Effect of Test Environment on Lifetime of Two Vacuum Lubricants Determined by Spiral Orbit Tribometry

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Abstract

The destruction rates of a perfluoropolyether (PFPE) lubricant, Krytox 143AC™, subjected to rolling contact with 440C steel in a spiral orbit tribometer at room temperature have been evaluated as a function of test environment. The rates in ultrahigh vacuum, 0.213 kPa (1.6 Torr) oxygen and one atmosphere of dry nitrogen were about the same. Water vapor in the test environment – a few ppm in one atmosphere of nitrogen – reduced the destruction rate by up to an order of magnitude. A similar effect of water vapor was found for the destruction rate of Pennzane® 2001A, an unformulated multiply alkylated cyclopentane (MAC) hydrocarbon oil.

Introduction

The destruction of liquid lubricant molecules by tribochemical attack (tribochemistry) is well-recognized, especially for perfluoropolyethers (PFPEs). The destruction or degradation can be manifested by the finite lifetime of a mechanism with a limited supply of lubricant. It is also indicated by the observation of chemical reaction films on the bearing surface, friction polymer and molecular fragments emitted into the environment. Destruction of PFPEs, in particular, has been observed in ball bearings for vacuum service in spacecraft and in eccentric bearing tests that operate in the starved or boundary lubrication regime, depleting the lubricant supply and causing bearing failure [1, 2]. Destruction of PFPEs is also a matter of concern in hard disk magnetic storage media [3]

The destruction rate of the lubricant molecules is a function of both the lubricant's chemical structure [4, 5] and bearing substrate chemistry [6, 7]. It can also depend on the test environment [8-10]. Understanding environmental effects on lubricant's destruction rate is vital to ensure that earth-based life tests of vacuum hardware provide meaningful results. Some tests are performed in 'inert' gas, such as dry nitrogen, because of significant cost and convenience advantages versus vacuum testing. However, the test chamber may still contain trace impurities that compromise the inertness of the test environment, even though the chamber may have been backfilled or purged with an inert gas such as nitrogen. Impurities such as oxygen or water vapor may be tribochemically active and change the lubricant's lifetime compared to what would be exhibited in vacuum.

In this paper, the destruction rates of Krytox 143AC™, a popular PFPE vacuum lubricant, in rolling contact with 440C stainless steel in a spiral orbit tribometer are studied for test environments of ultrahigh vacuum (UHV), dry oxygen, dry nitrogen, nitrogen containing water vapor and pure water vapor. The destruction rate is expressed as the lifetime of a finite charge of lubricant in a test and the results give a ranking of the lifetimes as a function of test environments. Some results are also presented for the effect of water vapor on the destruction rate of Pennzane® 2001A, an unformulated multiply alkylated cyclopentane (MAC) hydrocarbon oil.

Experimental

The test instrument is a spiral orbit tribometer (SOT) depicted in Fig. 1. This rolling contact tribometer is a retainerless thrust bearing with one ball and flat races whose elements and kinematics have been described [11]. The SOT was used to observe the tribochemical destruction of lubricants in vacuum and to give a ranking of the lifetimes, or degradation rate, of two different PFPEs (Krytox 143AC™ and Fomblin Z-25™) and the unformulated Pennzane® 2001A on 52100 steel [4].

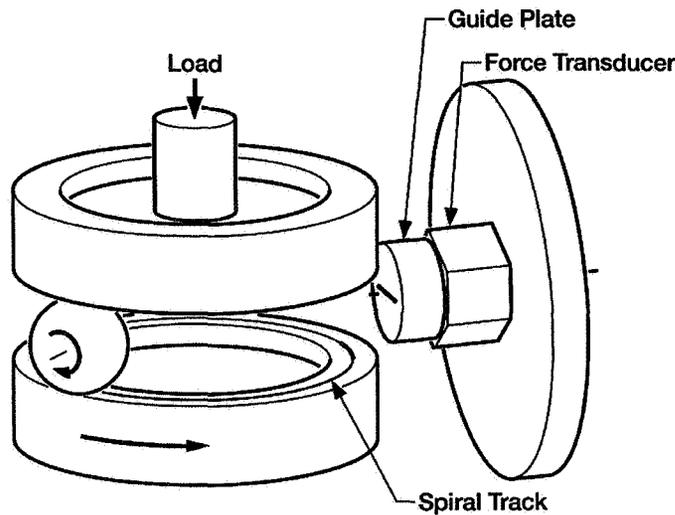* NASA Glenn Research Center, Cleveland, OH

Figure 1. Schematic of the Spiral Orbit Tribometer

The 12.7-mm (.5-in) diameter ball and the plate specimens were 440C steel. All tests were run at room temperature at a mean Hertz pressure of 1.5 GPa and a ball orbit rate of 30 rpm (rolling velocity 0.071 m/s). The stainless steel, metal-gasketed test chamber was evacuated to $<0.133 \times 10^{-8}$ kPa (1×10^{-8} Torr) with a turbomolecular vacuum pump. A gate valve between the test chamber and the turbomolecular pump could be closed to permit the evacuated chamber to be backfilled with a particular gas. The nitrogen and oxygen supply bottles were specified to have a water vapor content of < 2 ppm. The gasses were admitted into the test chamber through an evacuated and baked stainless steel transfer line and a variable leak valve. Pure water vapor was admitted into the test chamber through a variable leak valve from a water supply that had been thoroughly degassed by the freeze-pump-thaw method. Water vapor concentration in the nitrogen atmosphere test environment was determined with a thin film hygrometer (Kahn Cermet II) inserted directly into the test chamber. The hygrometer's readout in dewpoint temperature, T_d, could be converted to either partial pressure of water vapor or concentration of water vapor in ppm through the Magnus formula and then to relative humidity. Test chamber total pressure P was determined by a cold cathode ionization gauge for $P<1.064 \times 10^{-3}$ kPa (8×10^{-3} Torr), a Pirani gauge for 1.06×10^{-3} kPa (8×10^{-3} Torr)$<P<0.266$ kPa (2 Torr) and a diaphragm gauge for $P>0.266$ kPa (2 Torr).

The lowest reading of the hygrometer is $T_d = -99.9°C$ which corresponds to a water concentration of .014 ppm. This reading is achieved in vacuum and initially upon backfilling the chamber to an atmosphere of nitrogen. Eventually, however, water vapor accumulates in the valved-off chamber as shown in Figure 2. The accumulation is detectable after about 2×10^4 orbits (~11 hours) and continues to increase thereafter. This water vapor is due to desorption from the chamber's unbaked interior surfaces. The lowest rate of accumulation is observed after the chamber had been evacuated for many days and then exposed to room air for a minimal time – approximately 10 minutes – during insertion of test specimens.
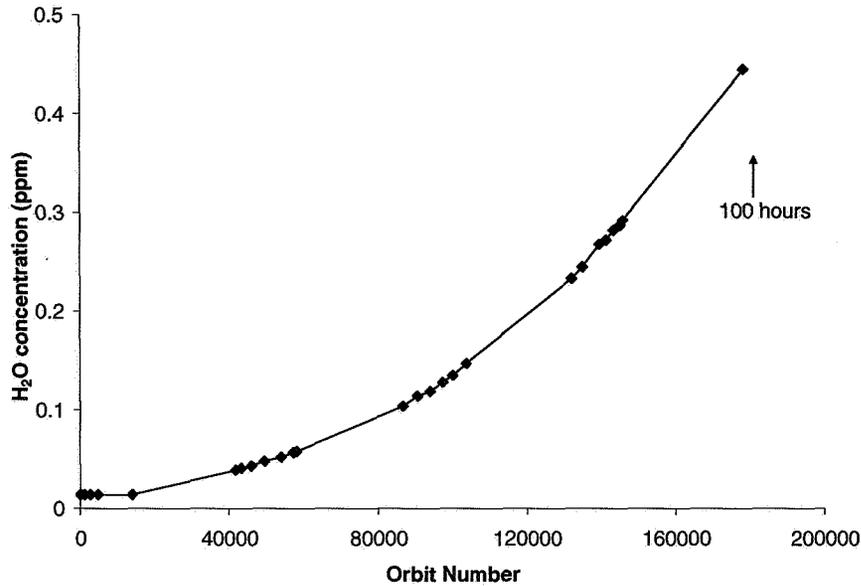
Figure 2. Accumulation of water vapor in an atmosphere of nitrogen

A lubricant charge of ~25 µg for the PFPE and ~20 µg for the MAC was deposited only on the ball from a gas-tight syringe containing a dilute lubricant solution in a volatile solvent. This lubricant amount was consumed in a reasonable time – from a few hours to a few days. The speed and temperature of the test are similar to values that would be seen in spacecraft bearings, with test acceleration achieved through limited lubricant. Friction is recorded as a function of ball orbit and results in a 'friction trace', shown in Figure 3.The trace exhibits constant coefficient of friction (0.134) until an abrupt increase at ~1230 orbits. A friction coefficient exceeding 0.2 is defined as test failure, the point when the lubricant is totally consumed. Normalized lifetime is obtained by dividing the orbits to failure by the initial lubricant charge. In this test, failure occurred at 1287 orbits and the initial lubricant charge was 25 µg, resulting in a normalized lifetime of 52 orbits/µg. Normalized lifetime is inversely proportional to the lubricant destruction rate.
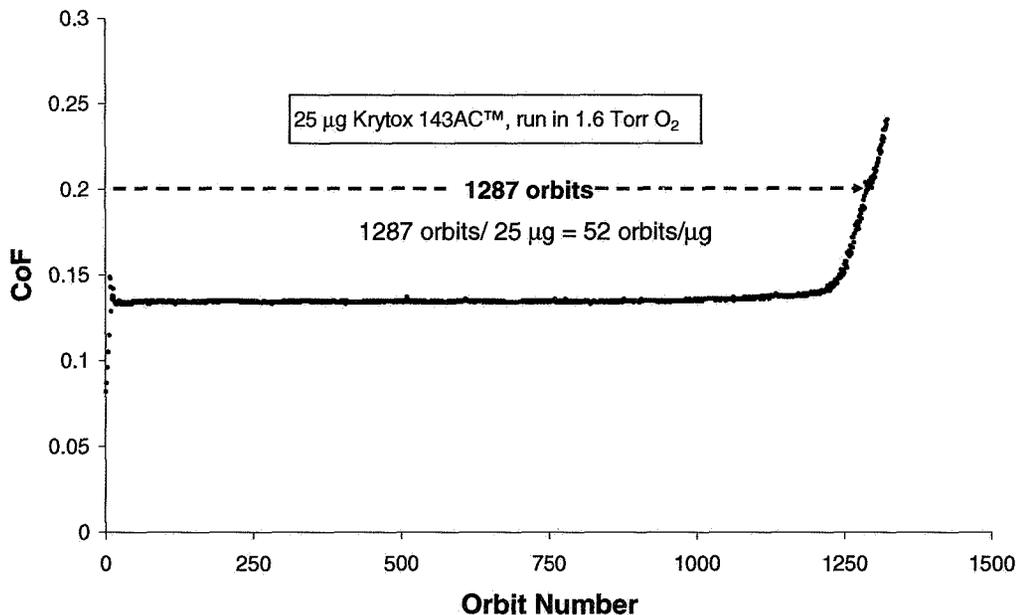

Figure 3. Typical friction trace in SOT tests

Krytox 143AC™

The results of four tests of Krytox 143AC™ run in each of the five specified environments are presented in Figure 4. The shortest lifetimes are exhibited by tests run in ultrahigh vacuum (UHV). The longest lifetimes are observed by running in the presence of water vapor, with increasing lifetime corresponding to increasing water vapor concentration in the test environment. Only 16 ppm water vapor in an atmosphere of nitrogen, corresponding to a relative humidity of <0.07%, is sufficient to extend the lifetime by an order of magnitude relative to testing in vacuum. Pure water vapor itself, without its being present in nitrogen gas, also leads to lifetimes much longer than testing in vacuum. Testing in one atmosphere of "dry" nitrogen, in which the hygrometer indicated no additional water vapor above its lowest reading of $T_d = -99.9°C$ (0.014 ppm), gives lifetimes greater than the tests in vacuum, but only marginally so. Testing in 0.213 kPa (1.6 Torr) dry oxygen, corresponding to ~0.2% trace contamination of oxygen in a nitrogen atmosphere, also has little effect on lifetime relative to that in vacuum. The results presented here thus indicate that water vapor in the test environment exercises a "protective" effect on the PFPE lubricant, permitting a longer life before failure. Finally, the coefficient of friction of 0.134 was independent of the test environment and thus of the lifetime.
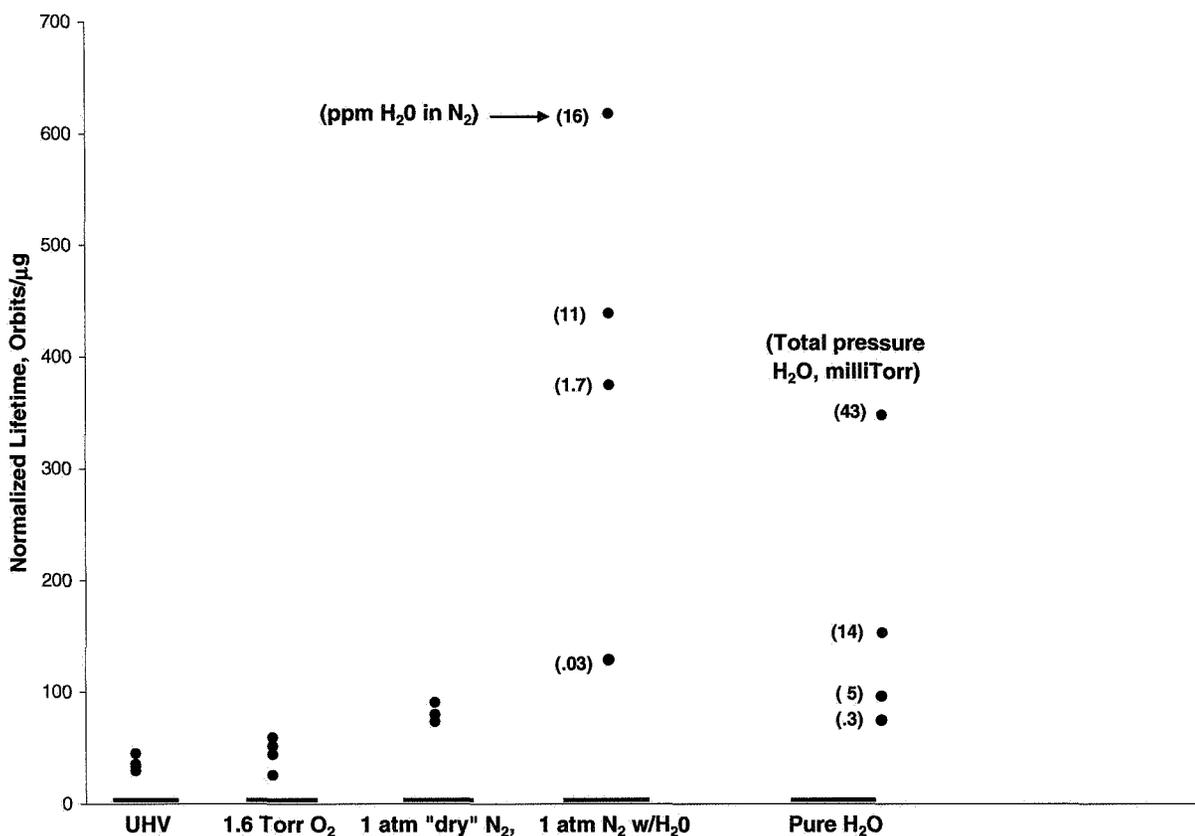

Figure 4. Normalized lifetimes of Krytox 143AC™ when testing in different environments

Pennzane® 2001A

Friction traces for Pennzane® 2001A are plotted in Figure 5 for testing in three environments – ultrahigh vacuum, an atmosphere of nitrogen with a minimum amount of water vapor and an atmosphere of nitrogen with a greater concentration of water vapor. The normalized lifetimes for the tests are indicated above the individual traces. The minimum concentration of water vapor in an atmosphere of nitrogen was achieved simply by closing the gate valve between the chamber and the turbomolecular pump and allowing the water vapor to accumulate in a nitrogen atmosphere as shown in Figure 2. The test at 75

ppm water vapor was achieved by deliberately admitting water vapor to the isolated test chamber from the degassed water vapor source and then backfilling with dry nitrogen. The test in ultrahigh vacuum lasted much longer than that of the test of the PFPE in ultrahigh vacuum as demonstrated in [4]. The tribodegradation rate of the MAC is much lower than that of the PFPE. The lifetime for the test in the minimum concentration of water vapor in the nitrogen atmosphere – whose evolution of concentration is shown in Figure 2 – is greater than the lifetime for the test in ultrahigh vacuum. The lifetime for the test in 75 ppm water vapor is greater still. Thus water vapor in the test environment extends the lifetime of the MAC as it does for the PFPE. As with the PFPE, the initial coefficient of friction of 0.08 is the same for all test environments, regardless of lifetime.
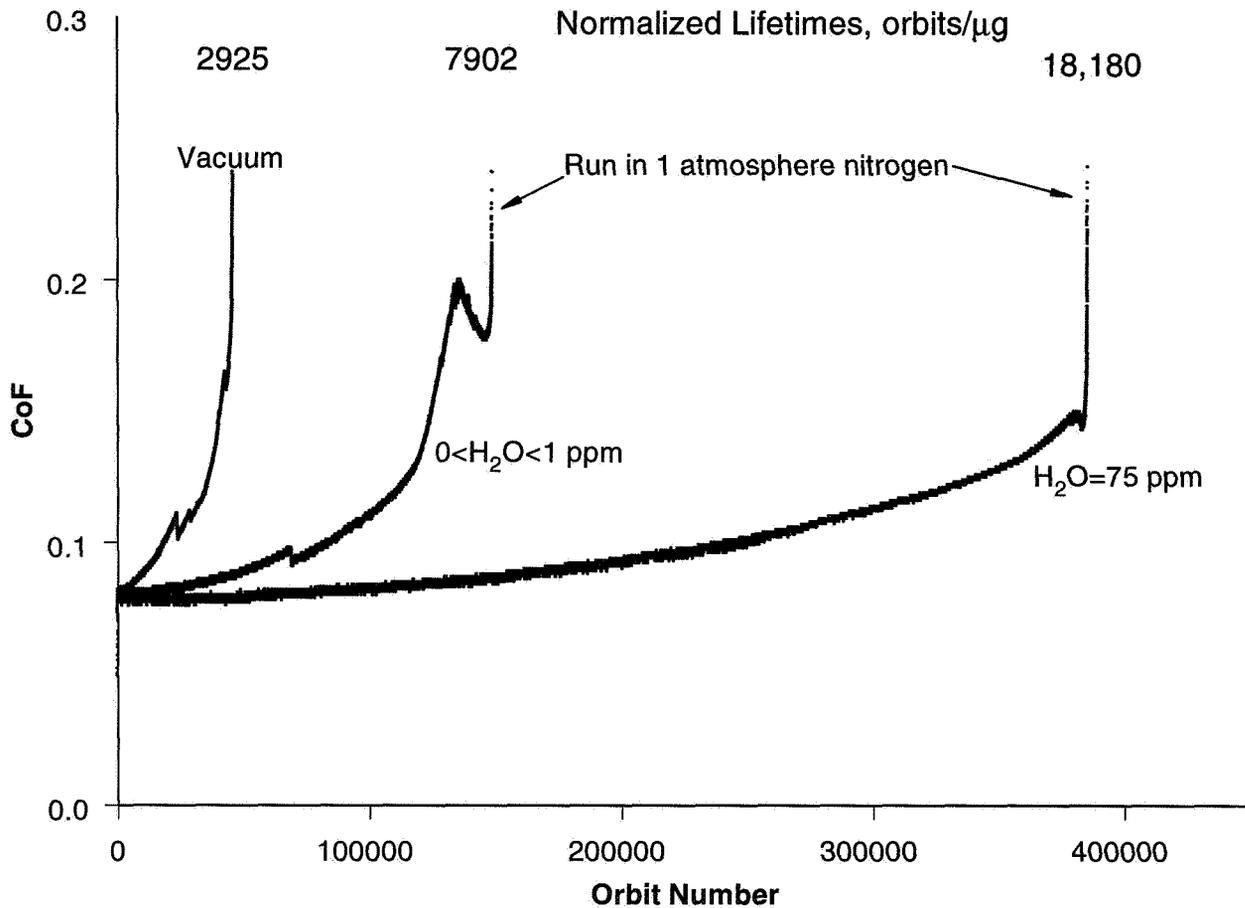

Figure 5. Friction traces of Pennzane® P2001A in different environments

Discussion

Contact Conditions

The low constant friction coefficient exhibited in the tests prior to failure is an indication that the contact is lubricated. However, the state of the lubricant in the contact is not known. Cann and coworkers [12] have studied similar systems under a state of reduced availability of liquid lubricant using optical EHL. Although the lubricant charge used in the SOT is three orders of magnitude smaller than used in their investigations, the SOT system still appears to be in a state of lubrication. Cann, et al, presented an expression for the film thickness in the contact in the fully starved regime. An evaluation of their expression for the present conditions yields a film thickness that is unphysically small (<<1 nm), confirming that the contact regime here is fully starved or parched [13]. The specific concentration of lubricant molecules in the contact is not known, except for the fact that there are enough of them to

lubricate the contact with a friction coefficient close to that exhibited by a fully flooded contact [14]. However, there are probably few enough so that an appreciable fraction of them are in direct contact with the substrate, where they are eventually consumed by tribochemical attack, indicating a failure by elevated friction (Figure 3).

In this study, the friction coefficient is independent of the degradation rate. Evidently, the process responsible for the establishment of the friction force (possibly of rheological origin) and the process responsible for the degradation (tribochemical origin) proceed independently of each other. The tribochemical events may be considered second order effects – events that occur relatively seldom compared with the rheological friction that is continuous in the contact. If the tribochemical rate of attack was higher, then the coefficient of friction might well be different for different test environments that determine different lifetimes.

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The lifetime increase is evident for even very low concentrations of water vapor in the test environment. A concentration of 0.03 ppm in an atmosphere of nitrogen corresponds to a partial pressure of water vapor of 0.02 milliTorr and lower concentrations may be difficult to achieve. Indeed, the somewhat longer lives for the tests in atmospheres of "dry" nitrogen (atmospheres in which the hygrometer maintained its base reading of T_d = -99.9°C) could be due to water vapor concentrations too low to be registered. The extrapolation of the data in Figure 2 to small orbit numbers indicates that there is some lifetime-extending water vapor present even for the relatively short lifetime exhibited by this PFPE. This would indicate that the lifetime tests conducted in this manner are more sensitive to water vapor than the hygrometer itself.

The tests conducted with Krytox 143AC™ in pure water vapor support the assertion that water vapor really is the cause for extended lifetimes in nitrogen atmospheres and not some other tribochemically active molecule that was introduced into the chamber along with the nitrogen. These results also indicate that life testing in "soft" vacuums of about 10^{-5} Torr or less (for which water vapor constitutes a majority of the residual gas) can be as valid as testing in a better vacuum.

The null result of testing in 0.213 kPa (1.6 Torr) oxygen establishes that such trace amounts of oxygen in nitrogen cannot protect the PFPE lubricant against tribochemical attack. This result relates to a current idea that tribological stress exposes clean metal by removing the native oxide, allowing the clean metal to initiate tribochemical attack on the lubricant. However, such clean metal would be oxidized by exposure to 0.213 kPa (1.6 Torr) oxygen thus quenching any tribochemical attack by clean metal. If the oxidation is fast enough to oxidize clean metal in the contact, then these results imply that the "exposure" mechanism is not operative here and that the ball is probably rolling on the native oxide of the steel during the test.

Pennzane 2001A®

The friction traces in Figure 5 indicate that water vapor in the test environment also extends the lifetime of the MAC. It would be desirable to determine if there was any effect on the lifetime by testing in an atmosphere of a truly inert gas or oxygen. However, the MAC's long intrinsic lifetime allows the accumulation of water vapor in the test environment – as presently constructed – that would mask the possible effects of these species. A study of the effects of oxygen or an inert gas must be conducted in the absence of water vapor and remains to be done.

Mechanisms

A consideration of the mechanism by which water vapor retards the tribochemical degradation of the lubricant molecules begins with the observation that the effect is present for both the PFPE and the MAC. The mechanism is not specific to the particular lubricant chemistry and attention is thus directed to the substrate. Substrate sites (probably on the steel's native oxide) are evidently passivated by the water vapor. Water molecules might adsorb on the sites physically, that is without chemical reaction, and simply sterically block the interaction of the site with the lubricant molecule. Although this physical adsorption is well known, appreciable coverage at room temperature occurs at much higher partial pressures of water vapor [15], rendering this physisorption approach unlikely. An approach that considers the passivating chemical reaction of water with the active surface sites may be more fruitful. Lewis acid sites have received much attention in the context of PFPE degradation [16]. This approach may also work out for the sites that can attack both the PFPE and the MAC. The purely tribological results presented here offer limited chemical insight.

Other studies [8, 9] of lubricant life extension under a nitrogen cover gas have emphasized the role of an oxygen impurity component in the cover gas interacting with both an additive in the lubricant and with clean iron exposed by tribological action. The results presented here on oils without additives indicate that neither oxygen nor clean iron is a necessary aspect of life extension under an impure cover gas. Neither is the presence of an additive an essential aspect of the life extension process. Rather, the passivation of active sites on the surface of the bearing steel by water vapor is the governing mechanism that reduces the attack on the lubricant molecule itself.

Application to Testing
The first implication of these results for testing of space mechanisms is that life-testing devices such as bearings in a nitrogen environment to simulate vacuum is permissible with sufficient absence of water vapor. However, the severe restrictions required on the water vapor levels may eliminate any cost savings versus vacuum testing. The second implication is that the device housing may contribute water molecules to the device's environment, since water always desorbs from an unbaked surface. This water flux captured in a housing with limited access to vacuum can provide a degree of protection to the lubricant that is not available in a more open geometry such as in the present test arrangement. In this sense the present test arrangement provides a very severe test.

Conclusions

Both the PFPE and the MAC lubricants are tribochemically degraded in vacuum as evidenced by the finite lifetimes they both exhibit in these tests. Tests in controlled environments indicate the lifetime of both lubricants is extended if water vapor is present in the environment. The effect of water vapor is evident at quite low levels (<1 ppm) in the present tests. These results imply that sites must exist on the bearing steel's surface that can attack the lubricant molecules. These sites are chemically passivated by water vapor, thus reducing the attack rate and allowing a longer lubricant life. An independent understanding and chemical characterization of these sites is not available at present. These results imply that testing of those mechanisms whose life is limited by lubricant consumption in an environment with water vapor, even at very low concentrations in a nitrogen atmosphere, can lead to mechanism lifetimes that are much longer than will be realized in vacuum service. Thus in terms of a "lessons learned", it is advisable to provide water and oxygen sensors for the mechanism test environment.

Acknowledgments

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