Development of a Space Grease Lubricant with Long-Term-Storage Properties

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Table S1: Technical info on tested PTFE powders provided by suppliers.

PTFE powders

Description	Average particle size [µm]	Primary particle size [nm]	Specific surface area [m^2g^{-1}]
PTFE-1	5	200-300	> 7.5
PTFE-2	D_{50}: 3 / D_{90}: 6	info not available	info not available
PTFE-3	min. size: 2-4 ; max. size: 22	200-250	info not available
PTFE-4	mean value: < 20	~ 200	6.0–8.0
PTFE-5	mean value: < 10	info not available	7.0–9.0
PTFE-6	mean value: < 6	< 800	9.0–15.0
PTFE-7	D_{50}: 2.9 / D_{90}: 7.6	200–300	info not available
PTFE-8	D_{50}: 3.5 ; max. size: 15.6	info not available	info not available
PTFE-9	max. size: 1	info not available	info not available
PTFE-10	D_{50}: 5.5 – 10.5 D_{90}: ~ 16	info not available	info not available
PTFE-11	D_{50}: ~4	info not available	info not available
PTFE-12	D_{98}: < 8 / D_{50}: ~ 4	info not available	info not available
PTFE-13	mean value: 4	200	12
PTFE-14	mean value 4	120	17

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Rheological measurements

Rheological characterizations were performed on an Anton Paar MCR 702 rheometer. For oils, the viscosity and viscosity indices were determined. For greases, viscosities were measured and amplitude sweeps were performed.

Amplitude sweep

Amplitude sweeps were performed to measure the shear dependent dynamic moduli of greases. The standard settings for performing amplitude sweeps were:

- Cone/plate measurement system, 1° angle;
- Test plate size: 25 mm diameter;
- Measurement gap/lubricant layer thickness: 1 mm;
- Test temperature: 25 °C;
- 10 minutes holding time at target temperature before measurement;
- Frequency: 1 Hz;
- Shear deformation range: 0.01–100 %

Viscosity and Viscosity index measurements

PFPE oils.

Tests were performed according to DIN 51810-1. The conditions for performing viscosity measurements for the base oils were:

- Plate/plate measurement system;
- Test plate size: 25 mm diameter;
- Measurement gap/lubricant layer thickness: 1 mm;
- Test temperature range: 20 – 100 °C;
- 10 minutes holding time at target temperature before measurement;
- Shear rate: 0 – 100/s.

Viscosity indices were determined by measurement of kinematic viscosity at 40°C and 100°C at a shear rate of 50/s. Calculations were performed according to ASTM D 2270-74, and the required base oil densities were taken from the technical datasheets.

Greases

Tests were performed in alignment with DIN 51810-1, but at modified shear rates

- Cone/plate measurement system, 1° angle;
- Test plate size: 25 mm diameter;
- Measurement gap/lubricant layer thickness: 49 μm.
- Procedure:
    - Hold sample at 20 °C for 5 minutes.
    - Pre-shear at rate of 5/s for 4 minutes.
    - Hold sample for 2 minutes.

- Shear rate sweep from 0 to 10/s within 1 minute.
- Hold sample at 10/s for 2 minutes.
- Shear rate sweep from 10 to 100/s within 1 minute.
- Hold sample at 100/s for 2 minutes.
- Shear rate sweep from 100 to 500/s within 1 minute.
- Hold sample at 500/s for 2 minutes.

Thermogravimetric analyses

Thermogravimetric analyses were performed with a Netzsch TG 209 F1 Libra thermo-microbalance. Tests were conducted in a N_2 inert atmosphere or in an air atmosphere. Depending on the analyzed compounds, different measurement profiles were specified.

PFPE oils and additives

- Heating from 25 °C to 700 °C at rate of 10 °C/min (atmosphere: N_2 or air).
- Heating from 700 °C to 1000 °C (atmosphere: air).

Greases

Measurements were performed in N_2 atmosphere according to the following protocol:

- Heating from 20 °C to 500 °C at rate of 10 °C/min.
- Holding time of 15 minutes at 500 °C.
- Heating from 500 °C to 700 °C at rate of 10 °C/min.

Measurements were performed in air atmosphere according to the following protocol:

- Heating from 20 °C to 120 °C at rate of 10 °C/min..
- Holding time of 120 minutes at 120 °C.
- Heating from 120 °C to 500 °C at rate of 10 °C/min.
- Holding time of 30 minutes at 500 °C.
- Heating from 500 °C to 700 °C at rate of 10 °C/min.

For the characterization of the preliminary formulation, the following parameters were defined. All aged and unaged formulations were stored openly under laboratory conditions for 24 hours to allow for an eventual water uptake. The following parameters were taken from the TGA measurements:

- Water content: Gathered from measurements in air atmosphere. Mass loss at 120 °C, 20 minutes after start of the measurement.
- 2 % mass loss: Gathered from measurements in air and N_2 atmosphere. Temperature, at which 2 % of the original weight is lost.

Corrosion testing

Corrosion testing was performed with the following metals: SAE 52100 steel (1.3505), AISI 440C steel (1.4125), 17-4 steel (1.4542), Al7075 (3.4365), Ti6AlV4 (3.7165). Therefore, round samples (height: 5 mm, diameter: 30 mm, surface roughness R_z: 6.3) were purchased.

The following procedure was followed:

- Cleaning of samples with Acetone;
- Weighing of samples;
- Application of grease evenly on both faces and the side, using a cling wrap-covered petri dish;
- Arrangement of greased samples on glass plate;
- Placing of plate in a Memmert HCP50 climate chamber (80 °C, 60% relative humidity) for 2 weeks. The test conditions were an acceleration to simulate 15–20 years of storage at ambient conditions;
- Cleaning of samples with fluorinated solvent (*Turmotempoil 480*);
- Weighing of samples and visual assessment.

Impregnation of phenolic resin

The porous phenolic resin (Krütex 100P) was tested for compatibility with the grease formulations according to the following procedure:

- Cutting of round specimen (thickness: 4 mm, diameter: 32 mm) from rod material;
- Weighing of samples;
- Cleaning in ultrasonic iso-propanol bath. Four times for 5 minutes at 20% amplitude;
- Drying in air for 15 minutes;
- Weighing of samples;
- Storage in air for 2 days and weighing;
- Cleaning in ultrasonic iso-propanol bath. Two times for 10 minutes at 20% amplitude. The procedure was performed three times, each repetition was performed with fresh iso-propanol;
- Drying in air for 15 minutes;
- Weighing of samples;
- Cleaning in ultrasonic iso-propanol bath. Two times for 10 minutes at 20% amplitude. The procedure was performed three times, each repetition was performed with fresh iso-propanol;
- Drying in air for 15 minutes;
- Weighing of samples;
- Storage in air for 3 days and weighing;
- 1st impregnation: Discs were put in a vacuum reactor at a temperature of 80°C and a pressure of 0,2mbar. PFPE oil was added dropwise on top of the samples. Due to the phenolic resin having a lower density than PFPE oil, a small glass dish was added to weigh the samples down and fully submerge them. Discs were then submerged in oil for 44 hours at a temperature of 80 °C and a pressure of 0.05mbar (pressure decreased during the procedure). Afterwards, samples were allowed to cool down to room

temperature in vacuum over a period of 4 hours. Samples were cleaned with a tissue and Turmotempoil 480 to remove excess oil. Then drying for 5 minutes was allowed.

- Weighing of samples;
- 2nd impregnation: The exact same procedure as for the first impregnation was applied
- Weighing of samples;
- 3rd impregnation: The exact same procedure as for the first impregnation was applied;
- Weighing of samples.

Tribological testing

All tribological was performed at ESR Technology (Manchester, UK).

Test Setup

The spiral orbit tribometer (SOT) is a test facility which reproduces the kinematics of an angular contact bearing and allows for the evaluation of friction and degradation rates (i.e. consumption/wear) of lubricants in detail. The facility has the ability to test liquid, solid, and grease lubricants. The arrangement of the SOT allows the ball to experience rolling, sliding, and pivoting—all motions experienced by a ball in an angular contact bearing.

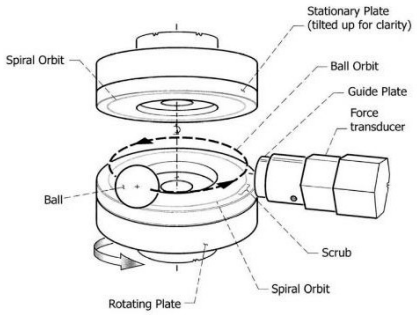

Figure S1: Internal arrangement of SOT, showing arrangement of sample set.

The SOT is essentially a thrust bearing, with an individual ball held between two interchangeable flat plates, located within a vacuum chamber. 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 rotate in a spiral path with a radius ~21 mm.

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 maintain a repeatable orbit. The region of each orbit for which the ball is in contact with the guide plate is denoted as the scrub. A force transducer behind the guide plate measures the force exerted by the ball onto the guide plate. From this, the friction coefficient is found, once for every orbit.

Test Samples

Prior to testing, all balls and plates were solvent cleaned using iso-propanol, acetone, and in a Kerry ultrasonic cleaning plant in Opteon SF80 solvent in accordance with standard ESTL practice [PRA-ESTL-PR-7301 03—Precision Cleaning Procedures].

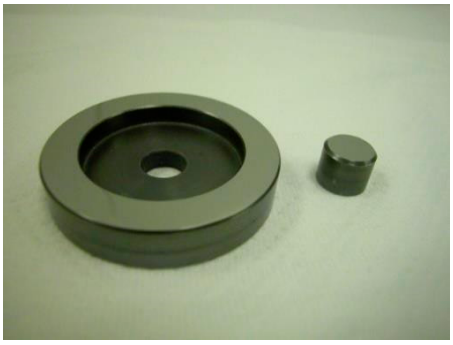

Figure S2: SOT flat and guide plate (before testing)

Lubrication

During this test program, various PFPE grease formulations were tested in the SOT. The lubricant was applied to the ball only.

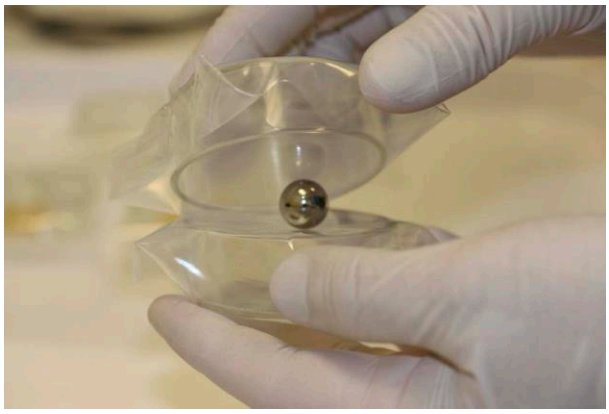

Figure S3: Lubrication of a ball with grease through rolling

Grease lubrication was achieved by the rolling of an individual ball between solvent cleaned Ultra Clean Level 100 Polyethylene tubing stretched over Petri dishes (**Error! Reference source not found.**). The ball was weighed dry using a microbalance, and a minimal amount of grease was applied directly to the surface (less than 1mm^3). The ball was then rolled between three pairs of sheets for 60, 30, and 15 seconds respectively. The ball was subsequently re-weighed, with the weight change being the grease uptake.

This method allows for the application of very small amounts of lubricant (~50μg) to the ball. Not only does this result in reduced test times, but ensures all tests take place under boundary conditions.

Residual Gas Analysis

An in-situ RGA system was operated in parallel to the friction assessment for a selection of the performed SOT tests. Such a technique has been successfully employed in the past to demonstrate the root cause of lubricant failure under similar test conditions for PFPE [ESA-ESTL-TM-0102 01—'Characterisation of Degradation of PFPE Based Lubricants'] lubricants.

A Hiden analytical HAL 201 RC Residual Gas Analyser (RGA) was used to directly monitor the gas species present during and produced by the lubricant under shearing at room temperature. This RGA was connected directly onto the side of the chamber. For each test, the RGA was degassed and operated at least 30 minutes prior to test start.

Table S2: Typical outgassing species identified in Fomblin Z25 (according to ESA-ESTL-TM-0102 01—'Characterisation of Degradation of PFPE Based Lubricants').

m/z	Degradation Species
28	CO (potentially CO and N_2)
44	CO_2
47	CFO
66	CF_2O
69	CF_3
119	C_2F_5
135	C_2F_5O

Table S3: Outgassing species identified in formulation-4.

m/z
28
44
47
51
66
69
85
97
100
104
119
131
169