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Research on Liquid Lubricants for Space Mechanisms

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Abstract

Four research areas at the NASA Glenn Research Center involving the tribology of space mechanisms are highlighted. These areas include: soluble boundary lubrication additives for perfluoropolyether liquid lubricants, a Pennzane dewetting phenomenon, the effect of ODC-free bearing cleaning processes on bearing lifetimes and the development of a new class of liquid lubricants based on silahydrocarbons.

Introduction

Most moving mechanical assemblies for space mechanisms rely on liquid lubricants to provide reliable long-term performance. Historically, these materials have been based on mineral oils, polyol esters, perfluoropolyethers (PFPEs) or polyalphaolefins (PAOs) [1]. Recently, a new synthetic hydrocarbon, a multiply alkylated cyclopentane (Pennzane), has seen increased use [2]. However, all of these materials have disadvantages that can limit their lifetimes in a lubricated contact. The PFPEs [3] are poor boundary lubricants and will not solubilize conventional additives. They are also susceptible to autocatalytic degradation [4]. Mineral oils have wide molecular weight distributions and thus, volatility problems [5]. Recently, Pennzane dewetting problems have been reported [6].

In addition, with the phasing out of ozone depleting chemicals (ODC), new concerns about bearing lifetimes have arisen due to the use of new, unqualified ODC-free cleaning techniques [7]. This paper reviews current research at NASA related to some of the above problem areas. These include: the development of a new series of soluble, low volatility, antiwear and anti-degradation additives for use in PFPEs, studies of the Pennzane dewetting phenomenon, and the use of the new NASA rolling contact vacuum tribometer and parched elastohydrodynamic (EHL) apparatus to study the effects of surface chemistry from ODC-free cleaning techniques on lubricated lifetimes. In addition, the development of a new class of synthetic space lubricants, based on the silahydrocarbons, is reported.

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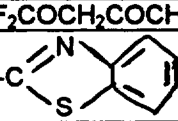
PFPE Boundary Lubrication Additives

Perfluoropolyethers (PFPEs) are widely employed as lubricants for space applications because of their excellent thermal and chemical stability, low volatility, spectral transparency and excellent EHL film forming characteristics [3]. However, when used as a boundary lubricant with steel surfaces, their performance is not always satisfactory [5, 8]. This is hampered further by the lack of soluble antiwear additives for this chemical class. Some soluble phosphorus based additives, carboxylic acids, esters and ketones have yielded mixed results in boundary lubrication experiments. For a more detailed discussion of these materials, see reference [9].

Tribological Tests — Undefined term —

Recently, NASA has developed a vacuum four-ball apparatus and a test protocol for the evaluation of liquid lubricants and greases for space applications [10]. As part of an SBIR program with Exfluor Corporation, six additives were synthesized and evaluated as boundary lubrication enhancers for PFPEs [9]. These additives included: a phosphate, a thiophosphate, a β-diketone, a benzothiazole, an amide and a sulfite. Formulae appear in Table 1.

Table 1. Additive Formulae

Name	*Formula*
Phosphate	$O{=}P(OCH_2CF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2CF_2CF_3)_3$
Thiophosphate	$S{=}P(OCH_2CF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2CF_2CF_3)_3$
ß-Diketone	$CF_3CF_2CF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2COCH_2COCH_3)$
Benzothiazole	$CF_3CF_2CF_2CF_2CF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2$-C 
Amide/Thiol	$CF_3CF_2CF_2CF_2CF_2CF_2OCF_2CF_2OCF_2CF_2OCF_2CF_2CONHCH_2CH_2SH$
Sulfite	$(CF_3CF(CF_3)CF_2CF_2CF_2CF(CF_3)CF_2CH_2O)_2S{=}O$

Additives were evaluated in a vacuum four-ball apparatus in a PFPE fluid (Krytox 143 AC) at an arbitrary one weight percent level. Tests were performed in vacuum (< 5.0×10^{-6} Torr), at room temperature, at an initial Hertzian stress of 3.5 GPa and a sliding velocity of 28.8 mm/sec. Test specimens were 52100 bearing balls. All additives yielded reductions in mean wear rates of at least 55 percent, with the exception of the benzothiazole which had no effect. Two of the additives, an amide-thiol and a sulfite, reduced the mean wear rate by at least 80 percent. These results are summarized in Figure 1.

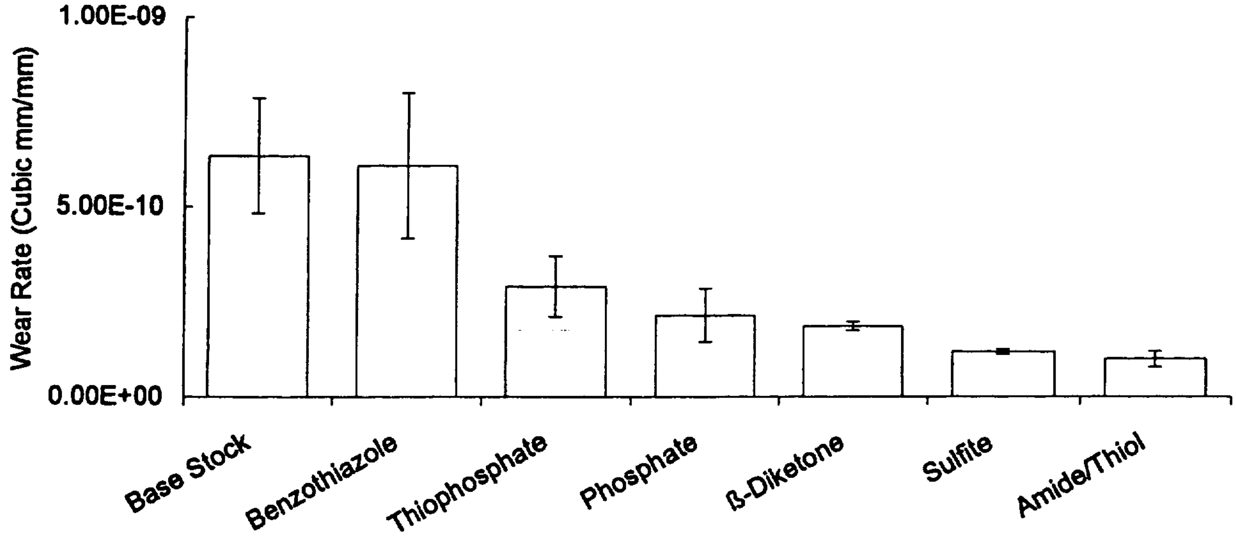


Figure 1. Mean wear rates from vacuum four-ball apparatus for Krytox 143AC and several additive formulations at one weight per cent. Error bars represent one standard deviation.

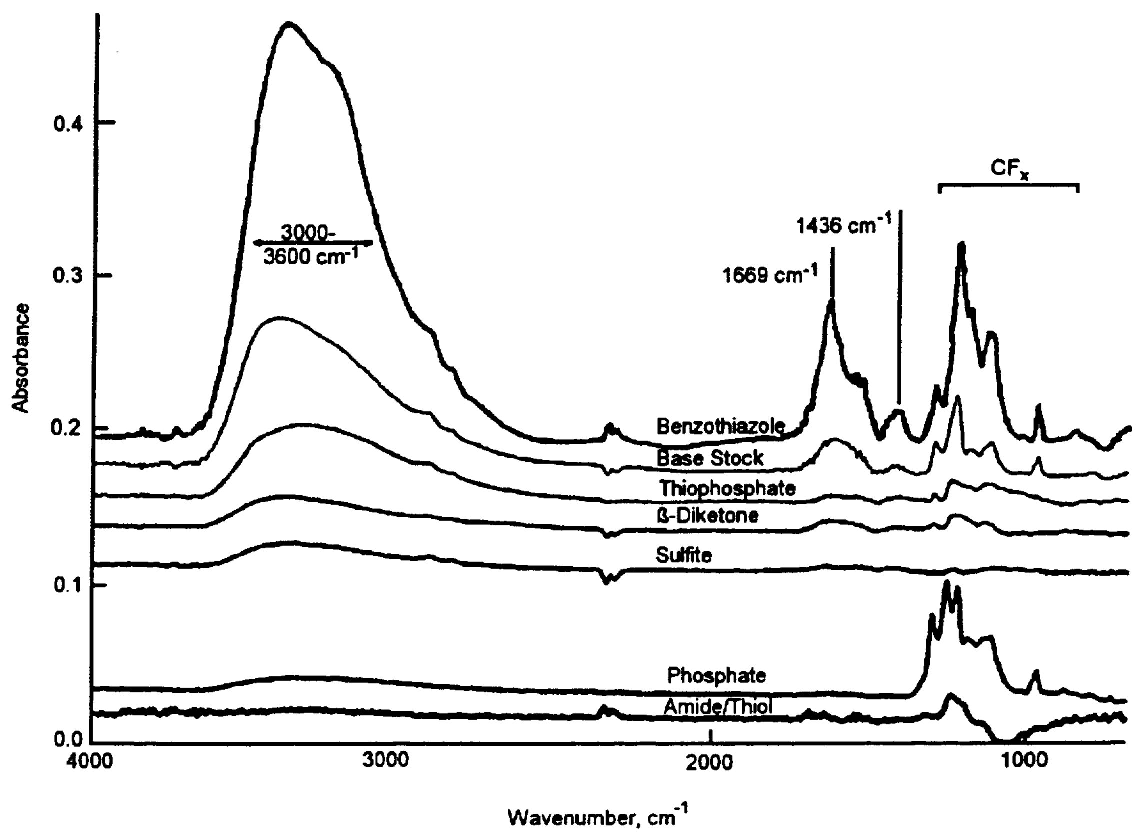


Figure 2. Infrared spectra of regions off the wear scar after solvent rinsing for formulated and unformulated tests

Surface Analysis

Infrared spectra of wear scars from each test were obtained using an IR microscope. These results appear in Figure 2 for the friction polymer region after solvent rinsing. In previous work, high wear with PFPEs have yielded IR peaks at 1436 and 1669 cm^{-1} and a broad band from 3000 to 3600 cm^{-1}. The broad band is associated with hydrogen bonded hydroxyl groups, while the other two bands are assigned to carboxylic acid species. In general, the greater the wear rate, the more pronounced are these bands. That is the case in Figure 2.

Pennzane Dewetting Phenomenon

For a lubricated contact, the supply of lubricant must be maintained throughout the life of the mechanism. If this supply is disrupted or reduced, the life of the mechanism may suffer. For elastohydrodynamic (EHL) contacts, the film thickness is determined by the EHL pressure generated in the convergent inlet region. If there is an insufficient supply of lubricant in this region, this pressure generation will be inhibited and the resulting film thickness will be diminished.

Effect of Dewetting on EHL Behavior

The inlet lubricant boundary is a function of several variables, including the quantity of lubricant, contact geometry, speed of the bearing surfaces, viscosity and surface tension. If the lubricant only partially wets the surfaces, this boundary can also be reduced, with an accompanying decrease in film thickness. If the contact is operating with a marginal film thickness, dewetting could drive the contact into the mixed or boundary film regime which would drastically affect bearing lifetime.

Dewetting Experiments

Researchers at L'Institut National des Sciences Appliquees de Lyon (INSA) first reported on the phenomenon of Pennzane dewetting in vacuum in 1996 [11]. Since that time, detailed studies at NASA Glenn have verified this unusual behavior and have identified a possible mechanism. This dewetting behavior is illustrated in Figure 3. Dewetting was initiated by placing a few drops of neat Pennzane on a UV-ozone cleaned 440C surface. The specimen was then axially centered on the driving shaft of a centrifuge, covered and allowed to stand for several minutes. Then the specimen was spun at 5000 rpm for 30 minutes. The specimen was then covered and allowed to stand in room air for several hours. Over this time period, all lots of Pennzane dewetted to some extent.

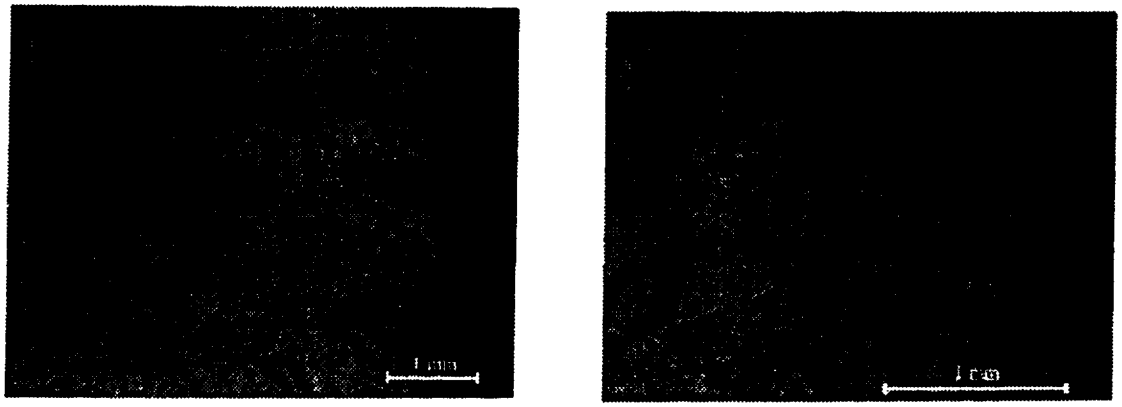


Figure 3. Dewetting of Pennzane on a clean 440C steel surface

Krytox Studies

Earlier studies [12] done on a particular lot of Krytox 143 AC yielded similar behavior (Figure 4). In that study, only one lot of Krytox exhibited the dewetting

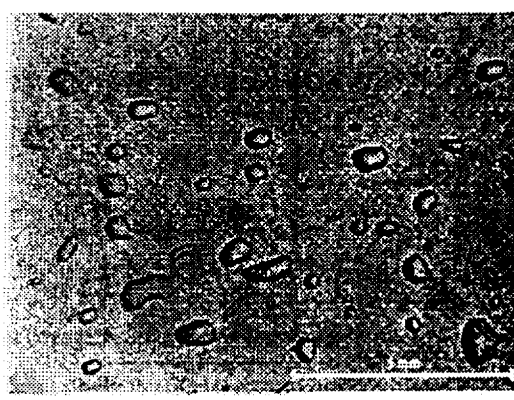


Figure 4. Dewetting of Krytox on a clean 440C steel surface

characteristics. In contrast, all Pennzane samples more or less exhibited dewetting properties. By pretreating the Krytox at high temperature (316°C) in oxygen or filtering it through a silica or alumina column, the dewetting could be completely eliminated. It was concluded that a low concentration of a surface active impurity was present which caused the phenomenon, probably a carboxylic acid.

Possible Mechanism of Dewetting

In discussions with the developers of Pennzane at Pennzoil, it was determined that a high molecular weight ester impurity is present in all samples at varying concentrations. This ester is generated during synthesis when one of the reactants, a C_{20} alcohol is partly oxidized to a C_{20} acid. The acid can then react with the excess C_{20} alcohol to produce a C_{40} ester. Since esters have been implicated in wettability problems in the past [13], it seems likely that this material is responsible for the phenomenon. The ester being more surface active than the hydrocarbon would adsorb at the metal interface. The ester would then hydrolyze to form an acid, which in turn would react with the metal to form a soap of lower surface energy than the bulk surface tension of the fluid, thus causing partial dewetting.

There has been only one report in the literature [14] alluding to a possible dewetting phenomenon with Pennzane SHF X-2000 in ballscrew tests in vacuum. It was stated that the Pennzane did not "cling" to the surface and thus required the application of a significantly larger quantity of oil. In addition, it was stated that the X-2000 formed "globules" on the ball screw surface and did not stop significant wear of the lead screw. Therefore, it would seem prudent to carefully observe bearing performance in life tests under EHL conditions when using this lubricant. However, it must be stated that this lubricant has performed very well in other tribological tests [17, 21 and 22] and has had some space heritage.

Effect of ODC-Free Cleaners on Bearing Life

<u>Preliminary Tests in Air</u>

The banning of the production of many ozone depleting chemicals (ODC) which includes CFC 113 by the Montreal Protocol has resulted in many new bearing cleaning techniques including: super critical fluid (SCF) CO_2, various perfluorinated solvents, UV-ozone and many aqueous based systems. Some of these cleaners can decrease bearing lifetimes compared to the conventional CFC 113 (Freon) cleaning [15]. This is shown in Figure 5. These were from accelerated tests run in air with a parched EHL simulator. Both SCF CO_2 and UV-ozone cleaned bearings yielded reduced lifetimes compared to Freon.

<u>Vacuum Tests</u>

Recently, a new rolling contact tribometer, ball-on-plate (BOP) has been developed [16]. This device simulates an angular contact bearing by replacing the curved raceways with flat plates (Figure 6). The device operates in vacuum without a retainer with a single bearing ball sandwiched between the plates. The test is accelerated by only lubricating the ball with microgram quantities of liquid lubricants. In the rolling and pivoting process, the lubricant is transformed into a friction polymer or into low molecular weight products and is eventually consumed, at which time friction increases and the test is automatically terminated.

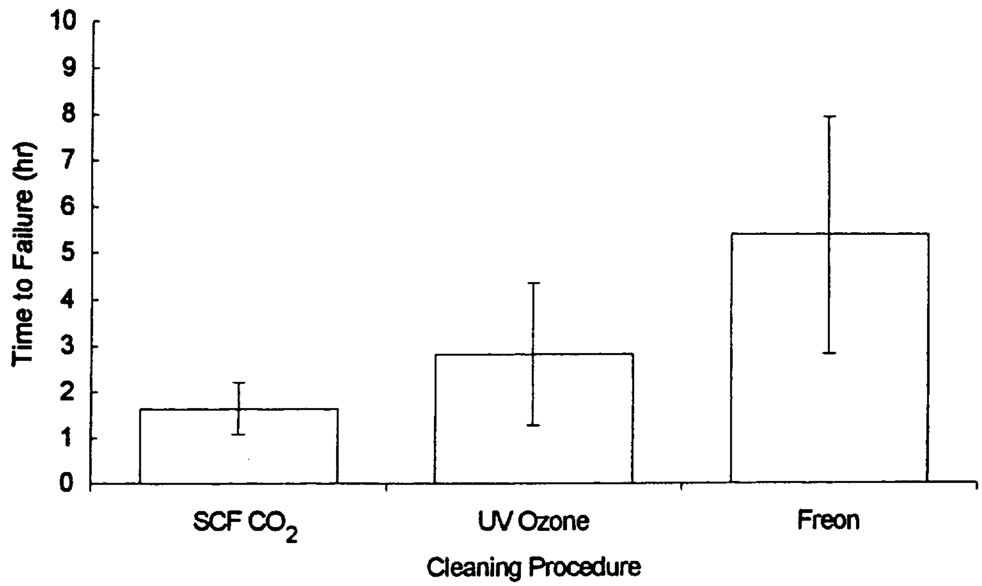


Figure 5. Effect of ODC-free cleaners on bearing lifetimes (Parched EHL apparatus, air, 4500 RPM, 23°C, Krytox 143AC)

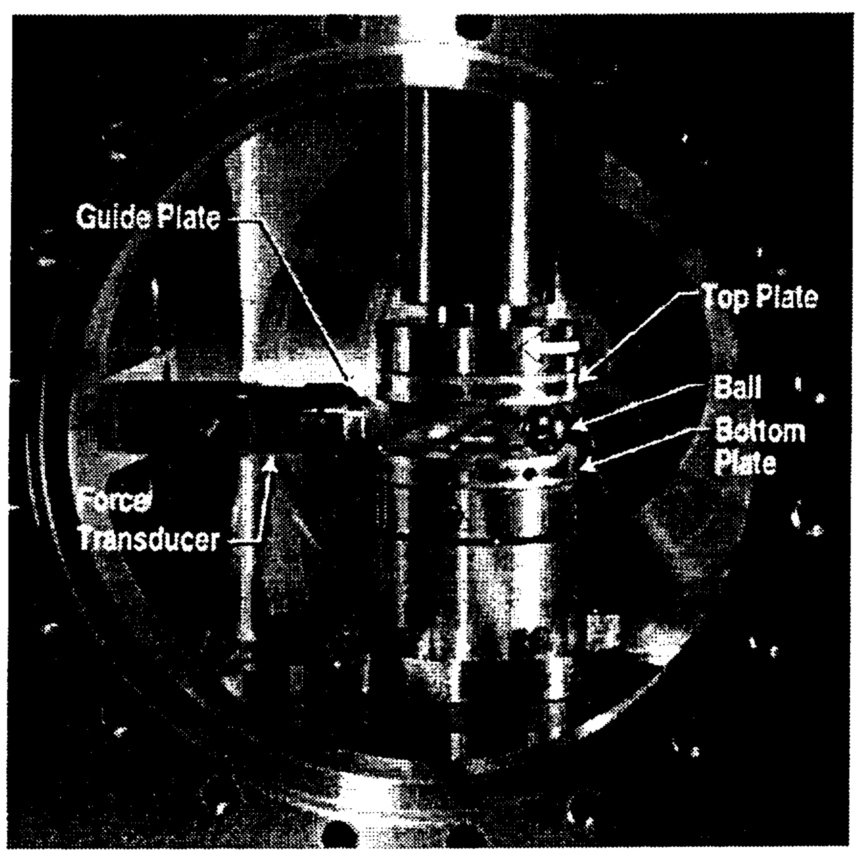


Figure 6. Ball on plate vacuum tribometer

ODC-Free Cleaning Techniques

Four ODC-free bearing cleaning techniques were studied (levigated alumina plus a water rinse, UV-ozone, SCF CO_2 and Brulin 815GD). These were compared to a standard Freon procedure. Lubricant lifetimes of a PFPE (Fomblin Z25), as a function of final specimen cleaning technique, appear in Figure 7. Two of the ODC-free processes, SCF CO_2 and aqueous Brulin 815GD, yielded longer lifetimes compared to the Freon standard. The UV-ozone and alumina results were comparable to Freon.

Comparison with Other Investigations

Preliminary data from accelerated bearing life tests at Lockheed Martin [17] showed that two ODC-free replacement cleaners (Vertrel XF, a perfluorinated solvent, and Brulin 815GD) yielded longer bearing lifetimes compared to Freon. The Brulin results correlate with the NASA results. In contrast, other accelerated bearing tests at Aerospace Corp. [18] have shown that Brulin cleaned bearings yielded lower lifetimes than the Freon standard. However, their Vertrel XF results do correlate with the Lockheed Martin data. The reasons for these discrepancies are not clear.

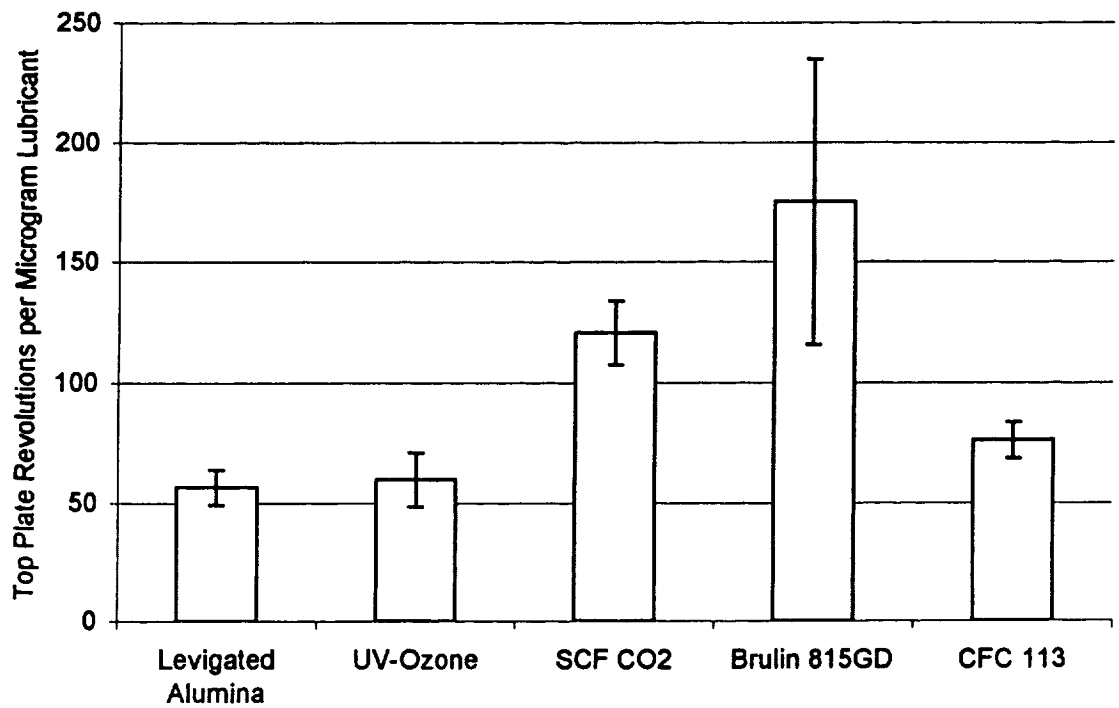
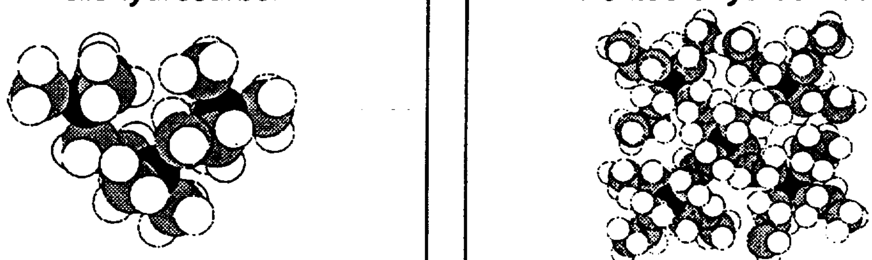


Figure 7. Lubricant lifetime for Fomblin Z25 from rolling contact tribometer for various cleaning techniques

Silahydrocarbons

Most liquid lubricants for space are either mineral oils, polyalphaolefins, PFPEs or synthetic hydrocarbons. Recently, a new class of lubricants containing only silicon, carbon and hydrogen (silahydrocarbons) have been developed at the Air Force Materials Laboratory [19]. These unimolecular materials have exceptionally low volatility and are available in a wide range of viscosities. There are three types based on the number of silicon atoms present in the molecule (i.e., tri, tetra or penta). Examples of a tri and a pentasilahydrocarbon appear in Figure 8.

Trisilahydrocarbon | *Pentasilahydrocarbon*



(a) $R_3Si(CH_2)_x - Si(R_2) - (CH_2)_x - SiR_3$
Where: $R = n\text{-}C_xH_y$

(b) $Si(CH_2CH_2CH_2SiR_3)_4$
Where: $R = n\text{-}C_xH_y$

Figure 8. Structures for two silahydrocarbons (a) trisilahydrocarbon (b) pentasilahydrocarbon

Viscosity Properties

A series of silahydrocarbons have been synthesized and their kinematic viscosities as a function of temperature have been measured (Figure 9). For comparison, a Pennzane plot has been included. As can be seen, the viscosity properties of the silahydrocarbons bracket the Pennzane data.

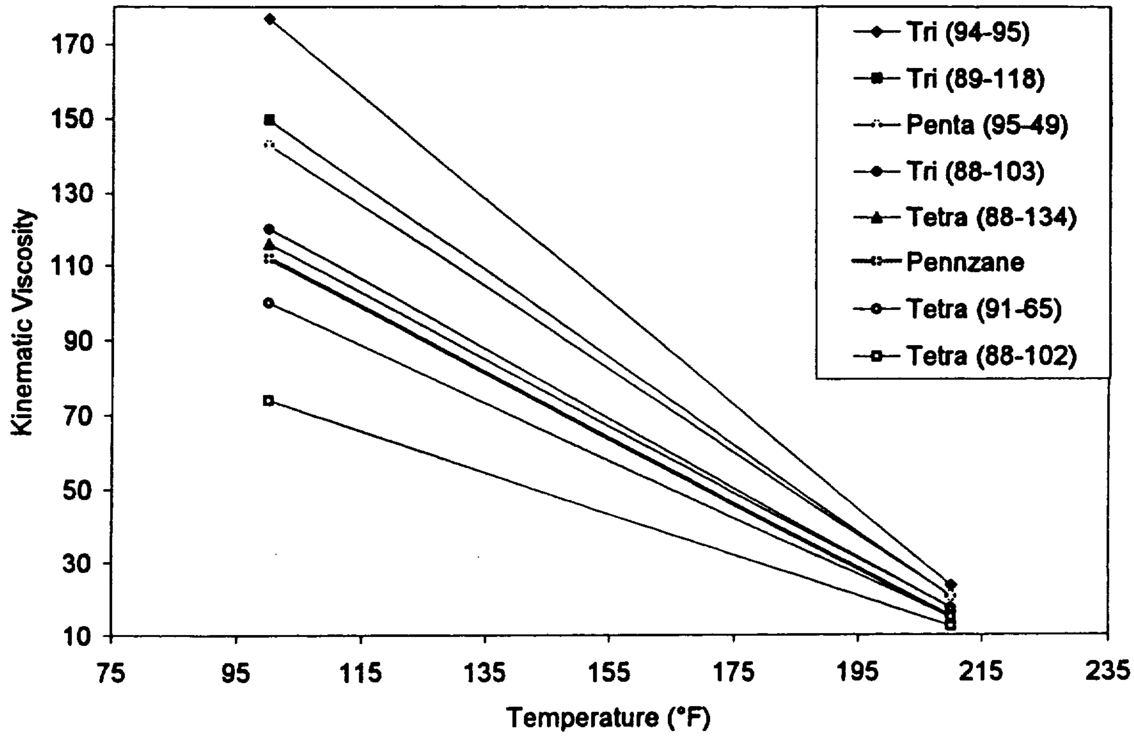


Figure 9. Kinematic viscosity as a function of temperature for a series of silahydrocarbons

EHL Properties

Elastohydrodynamic properties for two members of this class appear in Figure 10. These results were generated using a ball on plate optical EHL simulator [20]. Results were compared to a standard reference fluid of known pressure-viscosity properties. The trisilahydrocarbon has a pressure viscosity coefficient (α) of 16 GPa^{-1} ($\pm$ 0.3) at approximately 21 C, while the pentasilahydrocarbon has a value of 17 GPa^{-1} ($\pm$ 0.3). At 40 C, the trisilahydrocarbon has an α value of 11 GPa^{-1} ($\pm$ 1) and the penta, 13.5 GPa^{-1} ($\pm$ 1). For comparison, the α value for Pennzane at 30 C is 9.8 GPa^{-1} ($\pm$ 0.3), estimated by the same method. Therefore, these silahydrocarbons will generate thicker EHL films than Pennzane under the same conditions.

Tribological Properties

Using the vacuum four-ball tribometer, the friction and wear characteristics of the neat pentasilahydrocarbon were compared to the three commercially available PFPEs and an unformulated Pennzane (Figure 11) [21]. As can be seen, this unformulated silahydrocarbon has wear rates comparable to Pennzane and superior to the PFPEs.

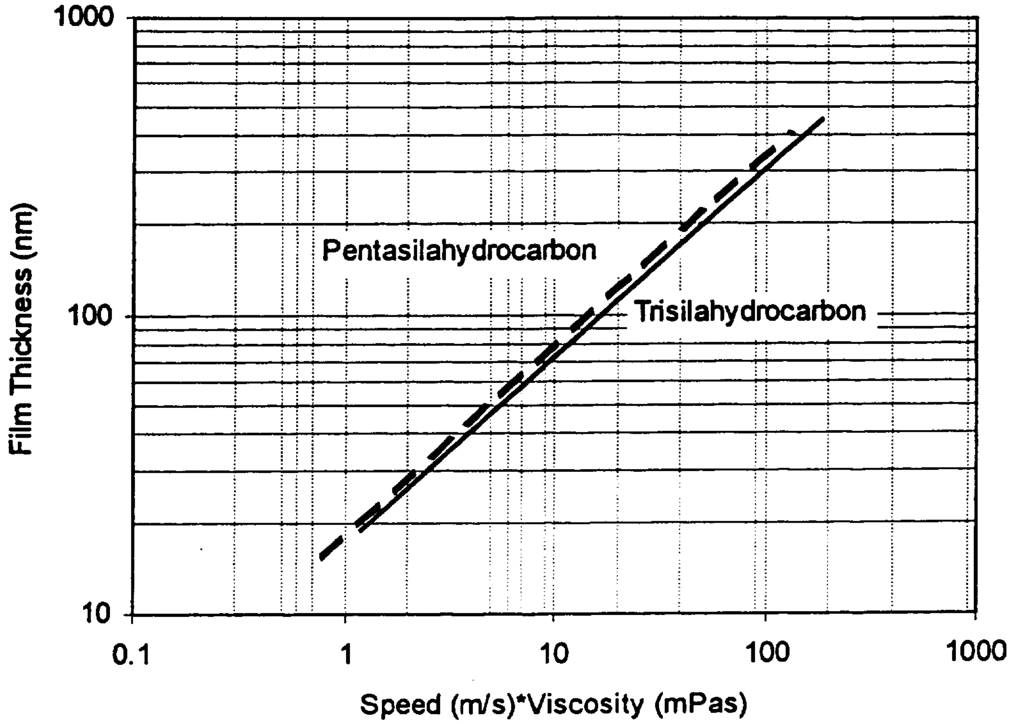


Figure 10. Elastohydrodynamic properties for a tri and a pentasilahydrocarbon

Future Work

Vapor pressure measurements are being performed on members of this lubricant class. In addition, some low volatility antiwear additives are being developed for incorporation into formulations.

Conclusions

A series of new soluble antiwear additives have been developed for use in perfluoropolyether space lubricants. Use of these materials under boundary lubrication conditions will reduce wear and thus extend bearing lifetimes. A dewetting problem with the synthetic hydrocarbon Pennzane has been verified and a possible mechanism proposed. The effect of several ODC-free cleaning processes on lubricant lifetimes has been determined using a vacuum rolling contact tribometer. Two cleaners, Brulin 815GD and super critical fluid CO_2, yielded longer lifetimes compared to a Freon (CFC 113) standard. Two other processes, alumina with a water rinse and UV-ozone, yielded comparable lifetimes compared to Freon. Finally, a new class of synthetic liquid lubricants based on the silahydrocarbons are described and some of their physical and tribological properties are reported.

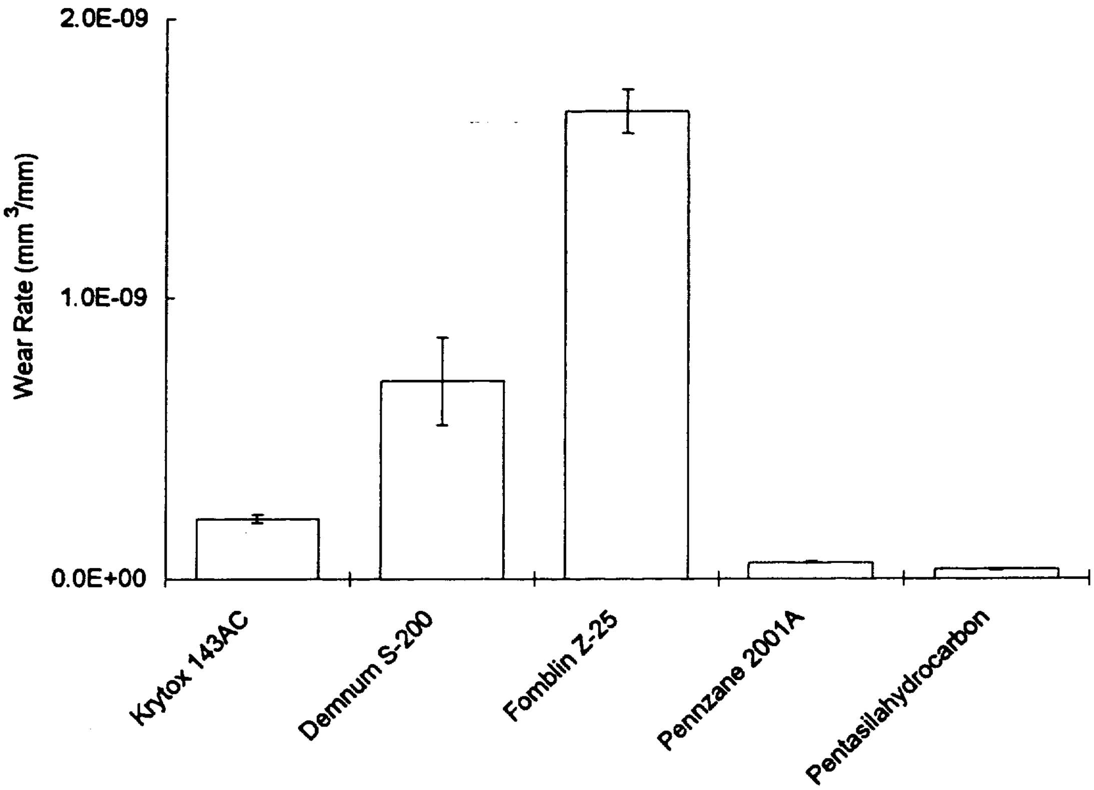


Figure 11. Mean wear rates for a series of space lubricants from vacuum four-ball apparatus

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