PFPE Lubricant Degradation – A New Method for its Assessment through Spiral Orbit Tribometry

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ABSTRACT

Z-type perfluorinated oils and greases are used extensively in spacecraft applications due, in part, to their uniquely low volatility. However, whilst their evaporation 'lives' are long, the period of operation over which they remain effective as lubricants is relatively short. This is because their lives under boundary lubrication conditions are limited as a result of degradation initiated by chemical reaction between components within the oil and bearing steels [1, 2]. Consequently there is great emphasis on understanding this relationship, and determining what factors can affect lubricant lifetime, and to what extent.

This paper presents and discusses the results of tests performed using a Spiral Orbit Tribometer (SOT), demonstrating the susceptibility of the lifetime of these lubricants to a range of variables (including load and temperature). A residual gas analyzer was implemented, demonstrating a technique for detecting the failure of a PFPE lubricant independent of the friction coefficient through in-situ monitoring of selected volatile gases throughout the tests.

In addition, the paper also describes pin-on-disc (POD) research efforts aimed at identifying the so called auto-catalytic effect of lubricant degradation.

Keywords: Spiral Orbit Tribometer, Vacuum Tribology, Fluid Lubricants, PFPEs, Mass Spectrometry

1. BACKGROUND

The subject of tribology, being the study of interacting surfaces in relative motion, is one which is reasonably well understood when operating under benign conditions. However the harsh environment of space produces a unique set of challenges, placing specific demands upon lubricants operating in such conditions. Most significant of these challenges are the vacuum environment, wide temperature ranges, and long life without, in most cases, the possibility of re-lubrication.

One popular tribological solution is the use of Z-type perfluoropolyether (PFPE) oils and greases. Such lubricants are composed of long-chain linear arrangements of perfluorinated monomers and are used extensively in spacecraft applications due primarily to their exceptionally low volatility, and hence long evaporative lives under vacuum conditions. However despite their good 'evaporative lives', PFPE lubricants are highly susceptible to chemical degradation through reaction with bearing steels, which tends to limit their operational lives [1, 2]. Hence there is great interest in understanding the process by which such lubricants chemically degrade, and how this can be influenced by external factors. This problem is particularly pertinent as longer and more demanding missions produce even greater requirements of space engineering.

1.1. PFPE Degradation Behaviour

The mechanism by which PFPE degradation is believed to occur is as follows [3];

- Fluorine is released from the oil as a consequence of the action of repeated shearing under high contact stresses

- The fluorine released reacts with the iron in the steel to form iron fluoride FeF_3

- Although PFPEs in general are regarded as chemically inert they suffer catalytic attack by FeF_3, causing further breakdown of the polymer chains, which results in the release of yet more fluorine.

- The rate of oil degradation increases, resulting in the production of a fluorocarbon polymer (referred to in the literature as 'brown sugar') which possesses poor lubricating properties, resulting in increasing torque, torque noise, and component wear.

The formation of FeF_3 and the degradation of the lubricant has been elucidated by Marchetti [3] and is summarized in figure 1 below;

$$F_3C - O - [CF_2 - CF_2 - O]_x - [CF_2 - O]_y - CF_3$$

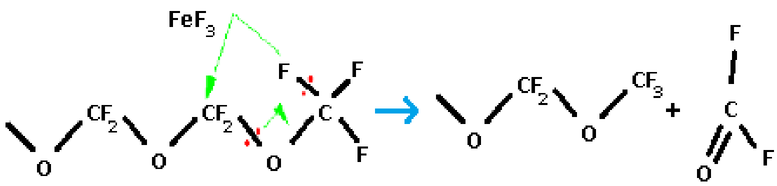
Stage 1. Molecular structure of Fomblin Z25, where y/x = 0.6 – 0.7

$$Fe_2O_3 + (...\text{-}F_2C\text{-}O\text{-}F_2C\text{-}O\text{-}F_2C....) \longrightarrow ...F_2C\text{-}O\text{-}CF_2^{\oplus} + {}^{\ominus}O\text{-}F_2C\text{-}O\text{-}...$$

Stage 2. Polymer chain breaking through reaction with iron oxides

$$Fe_2O_3 + 3COF_2 \longrightarrow 2FeF_3 + 3CO_2$$

Stage 3.Formation of FeF_3



Stage 4. Further rapid degradation of the polymer chains through reaction with FeF_3

Figure 1 Degradation of PFPE lubricants (After Marchetti [3].)

There is a significant desire to understand and characterize this mechanism further, particularly with regard to variables which may change the rate of this reaction, and subsequently affect the operational life of PFPE lubricated components.

2. TEST APPARATUS

2.1. Spiral Orbit Tribometer

The Spiral Orbit Tribometer (SOT) is essentially a thrust bearing, with an individual ball held between two interchangeable flat plates, located within a vacuum chamber (Fig. 2). A load is applied to the top plate via a spring-loaded linear translator. The lower plate rotates via a motor located outside the chamber, causing the ball to move in a spiral path with a radius ~21mm. This configuration causes the ball to spiral outwards, and a fixed guide plate is positioned to keep the ball within the flat plates and to produce a repeatable orbit. A force transducer behind the guide plate measures the force exerted by the ball onto the guide plate. From this a friction coefficient value is calculated, once per orbit.

The arrangement of the SOT allows the ball to experience rolling, sliding and pivoting – these are all the motions experienced by a ball in an angular contact bearing. This allows for a more representative testing of a lubricant than conventional pin-on-disc testing, which only recreates sliding motion. Lifetimes are given in units of orbits/micrograms, allowing for normalization of results should varying lubricant amounts be used.

Heating of the SOT was achieved through the implementation of an IR heating lamp directed through the front window of the SOT, controlled via an active control system. A mid-IR bulb, with wavelengths suited for transmittance through glass, was selected to minimize heating to the external surfaces.

In addition, an AccuQuad Kurt J. Lesker residual gas analyzer (RGA) was attached to the SOT to allow identification of gaseous species within the chamber during tests. The RGA was operated up to 140AMU with a resolution of 0.1AMU. The RGA was operated in analogue scan mode, with a full scan recorded every ~57 seconds. Prior to each test the RGA was degassed, re-calibrated, and tuned to maximize the signal-to-noise of each test.

SOT flat samples were manufactured from non-passivized 440C steel, polished to a roughness of R_a<0.05 micron. Balls were manufactured from 440C steel, of 12.7mm (1/2 inch) diameter, with the exception of tests involving TiC-coated balls for which 5.556mm-diameter (7/32 inch) 440C steel balls were used.

Prior to lubrication, all balls and plates were cleaned using Lenium ES solvent in accordance with standard ESTL procedure.

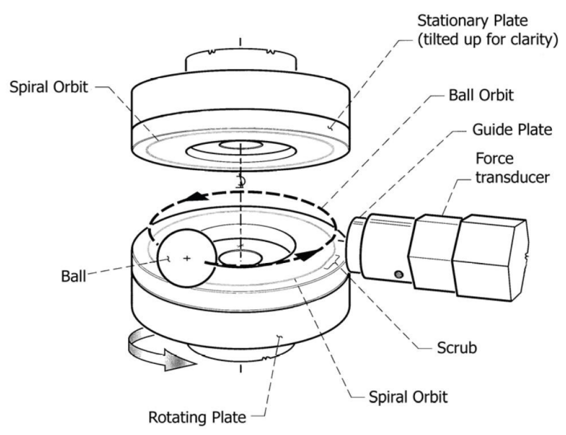


Figure 2. Internal arrangement of the SOT, image modified from [4]

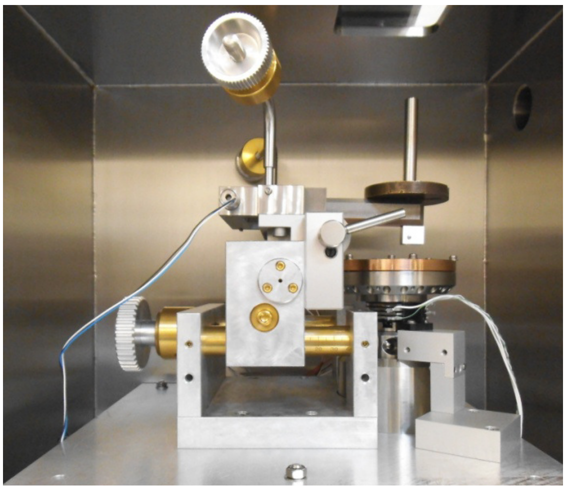


Figure 3. High temperature POD tribometer at ESTL

Lubrication was achieved through the preparation of a solution of lubricant diluted in an appropriate solvent to give a known concentration. This solution was applied directly to a rotating ball. The solvent was allowed to evaporate from the ball's surface, leaving the desired lubricant amount. This method allows for the application of very small lubricant amounts, typically 50µg. This minuscule amount of lubricant allows for reduced test times, and ensures all tests take place under boundary conditions.

2.2. Pin-on-Disc Tribometer

Sliding tests were carried out using a high temperature vacuum pin-on-disc (POD) tribometer. The experimental set up is shown in Fig. 3 above, and consists of a pin mounted on a balanced arm, loaded against the test disc using a dead-weight. The disc is rotated by a motor positioned outside the vacuum chamber. The frictional force is measured according to the sideways deflection of the pin-support arm, monitored using a PC-based data acquisition system. Heat is provided directly to the disc through a heating element, and monitored in-situ.

Test discs were manufactured from 440C steel, polished to a roughness ~0.1µm R_a. Test pins were also manufactured from 440C steel, of 3mm radius (achieving 1.20GPa mean, 1.80GPa peak Hertzian contact stress with 24N loading).

3. FACTORS AFFECTING PFPE LUBRICANT LIFE

Numerous SOT tests were performed under varying conditions to ascertain the influence of various factors on the degradation life of such lubricants. All SOT tests were performed with Fomblin Z25 oil (40-50µg), a popular European PFPE oil for space applications, and took place under high vacuum (<1.3×10^{-6} mbar).

Prior to commencing life-tests a single SOT test was performed under conditions designed to cause minimal tribo-degradation of the oil, such that failure would be due principally to the loss of oil by evaporation. This test, which was carried out at the highest test temperature, 100°C, demonstrated that the evaporative life of the Z25 oil was considerably longer than the 'tribological' life of the oil and therefore did not compromise the measurements of oil life due to tribo-degradation [5].

3.1. Contact Stress

Results clearly demonstrate a dependence upon contact stress for PFPE lubricants (Fig.4), with an exponential decrease of life with increasing load observed, irrespective of temperature and rotation speed. These observations are in-line with those previously demonstrated on similar liquid lubricants on the SOT at room temperature [6, 7]. In addition, friction coefficients were demonstrated to reduce with increasing contact stress.

3.2. Temperature

The results demonstrated a reduction in lubricant lifetime with increasing temperature for all loads and all tested rotation speeds (Fig. 4). The behavior of our evaporation test rules out the potential for loss through evaporation to be the cause of this reduction, strongly suggesting that the environment temperature plays a significant role in the degradation of these PFPE oils.

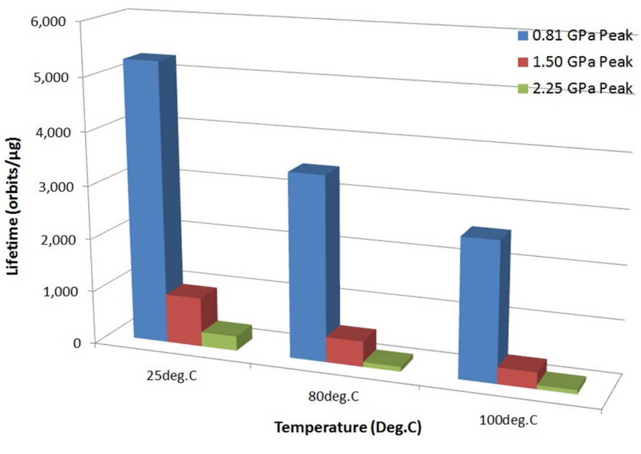


Figure 4. Lifetime results of SOT, showing dependence of life on contact stress and temperature

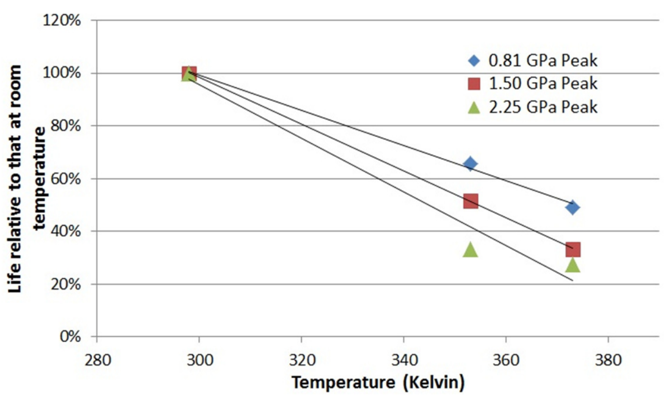


Figure 5. Lifetimes relative to room temperature with added trend lines

However this relationship appears to be linear, which is curious given that, if we assume that the degradation has an associated activation energy, the Arrhenius equation would predict an exponential relationship. This discrepancy may simply be a result of the limited temperature range tested however, and with a greater range of temperature a true exponential relationship may become apparent.

Fig. 5 plots the normalized lifetimes relative to the lifetime at room temperature for each load. From this plot we can see the high sensitivity of the lifetime of Fomblin Z25 to temperature. When loaded to 0.81GPa the lifetime at 373K is reduced to 49% of the room temperature lifetime, whilst at 2.25GPa the lifetime at 373K is reduced to only 27% of the room temperature lifetime. Therefore, it is also shown that the sensitivity of lifetime to temperature increases with increased loading.

Considering friction coefficient a decrease with increasing temperature is evident. This result is fairly well understood, and is related to the viscosity decrease (easier shear) of the oil with increasing temperature. We would expect to see a significant increase in friction should the ambient temperature be reduced to below 0°C [8].

3.3. Rotation Speed

Regarding speed, our test results (Fig. 6) showed no significant difference in the lifetime between 114RPM and 10RPM for Fomblin Z25 oil. This suggests that it is the ambient temperature of the test (i.e. the chamber temperature) rather than the temperature in the contact zones (influenced by speed) which affects lubricant lifetime. Considering friction coefficient we see reduced values for lower rotation speeds. This behavior is expected, and is due to the reduced shear strength of the oil as the rate of shear is reduced.

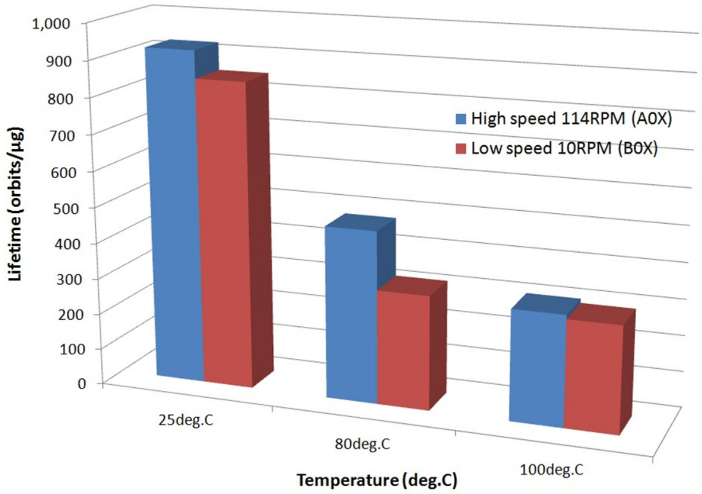


Figure 6. Lifetime comparison of tests performed at 1.50GPa peak, at varying speeds

3.4. Surface Coating

Our current model of PFPE degradation indicates that any form of protection of the oil from the reacting iron in the steel retards the tribo-degradation, and hence extend the workable lifetime of the lubricant. One proposed method of achieving this is to use the ceramic Titanium Carbide (TiC) in the form of a thin coating applied to the 440C steel balls within a PFPE lubricated mechanism. A past study by the European Space Tribology Laboratory (ESTL) has demonstrated that an order of magnitude increase in Z25 oil life is possible using this coating in comparison to raw 440C [9].

A direct "like-for-like" comparison between raw 440C and TiC-coated balls was performed using the SOT. These results demonstrate an increase in lubricant lifetime for the TiC-coated balls, but only a ~30% increase and far less than the magnitude reported in [9] using angular contact bearings.

A proposed explanation for this is that the ratio of the total contacting TiC and 440C surfaces are not the same as they would be in an angular contacting ball bearing when operating in the SOT. As the single ball moves along its orbit in the SOT, the lubricating oil comes into contact with both the TiC of the ball and the raw 440C of the track on the counter-faces. Summing the total contacting areas gives a ratio of approximately 3:1 of TiC against 440C (i.e. the ratio of the surface area of the SOT ball to the surface areas of the ball tracks). However in an angular contact bearing numerous balls will roll on an identical ball track. This will produce a higher ratio of TiC to 440C available for contact.

Taking into account the evidence that TiC retards the degradation of PFPE lubricants, and making the assumption that the oil will continue to degrade when in an unloaded state (i.e. due to auto-catalysis, see below), this higher ratio of TiC to 440C in the bearing will act to extend the lifetime of the PFPE oil in such an application beyond that suggested by the SOT.

3.5. Other Factors

The above list of influences on the lifetime on PFPE lubricants is not anticipated to be exhaustive, and it is likely that many more factors, beyond these discussed here, will affect their degradation. Some influences, such as contact geometry and bearing materials (e.g. ceramic balls) have been somewhat explored, but are outside the scope of this publication and are detailed elsewhere [10, 11]. Others, such as the importance of surface roughness, are scheduled to be investigated presently.

4. RESIDUAL GAS ANALYSIS

Further to the lifetime and friction analysis of the PFPE lubricants under varying conditions, effort has been made to analytically assess the method by which tribo-degradation occurs for these lubricants. Primarily this is achieved through the implementation of an in-situ residual gas analysis system on the SOT.

4.1. Preliminary Studies

A small number of prior investigations into the behavior of Fomblin Z25 using mass spectrometry were performed, including static and POD tests, and are detailed elsewhere [5, 12]. The main findings of this work can be summarized as follows;

- Significant mass loss and break-up of the lubricant polymer chains occur at temperatures between 180°C and 250°C under vacuum (under non-shear conditions)
- During such mass-loss periods in-situ mass spectrometry can identify a number of gas species believed to be related to the degradation of the PFPE lubricant
- POD tests demonstrated that when subjected to contact stress and sliding motion, degradation of the PFPE was observed at temperatures as low as 25°C

The above studies allowed a number of gas species suspected to be 'markers' of PFPE degradation, triggered through shearing alone, to be defined and identified for use in monitoring during a tribo-test. These species are listed in Table 1 along with their atomic mass unit (AMU).

Table 1. Volatile gas species measured in SOT tests

AMU	28	44	47	66	69	119	135
Species	CO	CO_2	COF	COF_2	CF_3	C_2F_5	C_2OF_5

4.2. SOT RGA Results

To aid analysis, specific gas species (as partial pressures) were plotted, along with friction coefficient, against time during SOT testing. An example of output data is shown in Figure 7 and a summary of the progression of this test is presented in Table 2

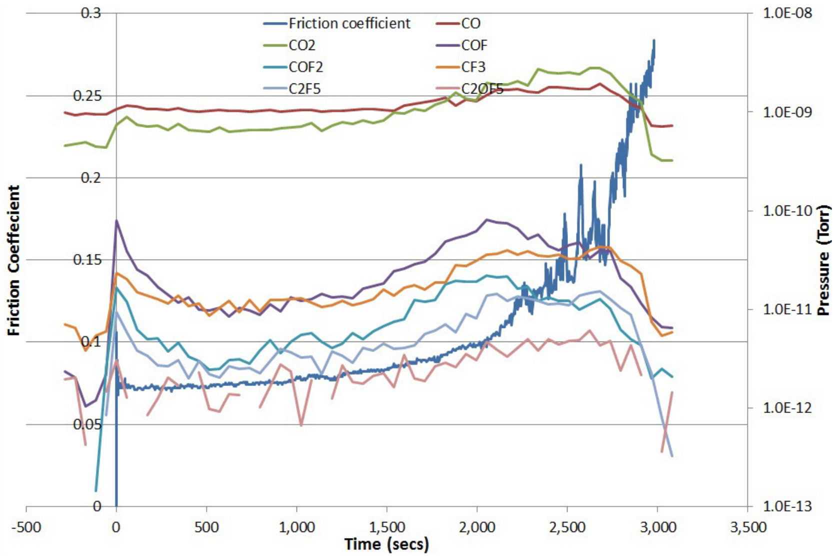


Figure 7. Friction and volatile gas evolution at 80°C, 2.25GPa Peak contact stress (SOT test)

Table 2. Evolution of gas species during SOT test (Fig. 7)

Time (seconds)	**Observation**	**Explanation**
-300 - 0	Low pressure prior to motion	No degradation occurring before rolling
0	Initial peak when rolling begins	Degradation begins upon starting motion.
100 - 1,800	Flat readings during 'steady-state'. Peaks most likely 'noise'	
1,800 - 2,000	Increase of the partial pressure values before significant increase in the friction coefficient	Majority of oil has been degraded, but enough still present to prevent significant increase in friction.
~2,000	Partial pressures peak.	Maximum creation of volatile gas species as remaining oil degrades.
2,000 - 2,900	Pressures reduce while friction coefficient increases	No un-degraded oil remaining. Volatile gas species being cleaned by the constant pumping of the chamber
2,900 - 3,200	A return to the steady, low values once motion is stopped.	No further oil degradation once motion has stopped

This progression demonstrates that the degradation state of the lubricant can be determined from the volatile gas partial pressures alone, and that the Z25 oil is fully degraded and no longer providing lubrication significantly prior to the friction coefficient increasing to our trip limit (0.28 in this case).

In addition, the work also demonstrates that through the monitoring of certain gas species released as the oil degrades, failure of the test can be predicted **before a significant increase in friction occurs**. Should this prediction method be used to assess lubricant failure in a mechanism, we would not expect significant wear to have taken place at the time the mechanism test is halted.

5. THE AUTOCATALYTIC EFFECT

It has previously been observed that when exposed to extended periods of dwell under vacuum, following a period of running, some mechanisms utilizing PFPE-based lubricants have displayed significantly higher torque on re-start [12]. One possible explanation for this is that once degradation of PFPE oil has begun, this reaction continues even when rotation is halted – the so called auto-catalytic effect (ACE).

5.1. Background

As discussed above, the degradation of PFPE oils is believed to be catalyzed by FeF_3 reacting with the fluorine released from the oil. This has been confirmed through a series of static sublimation tests performed at ESTEC, detailed in [12]. The findings of this work are summarized as follows;

- Introduction of raw FeF_3 powder to a quantity of heated Fomblin Z25 oil produces thermal (chemical) degradation at a lower temperature than pure Z25 oil alone under a N_2 environment

- A Z25/FeF_3 mixture heated to 230°C under N_2 showed evidence of spontaneous and sudden degradation after 80mins of dwell (Figure 8)

These results suggest that auto-catalysis is able to occur if FeF_3 is artificially introduced to the system. It was then interesting to establish if such an effect could be produced without artificial introduction, i.e. FeF_3 production through shearing.

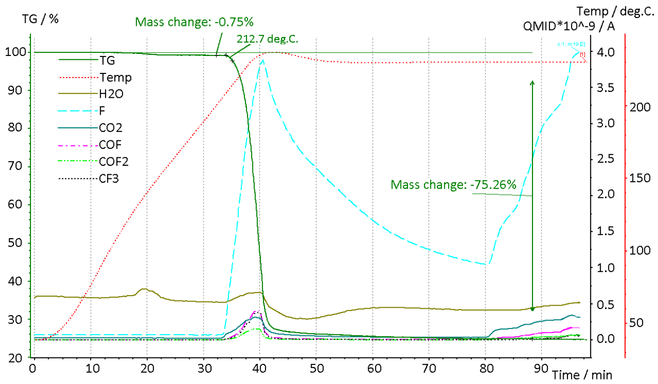


Figure 8. PFPE/Z25 mixture heated to 230°C in N_2. A spontaneous increase in gas species believed to be related to oil degradation occurs at 80mins

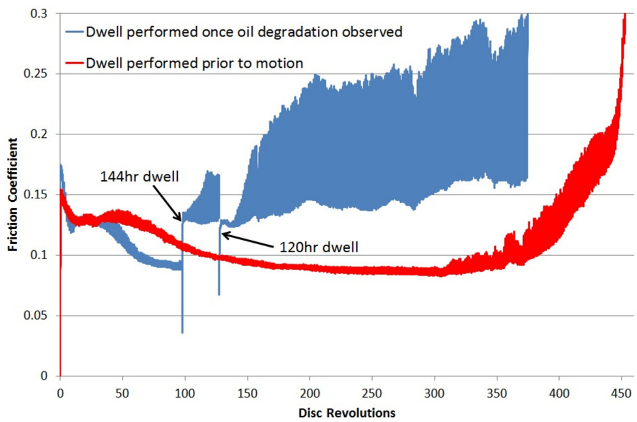


Figure 9. Dwell test on POD showing increase in friction following dwell period, once degradation of oil is initiated through shearing alone

5.2. Auto-catalysis on the POD

A series of POD tribometer tests were carried out to investigate the ACE. Tests were performed using ~400µg of Z25 oil which was applied to a 440C disc using a similar technique to that used for the SOT tests described above, and run at low speed (0.01ms^{-1}), 1.80GPa peak contact stress, at 100°C under vacuum. An RGA was used to monitor the degradation of the oil during the test. Once evidence of degradation was observed with the RGA, sliding motion was halted and the test subjected to an extended dwell of 144hrs under vacuum at temperature. Upon restart the friction coefficient was noticeably higher than prior to the dwell. The friction did not display signs of recovery with subsequent shorter dwells (Figure 9) and rapidly increased to failure.

In contrast, a second test was performed under identical conditions, but with the oil exposed to a 144hr dwell at 100°C prior to any shearing of the oil taking place. During this test no increase in friction coefficient was observed immediately following the dwell, and the oil did not display evidence of rapid failure.

These tests appear to demonstrate evidence of continued degradation of the oil during a dwell period, but only after degradation has been initiated by repeated shearing of the lubrication – the theory of auto-catalysis.

A third test was performed, in which the shearing and post-dwell exposure temperatures were reduced to 25°C under vacuum. This test did not display any evidence of auto-catalysis, implying that the reaction is temperature-dependent.

6. CONCLUSIONS

The main conclusions of the work are presented here are;

- The tribological behavior of the PFPE Fomblin Z25 oil is affected as tabulated below.

Table 3. Summary of factors affecting the tribological performance of Fomblin Z25

	Increase contact stress	**Increase temperature**	**Increase speed**	**TiC coating**
Degradation lifetime	Decrease	Decrease	No change	Increase
Friction coefficient	Slight increase	Decrease	Increase	No change

- Evidence of auto-catalysis has been observed in POD tests in which FeF_3 is produced through shearing of the oil alone.

In addition this work has demonstrated that through the monitoring of certain gas species released as the oil degrades, failure of the test can be predicted **before significant increases in friction occur**. Should this prediction method be used to assess lubricant failure in a mechanism, we would not expect significant wear of the contacts (e.g. ball and race) to have taken place at the time the mechanism test is halted. This potentially provides many advantages.

REFERENCES

[1] Baxter, B. H. & Hall, B. P., 'The Use of Perfluoroether Lubricants in Unprotected Space Environments', Proc. 19th Aerospace Mechanisms Symposium 2371, pp. 179-207 (1985)

[2] Carre, D. J., 'Perfluoropolyalkylether Oil Degradation: Inference of FeF_3 Formation on Steel Surfaces under Boundary Conditions', SLE Transactions, 29(2), pp. 121-125 (1986)

[3] Marchetti, M., Thesis: 'Aspects Globaux et Locaux de la Mise en Oeuvre del la Lubrification Fluide en Ambiance Spatiale', Institut National des Sciences Appliquées de Lyon (2000)

[4] Marchetti, M., Jones Jr., W. R. & Sicre, J., 'Relative lifetimes of MAPLUB Greases for Space Applications', NASA/TM-2002-211875, Glenn Research Center: National Aeronautics and Space Administration (2002)

[5] Buttery, M., Gaillard, L., Rajala, S., Roberts, E. W., Rohr, T. & Merstallinger, A., 'Fomblin Z25: A New Method for its Degradation Assessment & Proposal for Safe Operation in Space', Proc. 15th European Space Mechanisms and Tribology Symposium, SP-718 (2013)

[6] Jansen, M. J., Jones Jr., W. R., Predmore, R. E. & Loewenthal, S. H., 'Relative Lifetimes of Several Space Liquid Lubricants Using a Vacuum Spiral Orbit Tribometer (SOT)', NASA/TM-2001-210966, Glenn Research Center: National Aeronautics and Space Administration (2001)

[7] Buttery, M., 'An Evaluation of Liquid, Solid, and Grease Lubrication for Space Mechanisms Using a Spiral Orbit Tribometer', Proc. 40th Aerospace Mechanisms Symposium, NASA/CP-2010-216272, pp. 59-70 (2010)

[8] Cunningham, J. M. & Rimmer, A., 'Evaluation of the In-Vacuo Torque Performance of a Range of Space Compatible Oils in Bearing Tests, and a Function of Temperature, Speed and Oil Quantity', ESA-TM-227, ESR Technology (1998)

[9] Gill, S. & Price, W. B., 'In-Vacuum Performance of Fomblin Z25-Lubricated, 52100 Steel bearings with TiC-Coated Balls (Final Report), ESTL-TM-107, ESR Technology (1991)

[10] Buttery, M., 'Hybrid Ceramic Bearings Characterisation', ESA-ESTL-TM-0099 01-, ESR Technology (2012)

[11] Buttery, M., 'Further Spiral Orbit Tribometer Assessments of Space Greases', ESA-ESTL-TM-0089 02-, ESR Technology (2012)

[12] Gaillard, L., Mariot, A., Fotea, C., & Holzbauer, R., 'FeF_3 Catalytic Influence on PFPE Lubricant's Lifetime Under Loaded Conditions', Proc. 41st Aerospace Mechanisms Symposium, NASA/CP-2012-217653, pp. 147-154 (2012)