apparatus. These additives yielded some antiwear activity with the PFPE terminated acid being the most effective. Sharma et al (ref. 11) reported anti-wear activity for an additive (structure not disclosed) in Fomblin Z. Later, this additive was identified (ref. 8) as a PFPE alcohol. Reference 8 also reported wear reduction for a PFPE ketone. Recently, four-ball wear results (ref. 12) have been reported for two other PFPE derivatives: a polar amine salt and a phosphorus containing end group.

Recently, Draper Laboratory has developed a new class of soluble PFPE boundary additives (aryl esters) whose structure can be modified for specific applications. This approach has been successful for the development of a lubricant for sliding gold slip ring contacts (ref. 13). In addition, NASA Lewis has developed a vacuum four-ball apparatus for the evaluation of liquid lubricants for space applications (ref. 14).

Therefore, the objective of this work was to evaluate a series of PFPE soluble aryl esters for boundary lubrication activity in a PFPE basestock (at a one weight per cent concentration) by measuring steady state wear rates and coefficients of friction using a four-ball apparatus. Test conditions included: a dry air atmosphere, 200N load, a speed of 100 rpm, room temperature, 440C stainless steel bearing balls and a total test duration of approximately five hours. Due to the limited quantities of synthesized additives, only a few tests were performed in this preliminary study.

Experimental

Lubricant Basestock

A linear PFPE (Fomblin Z-25, lot P-67) was chosen as a basestock. This is a commercial fluid and is a random copolymer of perfluorinated methylene oxide and perfluorinated ethylene oxide, made by UV polymerization of tetrafluoroethylene in the presence of oxygen (ref. 15). Preliminary wear rates previously obtained for this fluid in dry air and vacuum appear in reference 14.

Lubricant Additives

Limited quantities of five different aryl esters were synthesized for this study. Their structures and designations appear in Table 1. All additives were evaluated at a one weight per cent level in Fomblin Z25. Aryl esters (figure 1) were chosen as the class of compounds for the following reasons:

1) The structure allows for the separation of fluorocarbon moiety (for solubilization) from an aryl moiety containing classical boundary lubrication functionalities.
2) This class is readily synthesized from PFPE derived acid fluorides and a variety of commercially available phenols.
3) The range of available phenols allow the evaluation of any functional group which may be attached to the ring.
4) This approach allows facile adjustment of physical properties such as density, viscosity, vapor pressure, etc.
5) The tribological moiety is insulated from the fluorocarbon moiety, avoiding effects from the electronegative fluorine atoms.
6) This structure lends itself to systematic functional group changes which may be evaluated for their tribological activity.
7) Tribological (aryl group) properties may be varied independently of physical properties (alkyl chain).

Synthesis

Two types of aryl esters were synthesized. One monoester (H_5PDFO) was prepared from a benzoic acid derivative and a fluorinated alcohol so that the carbonyl function is adjacent to the benzene ring. The other type (which includes the remaining four additives) was prepared from a phenol derivative and fluorinated acid fluoride so that the carbonyl group is separated from the benzene ring by an oxygen atom. Two mono and three diesters were prepared. Examples of the two types of synthesis appear in figure 2 (a) for 2,4,6-trimethyl E_2 and figure 2(b) H_5PDFO This initial study was limited to ring substitution having only hydrogen and methyl groups. More complex functional groups will be investigated in the future. All compounds were purified and characterized. The esters were greater than 99.9 per cent pure as measured by gas chromatography and mass spectroscopy.

Tribometer

A four-ball tribometer (figure 3), operating in the boundary lubrication mode, was used to measure steady state wear rates and friction coefficients for each lubricant formulation and the non-additive base stock. Specimen configuration (figure 4) is essentially the same as the ordinary four-ball apparatus, except for the use of 9.5 mm (3/8 in.) diameter precision bearing balls (grade 10). A complete description of this device appears in reference 14.

Procedure

Test balls made of AISI 440C stainless steel are cleaned by scrubbing with fine alumina powder under a stream of water followed by rinsing with de ionized water. The lubricant cup is cleaned similarly. The balls are further cleaned by exposure in a UV-ozone apparatus for 15 minutes just prior to the test. The lubricant cup is filled with the test lubricant after the three balls are fixed in it. The cup is placed on the stage inside the tribometer and the chamber is purged with dry air for 20 minutes. This stage is pneumatically loaded against the upper ball and rotation is started. Friction torque is recorded continuously. Wear is determined by measuring wear scar diameters on the three stationary balls using an optical microscope. A sample stage on the microscope is so designed that the wear scars may be measured without disassembling the balls from the cup. The experiment can then be continued using the same set of balls. After several measurements, a wear rate (mm^3/mm) is calculated from the slope of the straight line obtained by plotting wear volume as a function of sliding distance. An example for a Demnum PFPE fluid is shown in figure 5.

Results

Wear and friction results are tabulated in Table 2 and appear in figures 6 and 7, respectively. Due to the limited amount of additive, only a few tests were run on each lubricant formulation. However, it should be pointed out that one wear rate determination involves several separate wear scar measurements during the five hour test. As can be seen, the two monoester additives (2,4,6-trimethyl E_2 and H_5PDFO) yielded wear reductions of approximately 60 and 35 percent, respectively, compared to the unformulated Z25 basestock. One diester ($H_4[E2]_2$)(one test) had no effect and two other diesters (H-bisphenol A $[E_2]_2$ and $H_4[E_4]_2$)(one test) were actually pro-wear. Friction coefficients for the two monoesters were slightly greater than the base fluid, while the three diesters yielded similar results.

Discussion

Wear

As discussed in reference 3, PFPE base fluids under boundary lubrication conditions normal operate in the corrosive wear regime. For a detailed discussion of the boundary lubrication regime and corrosive wear effects, see references 16 and 17, respectively. In boundary contacts, PFPE fluids react with bearing surfaces producing a series of corrosive products, which, in turn, react with existing surface oxides producing metal fluorides (ref. 18). The presence of these fluorides usually prevent contact failure (scuffing) and also reduce friction. However, these fluorides also attack the PFPE fluids producing more reactive products. Surface fluoride is constantly removed from the sliding contact region, resulting in a high substrate wear rate (i.e. corrosive wear).

In contrast, conventional unformulated hydrocarbon and ester based lubricants are relatively unreactive and operate in the adhesive wear regime in boundary contacts. Therefore, these fluids are fortified with reactive anti-wear and extreme pressure additives so that surface films can be formed in order to reduce wear, and to a lesser extent, friction. But, it is unlikely that a similar approach would work with PFPE fluids. The addition of a reactive additive to an already reactive base stock, may actually increase wear rates.

One approach, that has been pursued, is the use of additives which have shown anti-degradation and anti-corrosion activity in high temperature static tests, such as phosphines and phosphatriazines (refs. 6 and 7). Indeed, these additives have yielded marginal improvements in bearing simulator tests with Krytox PFPE fluids (ref. 9). Their activity has been rationalized by assuming they react or block active sites on bearing surfaces, thus slowing the attack of the PFPE fluid. Other surface active materials include alcohols (ref. 19) and esters. Since the aryl esters had shown some promise in PFPE studies on slip rings (ref. 13), that was the approach used in this study.

As indicated above, the two additives which showed anti-wear activity in this study, were the monoesters, H_5PDFO and 2,4,6-trimethyl E_2. The three diesters either had no activity or were pro-wear. The reason for this diverse behavior is not known. A follow on study of the worn surfaces using sensitive surface analytical techniques is underway. The trimethyl E_2 additive was studied in Krytox in a ball-on-plate rolling contact device (ref. 20). Wear (measured by profilometry) was greatly reduced using a one weight per cent formulation and, therefore, lends support to the tentative conclusions reported here.

Friction

Boundary additives in conventional fluids can yield wear rate reductions of an order of magnitude or more (refs. 16 and 17). In contrast, the friction coefficient is relatively insensitive during steady state wear, as long as there is no contact failure (scuffing). For example, the addition of a fatty acid to an unformulated mineral oil may only lower the coefficient of friction from 0.15 to 0.09 (ref. 21). Therefore, the small changes observed with the additive formulations in this study was not unexpected.

Summary of Results

1. Monoesters (2,4,6-trimethyl E_2 and H_5PDFO) at a one weight per cent level in Fomblin Z-25 yielded wear reductions of 60 and 35 per cent, respectively, compared to the unformulated base stock.

2. Diesters ($H_4[E_4]_2$, $H_4[E_2]_2$, and H-bis Phenol A $[E_2]_2$) at a one weight per cent level in Fomblin Z-25 either had no antiwear activity or were pro-wear.

3. Friction coefficients for the monoester formulations were slightly greater than the base stock, while the diester formulations were similar.

Tentative Conclusions

Because of the limited number of tests, the following conclusions can only be considered tentative. They must be confirmed with additional tests when more material becomes available. At that time, effects of different additive concentrations, different atmospheres, and different base stocks, will be studied.

1. Aryl monoester additives exhibit antiwear activity in a PFPE base stock (Fomblin Z-25) in dry air under pure sliding conditions with 440C stainless steel.

2. Aryl diester additives do not exhibit antiwear activity in Fomblin Z-25 and may actually be detrimental.

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Table I. Designations and structures of aryl ester lubricant additives.

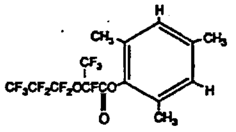
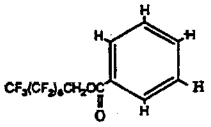
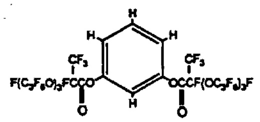
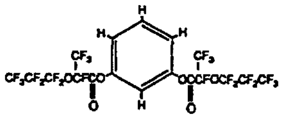
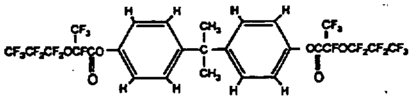
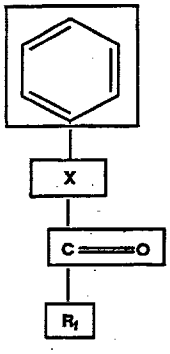
Designation	Structure
Monoesters	
2,4,6-Trimethyl E_2	
$H_5$5PDFO	
Diesters	
$H_4(E_4)_2$	
$H_4(E_2)_2$	
H-Bis Phenol A $(E_2)_2$	

Table II. Summary of friction coefficients and wear rates for lubricant formulations.

Test Fluid (Additive Conc. 1% wt.)	Average Coefficient of Friction	Average Wear Rate, $(mm^3/mm)x10^{-9}$
Fomblin Z-25 (Lot P-67) No Additive	0.08±0.01*	0.90±0.24*
2,4,6-Trimethyl E_1	0.11±0.005	0.34±0.06
H_5PDFO	0.11±0.004	0.58±.48
$H_4(E_4)_2$	0.08	3.3
$H_4(E_2)_2$	0.09	1.2
H-Bis Phenol A $(E_2)_2$	0.09±0.01	2.0±1.3

*Standard Deviation

- **Rationale for selection of basic molecular structure: allows systematic alteration of basic structural features**



- **Can hold 5 substituents for density, viscosity control, antioxidants (e. g., CHO), polar groups for surface attachment, lubricity enhancers, antiwear enhancers, etc.**
- **Connecting group**
- **Connecting group, increases polarity to enhance surface attachment**
- **Fluorocarbon moiety: lubricity, good low temperature properties, solubility**

Figure 1.—Aryl ester fluids.

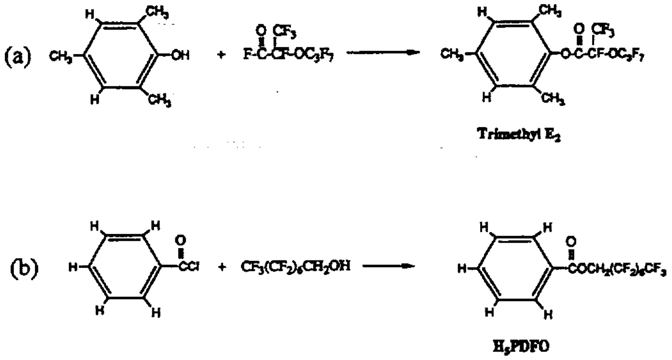


Figure 2.—Typical synthesis routes for two types of aryl esters.

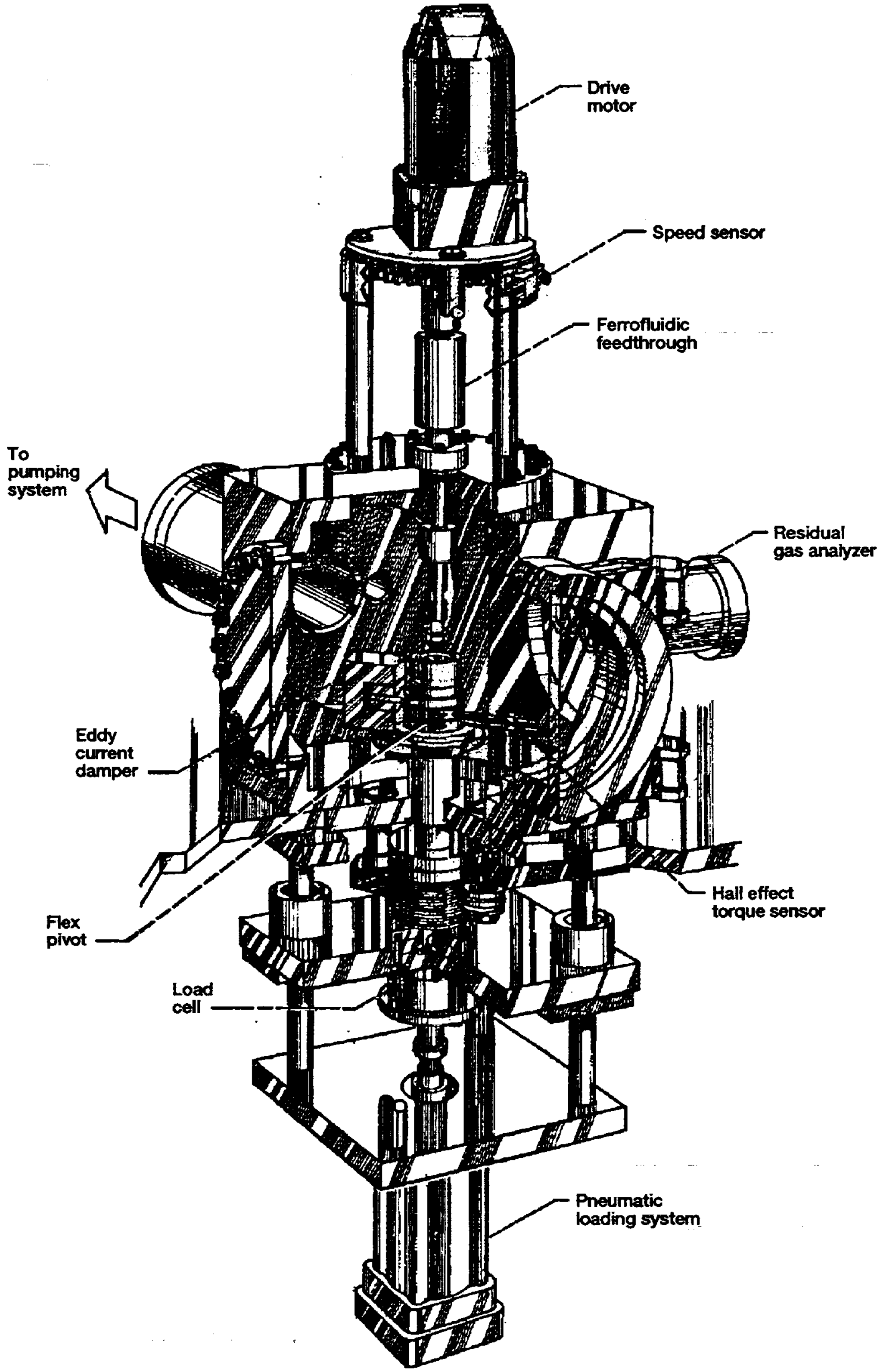


Figure 3.—Four-ball tribometer.

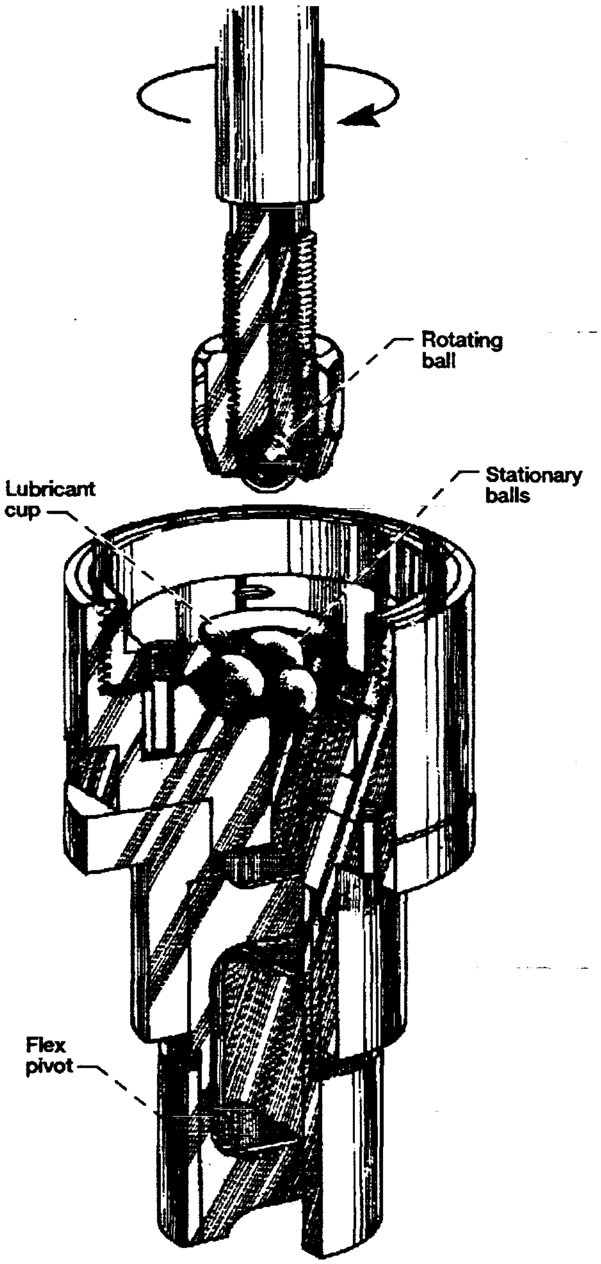


Figure 4.—Specimen configuration.

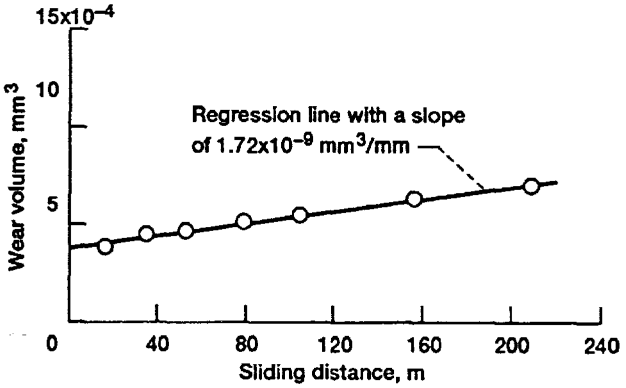


Figure 5.—Wear volume as a function of sliding distance (Demnum S-100; 600N, air).

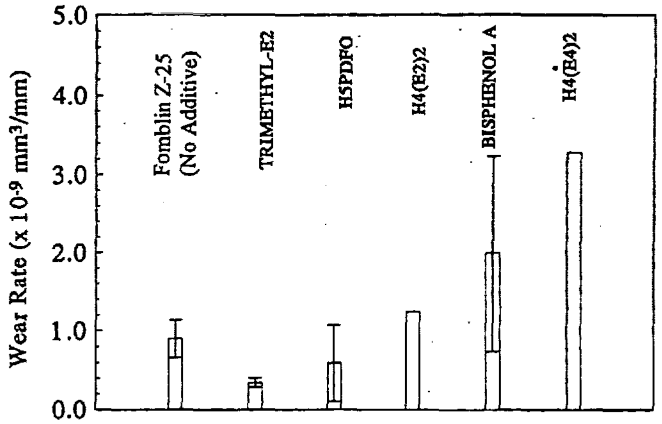


Figure 6.—Average wear rates for unformulated fomblin Z-25 base stock and various additive formulations (one wt. %) (dry air, 200N load, 100 rpm, 23 °C) error bars represent one standard deviation.

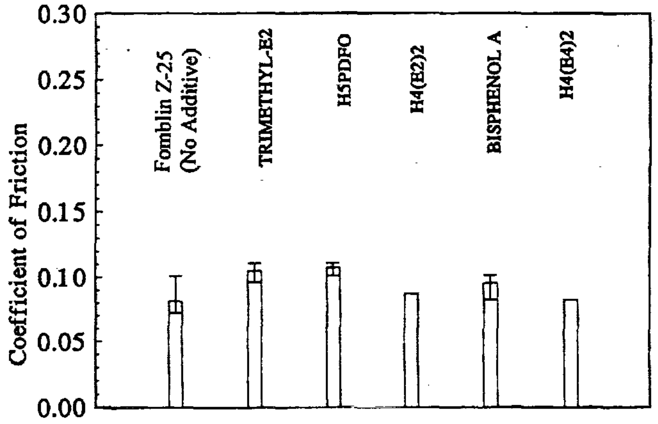


Figure 7.—Average friction coefficients for unformulated fomblin Z-25 base stock and various additive formulations (one wt. %) (dry air, 200N load, 100 rpm, 23 °C) error bars represent one standard deviation.

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13. ABSTRACT ***(Maximum 200 words)***

A series of additives were developed for evaluation as boundary lubrication enhancers for perfluoropolyethers. They are composed of a hydrocarbon aryl component (for lubrication improvement) and a fluorinated side chain (for solubility enhancement). The two moieties are joined by an ester linkage. Five boundary additives were evaluated in a perfluoropolyether basestock (Fomblin Z25) using a specially designed four-ball apparatus. Additives were evaluated at a one wt% concentration. Conditions included: an atmosphere of dry air at atmospheric pressure, a 200N load, a speed of 100 rpm, room temperature, and 440C stainless steel specimens. Two monoesters, 2,4,6-trimethyl E_2 and H_5PDFO yielded wear rate reductions of approximately 60 and 35%, respectively. One diester, $H_4[E_2]_2$, had no activity, while two other diesters (a diester of bisphenol A and $H_4[E_4]_2$ were pro-wear.

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