FeF_3 Catalytic Influence on PFPE Lubricant's Lifetime under Loaded Conditions

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Abstract

A Perfluoropolyalkylether (PFPE) oil was heated in an inert atmosphere under dynamic temperature control. The temperature profile allowed precise determination of the degradation onset temperature. The degradation temperature appears to be lower than literature values under the conditions used for this investigation. Other samples of PFPE oil were later tested with a Pin on Disk Tribometer under different temperature and loading conditions.

Introduction

While PFPE lubricants are widely used in mechanisms designed for aerospace industry because of their numerous advantages, it is known that they degrade quickly and heavily under boundary lubrication conditions, especially when in contact with 440C or 52100 stainless steels.

Numerous authors (1) (2) (3) (4) (5) (6) in the past decades suggested that degradation of PFPE oils under boundary lubrication conditions was catalyzed by the Lewis acid FeF_3 (Iron fluoride III). Some authors (3) even proposed the degradation mechanism was autocatalytic, which means it could continue for a while after the mechanical stress ceases.

In 1991, David J. Carré (2) proved indeed that PFPE does degrade in the presence of FeF_3 by reacting a branched PFPE and FeF_3 in a nickel-lined autoclave under inert atmosphere at high temperatures. The reaction is triggered in this instance at a temperature approximately 30°C below thermal degradation; however, high mechanical stress could have contributed to the high temperature excursions (7).

The recent experiment, on the other hand, has dealt specifically with the degradation temperatures and more importantly to precisely assess the triggering temperature for PFPE degradation. This is the first experiment that combined the precise temperature control for the heating ramp by using a state of the art Netzsch Simultaneous Thermal Analyser (STA) while monitoring the discrete changes that occur within the PFPE/FeF_3 mixture using Fourier Transform Infra-Red (FTIR) and a mass spectrometer. Furthermore, the experiment would provide further insight into the autocatalytic mechanisms as suggested by (3).

Experiment

The Netzsch STA consists of a dynamic temperature controlled furnace coupled with a Fourier Transform Infrared Spectroscopy and Mass Spectrometry (Figure 1 and Figure 2). The instrument is vacuum tight by design, the furnace is evacuated first at pressures of ca. 10^{-2} mbar and is continuously purged with N_2 gas therefore the pressure inside the furnace is atmospheric during continuous operation.

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Figure 1. Furnace (left) and mass spectrometer (right).

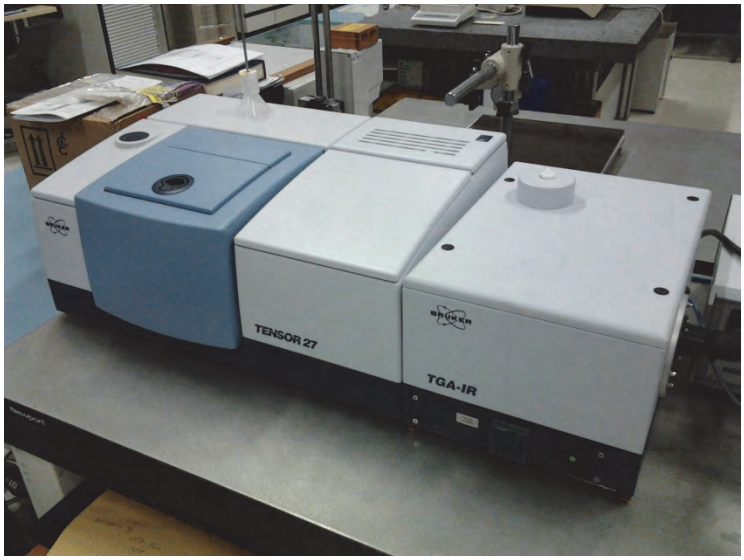

Figure 2. FTIR facility.

The fact that we were working at a more or less ambient pressure should not be an issue since even in high vacuum both FeF_3 and PFPE oil are expected to be present as a condensed form. In this case, the pressure dependence of the Arrhenius equation is low.

Approximately 5 mg of FeF_3 powder were mixed with ca. 100 mg of Fomblin Z25 PFPE lubricant in an aluminum crucible. Fomblin Z25 is a base oil used in various Maplub and Braycote greases. These quantities of FeF_3 were intentionally high to ensure that iron fluoride would be in excess. It was feared that the reaction rate with “realistic” amounts of FeF3 (which is supposed to form as a near-monomolecular layer on real-life mechanisms (3)) would be too slow to be measured during a reasonable timespan. A “witness” cup containing only Z25 oil was also prepared.

The temperature profiles used for this exercise are shown in (Figure 3).

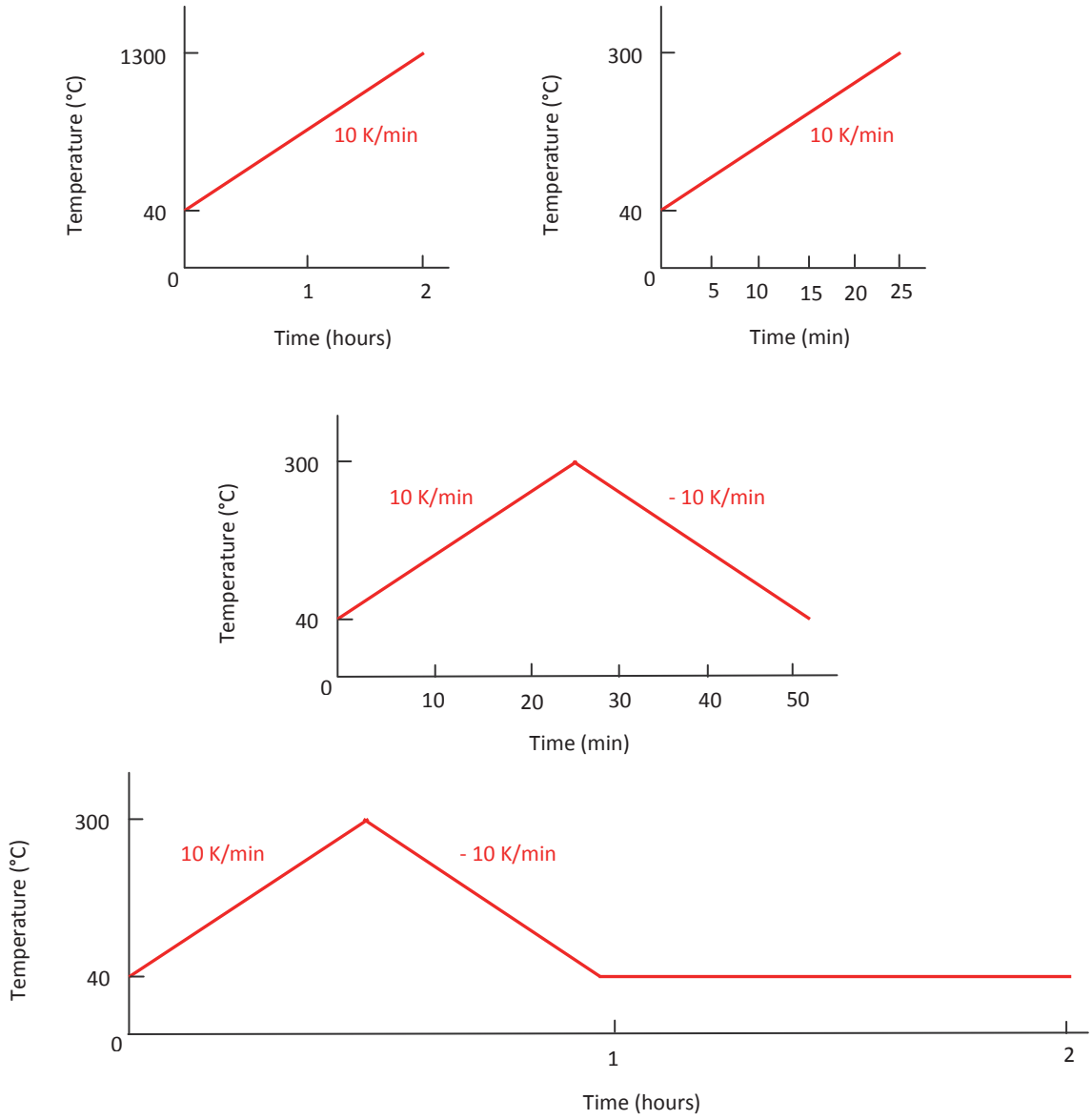

Figure 3. Temperature profiles.

At the time of writing this paper, the following tests were completed:

1. Neat Fomblin Z25 was heated to 1300°C using a 10 K/min ramp to assess the degradation temperature of the lubricant.
2. A mixture of Fomblin Z25 and FeF_3 was heated to 300° using a 10 K/min ramp.
3. A mixture of Fomblin Z25 and FeF_3 was heated to 300°C using a 10 K/min ramp and cooled down to 40°C using a -10 K/min ramp.
4. A mixture of Fomblin Z25 and FeF_3 was heated to 300°C using a 10 K/min ramp and cooled down to 40°C using a -10 K/min ramp, then maintained at 40°C for one hour.

The FeF_3 has never been clearly identified in an actual mechanism or test apparatus, even if its presence is very likely. Consequently, additional tests on a tribometer were run. The aim was to observe the gaseous compounds coming out of the degradation reaction. Although it would not be a definitive proof, finding the same degradation products and behavior as in the STA facility would greatly increase the

likeliness of the hypothesis. A Pin-on-Disc (PoD) tribometer was used in a high-vacuum chamber under temperature control, along with mass spectrometer analysis.

Results and discussion

The heating of neat lubricant to 1300°C determined the thermal degradation onset temperature of the Fomblin Z25 oil. Very precise onset points for the lubricant mass loss and the FTIR Gram-Schmidt reconstruction readings were observed. Figure 4 presents the temperature profile (red curve), the total mass loss of the oil (green curve), the differential scanning calorimetry (DSC) reading (blue curve), and the FTIR Gram-Schmidt reconstruction (black curve). The thermal degradation occurs at ca. 400°C.

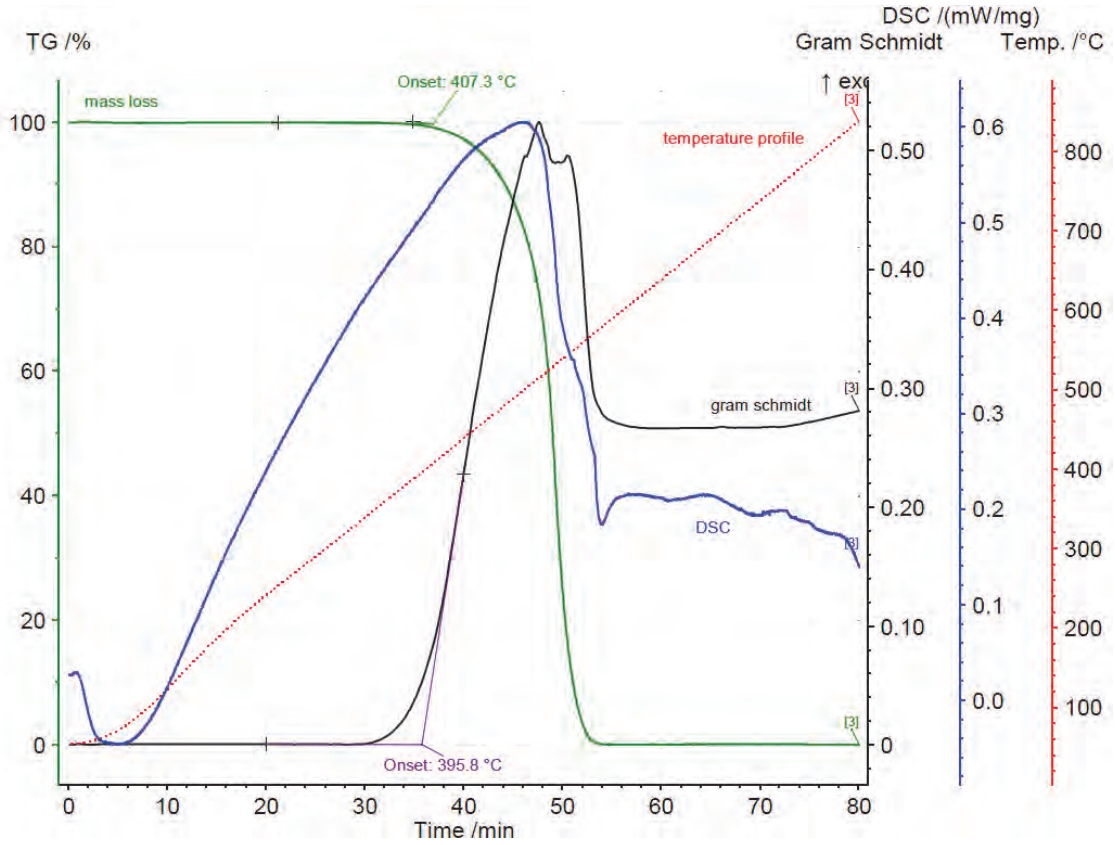

Figure 4. PFPE run to 1300°C.

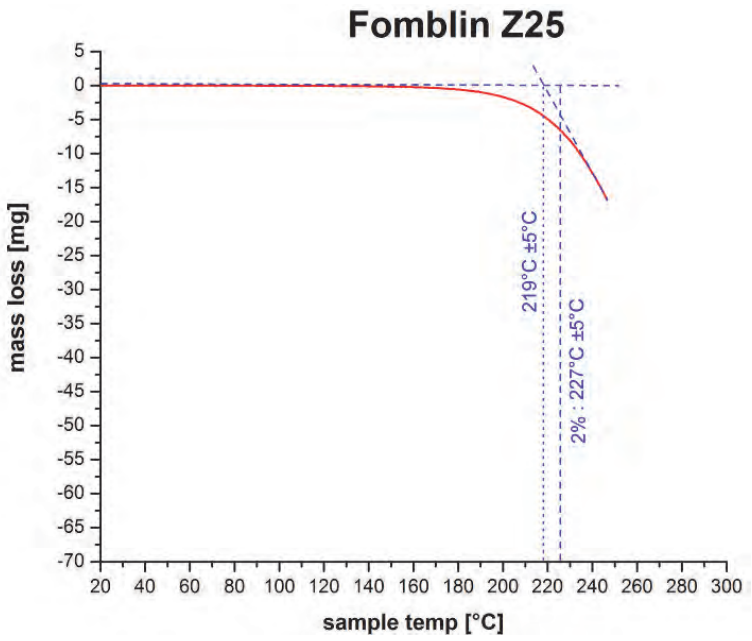

Figure 5. Z25 sublimation test under high vacuum.

Observation: the experiment was run at an ambient pressure, which means that under vacuum, sublimation will occur before the oil reaches 400°C. This was shown by a sublimation test run by AAC GmbH (Figure 5). Given those results, it was not necessary to go above the thermal degradation temperature, which led us to choose a 300°C maximum limit.

The second (PFPE and FeF_3 mixture heated to 300°C using a 10 K/min ramp) and third test (mixture of Fomblin Z25 and FeF_3 heated to 300°C using a 10 K/min ramp and cooled down to 40°C using a -10 K/min ramp) showed that some degradation was occurring at a much lower temperature. Figure 6 shows an onset point for the mass loss (green curve), FTIR Gram-Schmidt reconstruction (black curve) and mass spectrometer readings (dotted curves). Thus, the degradation appears to be triggered at ca. 220°C. Figure 6 presents the different gaseous products detected by the mass spectrometer as follows: the main peaks were observed at atomic mass units (amu) 19, 44, 47, 66 and 69. The 19 amu trace can be attributed either to electron-stimulated desorption (along with 1 and 16 peaks, not shown) (8) or to fluorine radicals coming out. The other traces are 44 amu: CO_2, 66 amu: COF_2 and its ionization product 47 amu: COF, all of them being predicted by the theory of FeF_3/PFPE reaction (3).

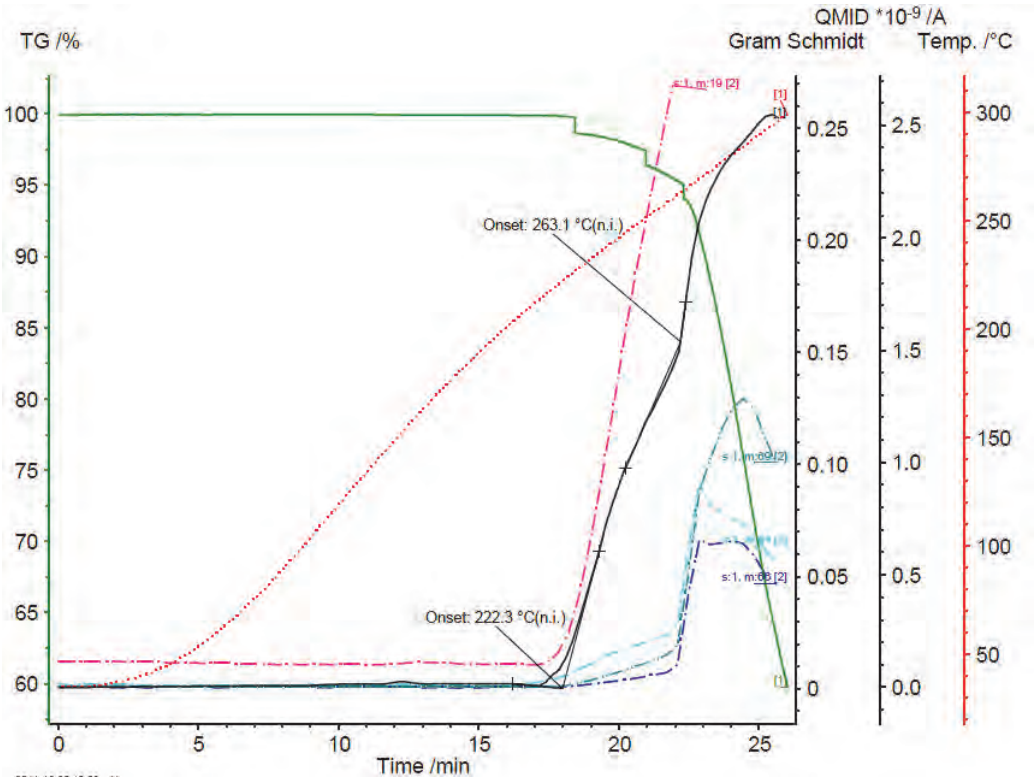

Figure 6. Second run with associated mass spectrometry data.

The final experiment used a mixture of Fomblin Z25 and FeF_3 heated to 300°C using a 10 K/min ramp and cooled down to 40°C using a -10 K/min ramp, then maintained at 40°C for one hour. We could not see any measurable decrease once the temperature dropped below 260°C, which makes us think that no catalytic reaction takes place at ambient temperature, or that its rate does not allow one to see it with the experiment/equipment used and the time spent.

The experiment has been made somewhat more difficult because of the absence of vacuum: gaseous compounds were noted to “contaminate” the test chamber, leading to sometimes false spectrometer readings. Moreover, some chemical species seem to be able to “stick” to the chamber from one test to another. This behavior has already been experienced within other test facilities such as the spiral orbit tribometer, even under a high vacuum.

Given the complex spectra of the studied compounds, it was difficult to identify each species. Care should be taken during mass spectrometer analysis to know in advance what are the expected compounds and to have a reference spectrum for each of them, especially when their spectra are overlapping (which was the case here).

The goal of the Pin-on-Disc experiments was to evaluate the influence of loading and temperature on the degradation mechanism. A total of 8 different experiments were conducted as shown in Table 1, using both temperature and mean Hertzian pressure as parameters.

Figure presents the results of one particular test run at a 1200 MPa mean Hertzian pressure and at a 120 °C temperature. Notably, traces at 28 amu: CO and 47 amu: COF (not shown) were noted accordingly to the degradation mechanism theory (3). Interestingly, there was a continuous increase of these traces during the rotation of the tribometer.

However, it has not been possible to compare the mass intensity of these traces between each experiment. Because of the presence of moisture inside the test chamber, the mass spectrum associated with water was exceeding the range of the mass spectrometer, thus rendering other readings inaccurate. Future tests should therefore carefully use amplification settings that do not make water traces exceed the range of the instrument.

Table 1. List of conducted PoD experiments.

Test 1 560 MPa, 20 °C	Test 2 560 MPa, 80 °C	Test 3 560 MPa, 120 °C
Test 4 850 MPa, 20 °C		Test 5 850 MPa, 120 °C
Test 6 1200 MPa, 20 °C		Test 7 1200 MPa, 120 °C
Test 8 1900 MPa, 20 °C		

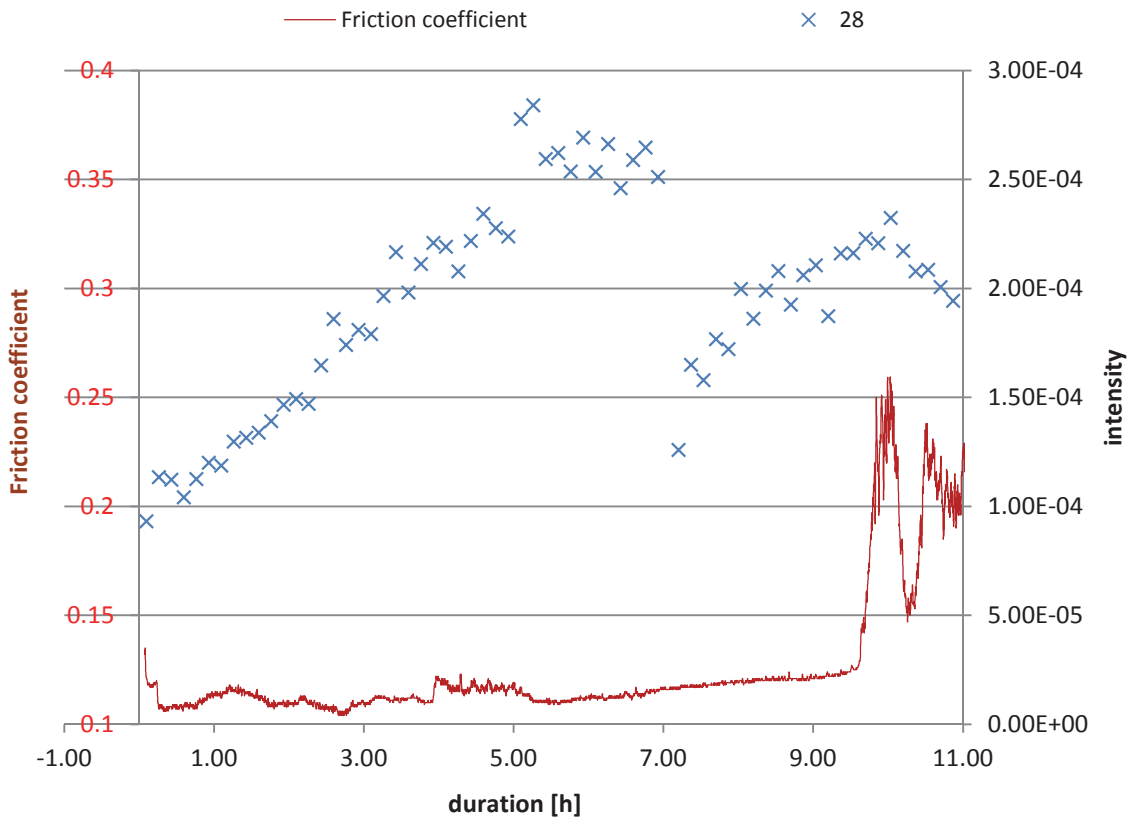

Figure 7. Example of MS readings from a Pin-on-Disc test (red curve: 28 amu, blue curve: 47 amu).

Conclusions

The current results have not allowed a precise reaction rate to be calculated at a given temperature, which would give a good estimation of this degradation mechanism's activation energy and therefore allowed us to propose a safe range for operating this grease in space mechanisms. This knowledge would also have allowed us to estimate whether the degradation reaction is truly negligible at ambient temperature or not. In this case, even stopped stages should be considered harmful for the lubricant. However, we did manage to show that the presence of FeF_3 in the mechanisms definitely and considerably lowers the lubricant's degradation temperature to a point that could be obtained through mechanical loading only (e.g., at ball/race micro contact level in a ball bearing).

Looking at the gaseous compound release during the Pin-on-Disk tests, it is also important to take into consideration that the outgassing rate of the grease under loaded conditions significantly differs from an unloaded grease. A prediction of grease outgassing for a long lifetime application shall take these effects into consideration and adapt the quantity of grease accordingly.

It has been noted that test facilities are easily contaminated by some chemical species. Care should be taken to follow proper "bakeout" procedures to ensure as much as possible that every trace of the previous test has been removed, especially in experiments where mass spectrometer data is important. Moreover, we would like to point out the importance of knowing in advance which spectra (and thus which peaks) are expected to be found in the mass spectrometer measurements, since expected species usually have complex spectra where various traces are overlapping.

Further tests within a pin-on-disc tribometer and/or the spiral orbit tribometer will now focus on observing a real-case degradation to assess if it can truly be correlated to the degradation reaction we studied here. In particular, the influence of mechanical loading and temperature will be monitored. During these tests, care shall be taken to carefully choose mass spectrometer settings that allow proper comparison of the readings coming from the different experiments. We expect that these tests will help us to better define safe ranges of operation for the Z25 grease, and conclude on the autocatalytic effect existence or not.

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