lubricants

Article

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

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Abstract: Controlled vacuum environments as in space applications represent a challenge for the lubrication of tribological components. In addition to common space lubricant requirements like, e.g., low evaporation, a broad operational temperature range and a high stability during operation, long-term-storage (LTS) properties have gained increasing attention recently. The term addresses the time-dependent stability of a lubricant under static conditions, which can mean chemical degradation processes such as oxidation on the one hand, but also the physical separation of oil and thickener in heterogeneous lubricants like greases. Due to the extended storage periods of lubricated components on-ground but also during a space mission for several years, it has to be ensured that a lubricant is still functional after LTS. This article depicts the development of a space lubricant grease with LTS properties. Firstly, LTS requirements and methods for their assessment are discussed. In the following, a systematic approach towards the design of a grease formulation compatible with LTS is described. Finally, the manufacturing of prototype formulations and their broad characterization by means of LTS behaviour, outgassing, and tribological performance is presented.

Keywords: grease; lubricant; aging; long-term storage; spacecraft

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1. Introduction

The extreme conditions encountered in space demand a unique set of requirements for fluid lubricants being used in mechanical components [1]. Due to the vacuum of space, and in particular in the presence of sensitive (e.g., optical) components, an extremely low volatility is required to limit evaporation or outgassing, which can lead to lubricant loss and contamination issues. Spacecraft components can experience extreme temperature ranges, and lubricants must remain functional over these wide intervals. Lubricants must be compatible with a wide range of spacecraft materials including metals, plastics, and elastomers to prevent corrosion or material degradation. Given the difficulty and expense of maintenance or replacement, long lifetimes and consistent performance over extended periods are needed to ensure the reliability of mechanisms [2–4].

The majority of fluids used for space applications is based either on perfluoropolyether (PFPE) or multiple alkylated cyclopentanes (MAC) [5]. PFPE lubricants have a long history in space mechanisms, and they benefit from their robust chemical structure, which is reflected in an extremely high chemical and thermal stability, and also in their extremely low vapor pressures [6,7]. However, PFPE fluids suffer from a tribochemical autocatalytic degradation in the presence of Lewis acids, in particular on ferrous surfaces, which drastically reduces their lifetime during operation [7–11].

MAC oils, on the other hand, are also known for low vapor pressures, good wear protection, and a low tendency to creep [12–14]. It has been demonstrated that MAC oils show degradation which results in enhanced evaporation during operation, in particular in the presence of metal ions, but that the fluids do not lose their lubricating properties, which reflects in their long lifetimes [15–18]. The susceptibility of the hydrocarbon structure to chemical attack also reflects in its tendency towards thermo-oxidation [19]. Stability can be improved by the use of suitable additives; however, these can notably increase the outgassing. This is demonstrated in Table 1, where the outgassing data of pure Fomblin Z25 and the additive-containing Nye Synthetic Oil 2001 are compared.

Table 1. Outgassing parameters of Fomblin Z25 PFPE and Nye 2001 MAC according to ECSS-Q-70-02 [20].

Lubricant Oil	TML [%]	RML [%]	CVCM [%]
Fomblin Z25	0.06	0.01	0.01
Nye Synthetic Oil 2001	0.61	0.58	0.07

It is well known that lubricants being in operation can change in their properties over time due to chemical reactions like oxidation or degradation; evaporation (also as a result of chemical reactions) and outgassing; lubricant creep, or oil separation (in the case of greases), and it is obvious that such property changes can severely impact the functionality of a tribological system (though this is often very difficult to quantify). However, due to the extended storage periods of lubricated components, the long-term-storage (LTS) properties of lubricants have recently gained increasing attention [7,21]. The term LTS addresses the stability of a lubricant under static and controlled conditions on-ground for several years. The Meteosat Third Generation mission provides a good example of LTS due to planned periods of 5 years of assembly, testing and integration on ground, 17.5 years of on-ground storage for recurring models, and at least 8.5 years of operation in orbit [22]. Real-time data for LTS are hardly available, and predictions based upon accelerated models typically lack verification. The retainment of tribological properties of the PFPE-based grease Braycote 601 EF (Castrol) after 17 years of storage was presented in a NASA study, and the findings were confirmed in a recent publication [23,24].

In particular, the demixing of greases due to the separation of oil and filler is regarded as a major LTS concern. Greases are dispersing systems that consist of a base fluid, additives, and a thickener (particles or soap), which form a self-assembled network [25]. Due to their heterogeneity, fluid and solid components can separate over time. The separation of oil (also: "oil bleeding") is even an essential function, since it provides a lubricated contact with fluid [26]. During operation, when the external shear forces exceed a grease's yield stress, the internal structure collapses and releases the oil [27]. This is a reversible process, as oil and thickener also remix. In comparison to this, during a static situation as in LTS, the oil separation is slow, and is the result of metastability. It can proceed to a critical extent, especially when no remixing is performed and when the oil can migrate out of the lubricated areas. Therefore, exercising—the conduction of routine motions to recover pre-storage levels of performance or detect incipient storage issues at a time when preventative action or rectification measures may be implemented—is recommended for lubricated components on-ground (though the ideal periodicity of on-ground exercising remains an open question). The use of anti-creep coatings with a lower surface energy than the lubricating fluid can support the prevention of oil migration and a reduction in fluid evaporation.

A distinct elasticity of the network and a high affinity of oil and thickener are the key properties of a grease to show little demixing during LTS. From the perspective of physical chemistry, greases are concentrated colloidal suspensions, and their stability is characterized by the capacity of the system to withstand sedimentation, which is originated by gravity and agglomeration. High dispersion stability can be achieved when the properties of the disperse phase (thickener), the continuous phase (oil), and their interface are optimized.

In the context of a formulation development, the most important parameters for material selection are [28–30]:

- Primary particle size of thickeners < 1 µm and narrow size distribution to decrease Van der Waals attraction energy, which allows for effective stabilization by steric hinderance and reduces the impact of gravity.
- Particles with high roughness exhibit increased surface area and show better wettability.
- High oil viscosity reduces the speed of sedimentation.
- High wetting of the particle surface, achievable by use of surfactants or adjustment of surface energy of oil and thickener. The surface energy of the continuous phase should be similar but lower than the surface energy of the dispersed phase.
- Minimum density difference between oil and thickener compounds.

This article describes the systematic development of a lubricant grease formulation suitable for space application and with a focus on LTS stability. The grease was designed with the base compounds PFPE and PTFE due to their known chemical inertia. The use of additives for the mitigation of autocatalytic degradation and prolongation of tribological lifetime was considered and investigated. The study is divided into three sections: Firstly, the specified requirements for the lubricant to be developed and methods for their assessment are presented. Then, the systematic evaluation of relevant parameters and the development of grease formulations is discussed. The article concludes with the extensive characterization of a final and optimized formulation and its comparison with the space-proven commercial LTS grease Braycote 601 EF.

2. Materials and Methods

2.1. Raw Materials and Grease Manufacturing

The PFPE oils Fomblin Z25 and Fomblin YR1800 were procured from FenS (Goes, The Netherlands). Various PTFE powders and additives were sourced (see Table S1). Greases were prepared with an EXAKT 50i ointment mill by repeated rolling at various speeds and gap widths in quantities between 20 and 200 g.

2.2. Characterization of Formulation Properties

Rheological characterization

Rheological characterizations were performed on an Anton Paar MCR 702 rheometer. For oils, the viscosities were measured according to DIN 51810-1 and viscosity indices were determined according to ASTM D2270. For greases, viscosities were measured in accordance with DIN 51810-1. In addition, amplitude sweeps were performed for an assessment of grease stability and the expected oil separation [26,31]. The amplitude sweep is a dynamic rheological experiment, yielding a strain-dependent storage modulus G' and loss modulus G'' (see Figure 1). The formation of a filler network is indicated by the existence of a linear viscoelastic (LVE) regime, where moduli are independent of deformation. High G' values in the LVE regime indicate a high network elasticity, and low $\tan \delta$ values pronounce the domination of elastic over viscous properties. The yield stress is an indicator for the deformation at which a grease begins to flow. Test details can be found in the Supplementary Information.

Thermogravimetry

Thermogravimetric analyses (TGA) were performed with a Netzsch TG 209 F1 Libra thermo-microbalance. Tests were conducted in an N_2 inert atmosphere or in an air atmosphere. The main parameters taken from TGA measurements were water content (mass loss at 100–120 °C) and the 2% mass loss (temperature at which 2% of the original weight are lost). Test details can be found in the Supplementary Materials.

Oil separation tests

Oil separation tests were performed with an apparatus as defined by ASTM D 6184. Greases were placed in a sieve and stored in an oven. The amount of oil that separated from the grease and flows through the sieve was weighed. Tests were performed at different temperatures and durations.

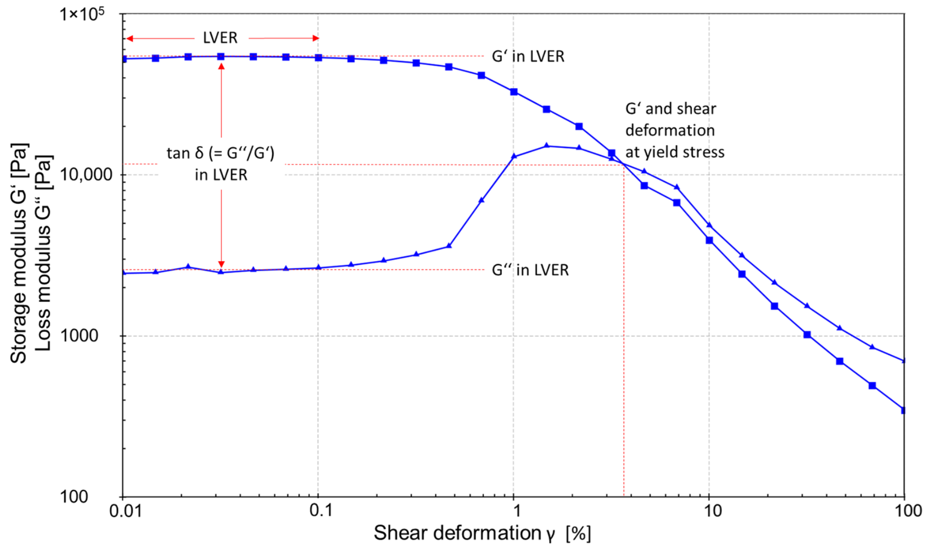


Figure 1. Depiction of a representative amplitude sweep and extractable output parameters.

2.3. Validation of Lubricant Properties for Space Application and Verification of LTS Properties

Recently, guidelines for testing of new fluid lubricants for space application have been proposed by ESR Technology [32]. These guidelines suggest a sequential process for the validation of lubricants for space mechanisms. In alignment with these guidelines, testing of the final lubrication formulation was planned. Furthermore, and based upon the available data for commercially available lubricants used in space mechanisms, a range of desired lubricant properties was specified. The performed tests are listed in Table 2 and described in the following sections. Outgassing tests were performed by DLR (Bremen, Germany) in accordance with the ECSS-Q-70-02 standard. Pour point, dropping point, and evaporation loss were measured at Intertek.

Table 2. Desired range of grease formulation properties.

Test Category	Test Parameter	Test Standard	Desired Property Range
Base oil parameters	Pour point	ASTM D5950	<−50 °C
	Viscosity	DIN 51810-1	100–400 cSt (20 °C) 80–200 cSt (40 °C) 20–70 cSt (100 °C)
	Viscosity index	ASTM D2270	>130
	Viscosity	DIN 51810-1	ca. 40 Pa·s (20 °C, 10 s^{-1}) ca. 5 Pa·s (20 °C, 100 s^{-1})
Grease parameters	Evaporation	ASTM D972	<1 wt.-%
	Outgassing	ECSS-Q-ST-70-02	TML < 1%, RML < 1%, CVCM < 0.1% *
	Dropping point	ASTM D566	20 °C above maximum use temperature
	Oil separation	ASTM D6184	<10% (204 °C, 30 h)

* TML = total mass loss, RML = recovered mass loss, CVCM = collected volatile condensable material.

Tribological testing

Tribological characterization was performed under vacuum conditions (10^{-6} mbar) and in cleanroom air, at varying tribological loads and temperatures by use of a spiral orbital tribometer (SOT) at ESR Technology (Manchester, UK) [33,34]. This test facility 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 under representative environments. The arrangement of the SOT is depicted in Figure 2. The rig allows the ball to experience rolling, sliding, and pivoting—all motions experienced by a ball in an angular contact bearing.

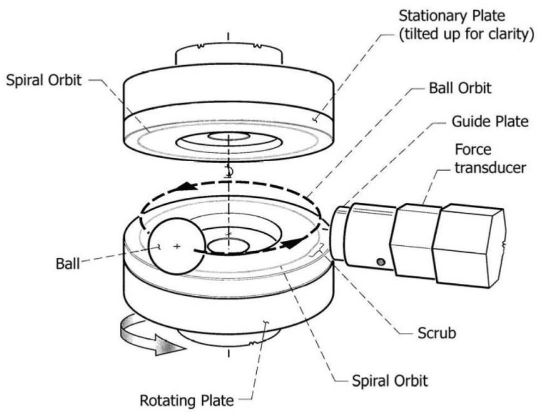


Figure 2. Schematic depiction of the spiral orbital tribometer (SOT) [33].

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. Surface materials can be altered, and for these tests were made from AISI 440C steel. More detailed information about the test procedure can be found in the Supplementary Materials.

The SOT data on friction coefficients are used to determine a SOT lifetime, which allows for the relative comparison of lubricants. The failure condition of a test is reached when the friction coefficient is $\geq$0.28 for three consecutive points, and the number of achieved orbits describes the lubricant's lifetime. This value is normalized by the amount of grease lubricant applied per test, providing a result in the units "orbits per µg of applied lubricant".

Corrosion testing

Corrosion testing was performed on materials representative of those commonly employed within spacecraft mechanisms: 100Cr6 (1.3505), AISI 440C (1.4125), 17-4PH (1.4542), EN-AW 7075 (3.7075) and Ti6Al4V (3.7165). Flat sample plates were coated with grease and stored in a Memmert HCP50 climate chamber for two weeks at 80 °C and 60% relative humidity. Samples were analysed for weight changes and visual appearance.

Lubricant creep testing

Creep is a known phenomenon for PFPE-based lubricants that can become critical when oil migrates out of the tribological system. Oil migration tests were performed with use of the creep barriers Acota EGC 2708 (equivalent to 3M Novec 2708) and Dr. Tillwich Antispread E2 Concentrate. Therefore, the materials were applied on a steel plate using a strip of adhesive tape and a pipette to form a "U" shape. The creep barrier solvent was allowed to evaporate for 30 min at room temperature. Then, one drop of the base oil mixture, 67% Fomblin Z25/33% Fomblin YR1800, was applied inside the formed shape of the creep barrier. The steel plate was placed in an oven at 100 °C and tilted at an angle of 7°. After 24 h, the anti-creep barrier was observed to still be successful in preventing lubricant migration.

Impregnation testing of phenolic resin

Bearing cages often consist of phenolic resin and are typically vacuum impregnated with an appropriate oil prior to assembly. It is a known difficulty to achieve a full saturation of cages with oil. The impregnation of the material Krütex 100P with the base oil mixture 67% Fomblin Z25/33% Fomblin YR1800 was investigated in a multistep process (see Supplementary Materials).

Verification of LTS properties

Storage over a period of multiple years was simulated by an accelerated aging experiment using an empirical rule based on the Arrhenius equation, which approximates that a temperature increase of 10 °C enhances the reaction rate by a factor of 2 [35]. Knowing that this approach is not accurate and cannot replace real-time testing, it actually represents a worst-case scenario for the lubricants due to their decrease in oil viscosity with temperature. Hence, grease samples were aged in an oven at 100 °C for 22 days, which aimed to mimic the behaviour at a room temperature of 20 °C for ~15 years. Afterwards, the grease was homogenised manually. Since LTS properties are defined as the conservation of properties before and after storage, the greases were characterized before and after aging.

3. Results and Discussion

3.1. Screening of Formulation Parameters

Selection of base oil

Fomblin Z25 belongs to the group of Z-type PFPEs and is a well-known PFPE oil with long heritage in space applications due to its low viscosity and high viscosity index, thermal stability, and extremely low vapor pressure. Z-type PFPEs are very susceptible to shear-induced tribochemical degradation, accelerated by Lewis acids. Y-type PFPEs, on the other hand, are known to be less reactive under such conditions due to a lower acetal content in their structure [36–38], but they exhibit lower viscosity indices and display significantly higher viscosities when being compared with Z-type PFPEs of the same molecular weight. At equivalent viscosities, Y-type PFPEs show much higher evaporation. The properties of Fomblin Z25 and the Y-type Fomblin YR1800 are compared in Table 3. The blending of suitable Z-type and Y-type PFPE bases was investigated in order to receive an oil with a high viscosity and robustness against Lewis acid attack at acceptable viscosity indices and evaporation rates. Fomblin YR1800 was identified as a promising oil for blending with Fomblin Z25.

Table 3. Properties of Fomblin Z25 and Fomblin YR1800 taken from technical datasheets.

Property	Fomblin Z25	Fomblin YR1800
Density (20 °C)	1.85 g/cm^3	1.92 g/cm^3
Average molecular weight	7300 g/mol	17,100 g/mol
Kinematic viscosity (20 °C)	223 cSt	1850 cSt
Viscosity index	350	148
Pour point	−75 °C	−20 °C
Vapor loss (204 °C, 22 h)	0.4 mass-%	0.5 mass-%

Different mixtures from both oils were analysed in order to identify a composition with a viscosity of ca. 400 cSt at 20 °C. The impact of composition on viscosity is depicted in Figure 3. A blend of 67% Fomblin Z25 and 33% Fomblin YR1800 was found to exhibit the targeted properties.

Greases with a PTFE content of 30% were manufactured with the blend oil and with pure Fomblin Z25 in order to investigate the postulated beneficial effect on dispersion stability. Rheological amplitude sweeps revealed higher storage moduli in the LVE regime for the grease made from the oil blend, and also in oil separation testing at 100 °C for seven days, the grease with the higher viscosity displayed a slightly higher stability.

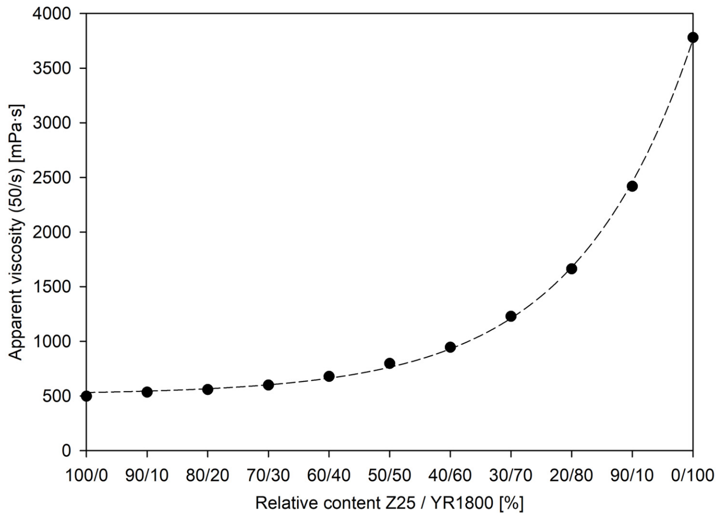
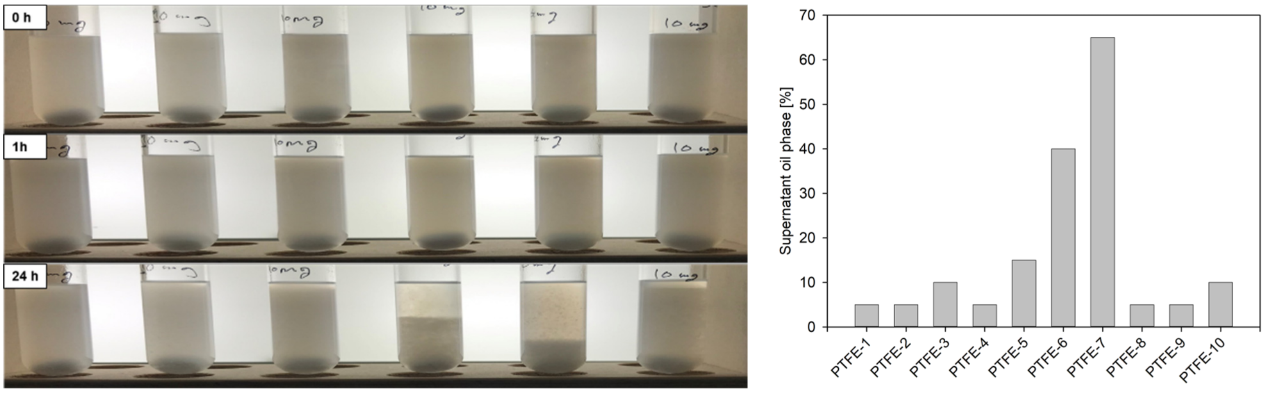


Figure 3. Viscosity of blends from Fomblin Z25 and Fomblin YR1800 at different compositions.

Selection of PTFE type and optimization of PTFE content

PTFE micropowders with primary particle sizes < 1 μm are well-known and commonly used thickeners of greases for long-life applications. They can be produced via different process routes, which result in products of different molecular weights, particle morphology, size, and size distribution, which then has a significant effect on their ability to be dispersed in a lubricant fluid [30]. Ten different commercially available PTFE powders were therefore compared. In a first preliminary experiment, the stability of dilute micropowder dispersions was investigated. A small amount of 50 mg PTFE was mixed with 10 g of PFPE oil, and the mixture was ultrasonicated. Turbid dispersions formed, and phase separation was monitored (see Figure 4a). The supernatant oil phase above the turbid dispersion was measured after 24 h. Its content relative to the overall height of the dispersion was calculated (see Figure 4b).



(**a**) (**b**)

Figure 4. (**a**) Settling of dilute PFPE/PTFE dispersions at different times. (**b**) Calculated relative height of supernatant oil phase of sedimented dilute PFPE/PTFE dispersions.

In addition, greases were manufactured at a PTFE mass content of 25%, but not all powders displayed a sufficient thickening effect. All stable greases were analysed by rheological amplitude sweeps and oil separation testing. The results from the preliminary experiment and the amplitude sweep were in good correlation, since the powders with the least phase separation showed high G' values in the amplitude sweep.

Oil separation tests were performed with the most promising candidates. The best overall results were received for PTFE-1, PTFE-5, PTFE-6 and PTFE-10, as visualized in

Figure 5. The best results were received for PTFE-1, which was selected as the thickener for all upcoming investigations.

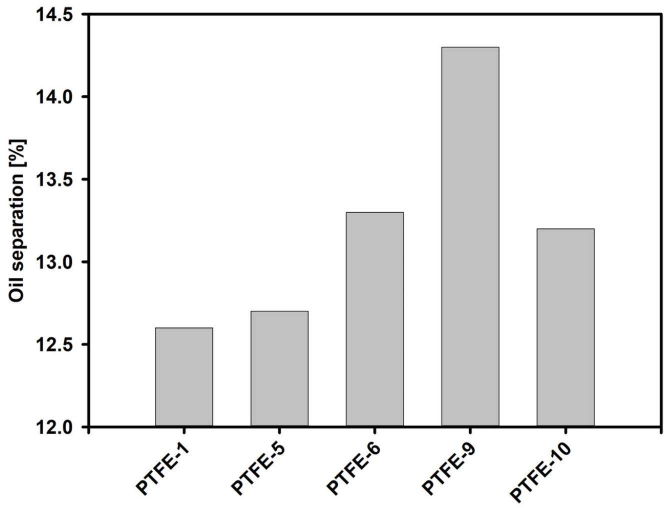
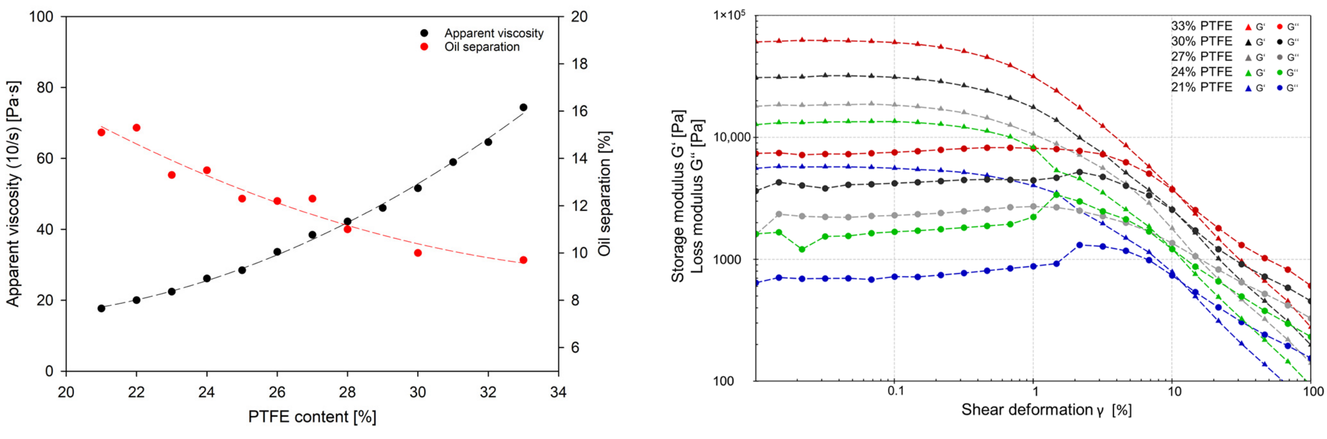


Figure 5. Oil separation of greases with different PTFE powders at 25% mass content and PFPE as base oil.

In the next step, an optimum PTFE content was investigated. Similar to oil viscosity, the viscosity of a grease also improves dispersion stability, and it is known that the viscosity of a dispersion increases with its solid content. Greases with a PTFE mass content between 21 and 33% were produced and analysed by oil separation tests and rheological amplitude sweeps (see Figure 6). It was found that a PTFE content between 27 and 31% is the most favourable compromise between a high grease stability with little oil separation and an acceptable viscosity.



(**a**) (**b**)

Figure 6. (**a**) Viscosity and oil separation of greases with different PTFE content. (**b**) Rheological amplitude sweeps of greases with different PTFE content.

Screening of additives for stabilization of PFPE

The use of additives for an improvement in robustness against autocatalytic PFPE degradation was investigated by TGA measurements of mixtures with Fomblin Z25. This approach was presented in a former publication [39] and is based on the expectation that a stabilized PFPE starts to decompose at higher temperatures, or that the decomposition proceeds slower. All tested additives were solid and immiscible with PFPE, and had sufficiently high melting points to ensure a low vapor pressure. It was a common observation for all compounds with a stabilizing effect that they initiated a mass loss at lower temperature compared to the pure oil, but then supported a delayed composition at higher temperature. The tests revealed that the combination of an antioxidant and a metal deactivator showed a synergistic effect in the TGA tests. This can be seen in Figure 7.

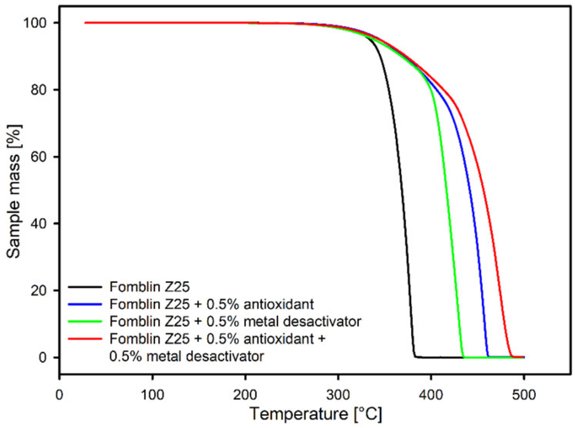


Figure 7. Temperature-dependent mass loss of Fomblin Z25 and its mixtures with additives.

Testing of preliminary formulations

Several preliminary formulations have been produced and characterized, applying the findings from formulation development investigations. The formulations consisted of mainly PFPE and PTFE, and in some cases a functionalized bentonite, an antioxidant, and a metal deactivator were added. For a concise presentation of the most important results, four out of twelve overall preliminary formulations are presented in Table 4. Two SOT tests were performed with formulations-1–3, respectively, and three with formulation-4.

Table 4. Comparison of SOT lifetime, oil separation, and viscosity of grease formulations.

Grease	Base Oil	PTFE Content	Additives	Average Lifetime (SOT)	Oil Separation (204 °C/30 h)	Viscosity (10/s)
Formulation-1	Fomblin Z25	25%	-	77 ± 6 orb/µg	12.5%	27.9 Pa·s
Formulation-2	Fomblin Z25	30%	-	103 ± 27 orb/µg	10.6%	52.4 Pa·s
Formulation-3	Fomblin Z25	27%	Bentonite 3% Antioxidant 2%	137 ± 8 orb/µg	10.9%	45.8 Pa·s
Formulation-4	Fomblin Z25/Fomblin YR1800	27%	Bentonite 3% Antioxidant 1% Metal deactivator 0.5%	269 ± 21 orb/µg	8.0%	53.6 Pa·s

The main findings from formulation development were:

- A higher PTFE content increases viscosity, reduces oil separation, and enhances tribological SOT lifetime.
- The partial substitution of PTFE with an organo-modified bentonite slightly reduces viscosity and increases oil separation, but improves SOT lifetime.
- The use of an oil blend from Z-type and Y-type PFPEs significantly reduces oil separation and increases SOT lifetime.
- The combination of an antioxidant and a metal deactivator significantly increases SOT lifetime.

Based on these findings, it was decided to define formulation-4 as the final formulation.

3.2. Formulation Validation

In the following, final formulation-4 was characterized extensively in alignment with the proposed guidelines for lubricant validation prepared by ESR technology. This included various tests to confirm that the grease fulfils fundamental requirements for use in space applications. In addition, further experiments were performed to address concerns that relate to LTS. A comparison was made with Braycote 601 EF, a grease with long space heritage and proven LTS properties.

Base oil properties

Analyses with the base oil were performed to investigate pour point, viscosity, and viscosity index. The density was calculated from the relative content of the base components Fomblin Z25 and Fomblin YR1800 and their individual density. Vapor pressure measurements for the blend could not be performed, and the vapor pressure of the individual components was provided by the supplier. The comparison with Braycote 601 EF was performed on the basis of technical datasheet values.

All tested parameters for the base oil blend of formulation-4 are listed in Table 5 and could meet the range of the desired properties that are given in Table 2.

Table 5. Base oil properties of formulation-4 and Braycote 601 EF.

Property	Formulation-4	Braycote 601 EF
Density (20 °C)	1.85 g/cm^3	1.97 g/cm^3 *
Kinematic viscosity (20 °C)	223 cSt (20 °C) 167 cSt (40 °C) 36 cSt (100 °C)	110–170 cSt (38 °C) * 40–50 cSt (99 °C) *
Viscosity index	262	340 min. *
Pour point	−71 °C	−73 °C max. *
Vapor pressure (20 °C)	2.1×10^{-13} mbar (Fomblin Z25) * 4.0×10^{-12} mbar (Fomblin YR1800) *	<5.3×10^{-13} mbar *

* Values taken from supplier datasheet.

Outgassing and thermal stability

The ECSS-Q-ST-70-02C standard is applicable to thermal vacuum tests to analyse outgassing properties for space materials [40]. In this test, a material is heated at 125 °C for 24 h and at a pressure of 10^{-7} mbar, and the mass loss is investigated. The total mass loss (TML) indicates the total amount of outgassing. The recovered mass loss (RML) represents the total mass loss without the amount of adsorbed water. The collected volatile condensable material (CVCM) is the quantity of outgassed matter that condensed on a collector plate that has a temperature of 25 °C. While RML is a general indicator for the amount of organic outgassing material, the CVCM represents the amount of compound that would be harder to remove by evaporation, which would cause a greater concern for sensitive surfaces. The standard specifies the allowable outgassing to be TML < 1%, RML < 1%, and CVCM < 0.1% for typical (i.e., non-optical) cases. The evaporation loss test according to ASTM D972 assesses the mass loss of grease at an elevated temperature, and the dropping point test according to ASTM D566 is an indicator for the temperature limits of the thickener system.

All of the discussed tests were conducted with formulation-4, and reference data for a comparison with Braycote 601 EF were taken from the technical datasheet or from the Space Materials Database [20]. In Table 6, the results are compared.

Table 6. Outgassing properties of formulation and Braycote 601 EF (Braycote data taken from [20]).

Property	Formulation-4	Braycote 601 EF
TML	0.16	0.19
RML	0.12	0.16
CVCM	0.03	0.05
Dropping point	200 °C	182 °C min. *
Evaporation loss	0.68%	2% max. *

* Values taken from supplier datasheet.

The outgassing data for Braycote 601 EF were taken from the Space Materials Database [20] and are an average from multiple batches. Testing revealed that formulation-4 could pass the outgassing requirements of ECSS-Q-ST-70-02C and is competitive with the commercial grease.

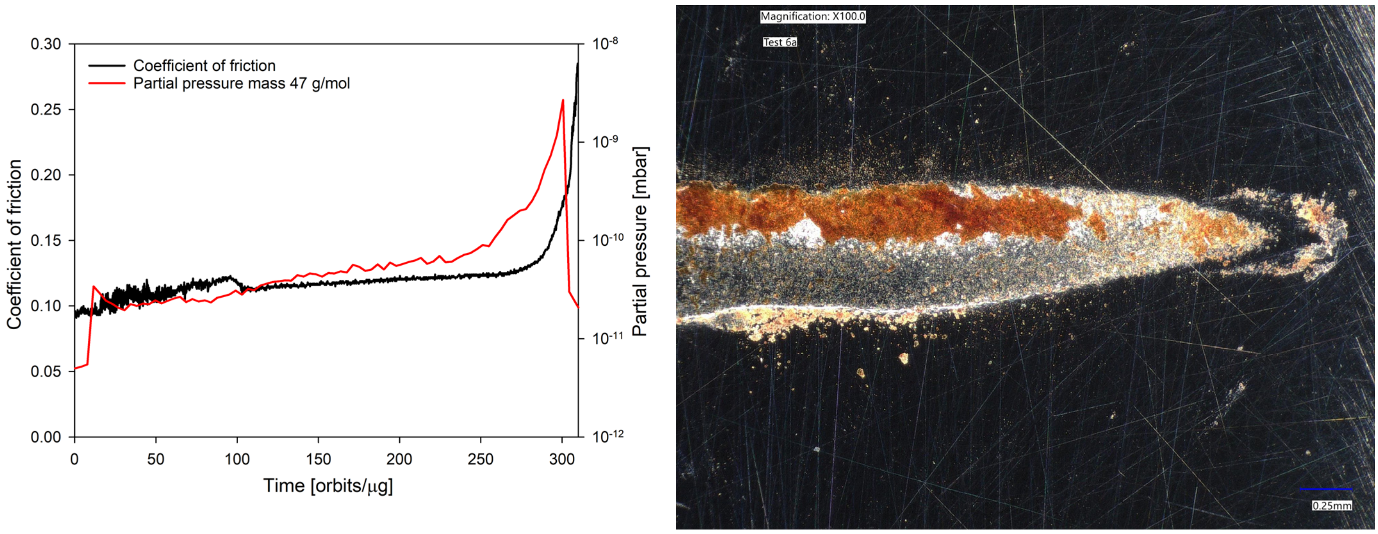
Tribological characterisation

Spiral orbital tribometer tests were performed with the final formulation-4, and the results were put in perspective to earlier equivalent tests with Braycote 601 EF. In situ residual gas analysis (RGA) measurements were performed in specific cases to gain further insight into the degradation of the lubricant and the progression of vapor pressure during the experiment. All results from SOT testing with varied parameters are listed in Table 7.

Table 7. Results from tribological SOT testing.

Peak Hertzian Contact Stress	Environment	Temperature	Number of Tests	Average Lifetime	Average Steady State Coefficient of Friction
2.25 GPa	<1.3·10^{-6} mbar	22 ± 3 °C	3	269 ± 25 orb/μg	0.117
1.88 GPa	<1.3·10^{-6} mbar	22 ± 3 °C	2	658 ± 6 orb/μg	0.119
1.50 GPa	<1.3·10^{-6} mbar	22 ± 3 °C	2	1541 ± 2 orb/μg	0.119
2.25 GPa	<1.3·10^{-6} mbar	50 ± 3 °C	2	207 ± 18 orb/μg	0.108
2.25 GPa	<1.3·10^{-6} mbar	80 ± 3 °C	2	157 ± 6 orb/μg	0.092
2.25 GPa	1013 mbar	22 ± 3 °C	2	5639 ± 377 orb/μg	0.113

An extension in lifetime occurred with a reduction in contact stress, and a reduction in lifetime with an increase in test temperature. These are known and anticipated relationships when considering fluid lubricants with the spiral orbit tribometer [41]. Also, an increase in the lifetime when testing in air was observed, which is also in line with previous testing of PFPE lubricants. Review of tribological data, RGA curves, and microscopic post inspections of the wear scars consistently indicated an expected and typical degradation pattern. At the end of the grease life, the coefficient of friction increased drastically, and the same was seen for the partial pressure in the test chamber (see Figure 8a). The majority of detected mass fragments in the RGA analysis are known from analysis of Z-type PFPE oils [42], while some additional signals indicate the degradation of Y-type PFPE structures (see Tables S2 and S3).



(**a**) (**b**)

Figure 8. (**a**) Representative picture for evolution of coefficient of friction and partial pressure of a characteristic mass fragment 47 g/mol (CFO) during an SOT test with a PFPE lubricant. (**b**) Typical example of a wear scar showing the presence of lubricant degradation product ("brown sugar").

Visual inspection of PFPE lubricants revealed the typically observed degradation product ("brown sugar") within the wear tracks (see Figure 8b). This debris is a mixture from PFPE degradation products and inorganic fluorides, oxides, and carbides (mainly iron based) [43,44].

The comparison between formulation-4 and Braycote 601 EF revealed that the relationship of lifetime against peak contact stress is very similar for the two lubricants (Figure 9a). Under ambient conditions, formulation-4 achieved a more than six-times-longer lifetime compared to Braycote 601EF (Figure 9b). Across all test conditions, the lifetime measured for formulation-4 is significantly greater than that of Braycote 601EF.

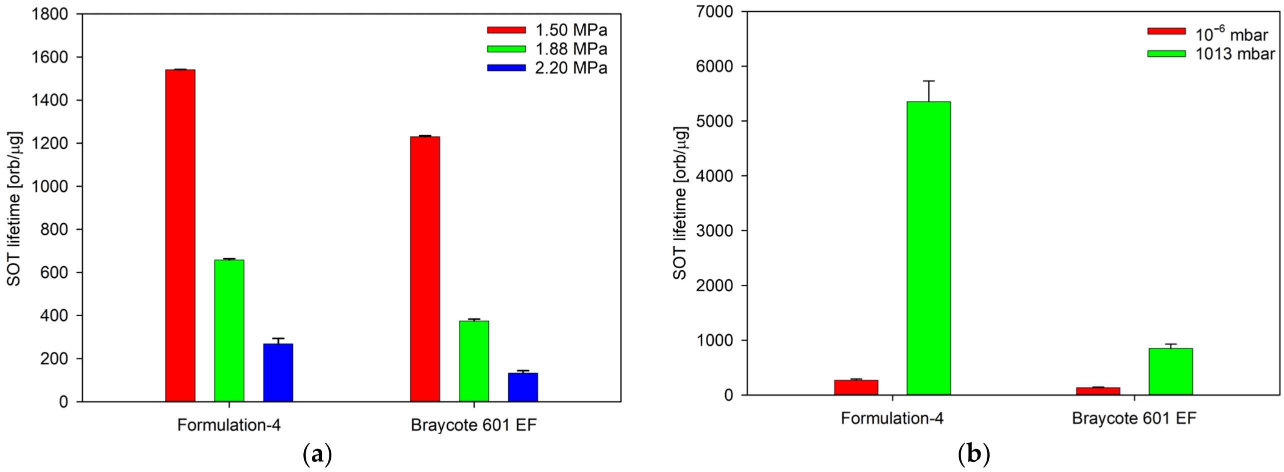


Figure 9. Comparison of tribological lifetimes from SOT test for formulation-4 and Braycote 601 EF (**a**) at different peak Hertzian contact pressure in high vacuum (10^{-6} mbar) and (**b**) at different pressure with a peak Hertzian contact pressure of 2.20 MPa.

Oil separation tests and accelerated aging

While the separation of oil and thickener is a general major concern with regard to LTS, it is the most significant risk for a PFPE/PTFE-based grease. This concern was addressed by standard oil separation tests on the one hand and accelerated aging experiments on the other. While a low oil separation is an advantageous property, the feasibility to re-homogenise separated material is of as-high importance. For a grease being stored in a container, this can be performed by manual remixing. In the case of lubricated components that are still on-ground, this can be performed upon initial actuation of the mechanism (and subsequently through periodic exercising). In accelerated aging tests, oil separation was enhanced artificially by oven storage at 100 °C for 22 days, and the retainment of grease properties after a remixing procedure was investigated.

A long-term oil separation experiment at room temperature was performed with Braycote 601 EF and formulation-4. The mass loss of Braycote 601 EF was recorded over a period of 24 weeks, and the experiment for formulation-4 is still ongoing, with 30 weeks having passed. It can be seen from Figure 10 that both greases show a low level of oil separation even after several weeks, and that values seem to converge against a maximum value. The oil separation of Braycote 601 EF after 24 weeks was at 2.60%, and for formulation-4 after 30 weeks was at 1.98%.

Accelerated aging was performed by storing the greases at 100 °C for 22 days. Prior and after the aging, oil separation tests at 100 °C and 204 °C as well as viscosity measurements were performed. Table 8 reports the results by comparing formulation-3, 4, and the Braycote 601 EF witnessed grease. An eventual impact of aging at elevated temperature on chemical degradation was monitored with TGA measurements. All the results are summarised in Table 8.

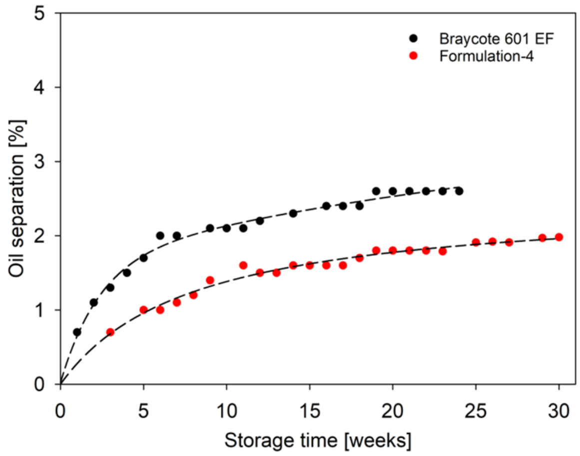


Figure 10. Results of long-term oil separation tests according to ASTM D6184 at room temperature for formulation-4 and Braycote 601 EF (dashed lines indicate trend).

Table 8. Comparison of grease formulations before and after accelerated aging.

Grease	Oil Separation (100 °C, 22 d)	Oil Separation (204 °C, 30 h)	Viscosity (10/s)	Viscosity (100/s)	Average Lifetime (SOT)	T 2% Mass Loss (TGA)
Formulation-4 before aging	7.1%	8.0%	53.6 Pa·s	9.1 Pa·s	269	332
Formulation-4 after aging	8.1%	9.5%	64.2 Pa·s	10.4 Pa·s	-	317
Formulation-3 before aging	8.4%	10.9%	45.8 Pa·s	7.5 Pa·s	137	328
Formulation-3 after aging	9.5%	11.7%	46.6 Pa·s	7.6 Pa·s	198	325
Braycote 601-EF before aging	6.0%	12.4%	55.4 Pa·s	8.5 Pa·s	133	369
Braycote 601-EF after aging	7.6%	-	-	-	-	375

Thermogravimetric analyses did not provide any indication of a chemical degradation that might have impacted the oil separation. For all greases, and during both tests with different temperatures, the oil separation after re-homogenization was higher than before the aging. On the other hand, the rheological viscosity measurements of the greases did not reveal significant changes, taking into account that the measurements are more sensitive to variation than measurements with oils. The tribological lifetime in SOT testing yielded higher lifetimes after aging of the grease than before. While no deeper analysis could be performed in the context of this work, we present a hypothesis that an "impregnation" of the PTFE particles occurs when grease is being stored for a longer period of time (in particular at elevated temperatures). While no indications of a major impact on the grease properties could be seen, altogether the results from the accelerated aging and re-homogenization failed to provide clear answers. More work dedicated to this particular subject is required and should involve not only the development of a more standardized re-homogenization procedure, but also a more extensive review of the accelerated aging test and of the verification methods.

Nonetheless, the results from the oil separation testing and accelerated aging suggest that formulation-4 is a promising candidate for LTS, in particular due to the comparison with the grease Braycote 601 EF.

Material compatibility testing

Different analyses for an investigation of the grease compatibility with typical space materials were conducted. Corrosion tests were performed with common alloys. LTS concerns that regard the potential loss of lubricant oil from the tribological system were addressed by migration experiments with creep barriers on the one hand, and by impregnation tests with phenolic resins that are typically employed in bearing cages on the other hand.

For corrosion tests, plates of 27 mm diameter of the following alloys being used as construction materials in space mechanisms were applied: 100Cr6 (1.3505), AISI 440C (1.4125), 17-4PH (1.4542), EN-AW 7075 (3.7075), and Ti6Al4V (3.7165). Therefore, different metals and polyimide polymer (Tecasint 4011) were coated with grease and stored in a climate chamber for 2 weeks at 80 °C and 60% relative humidity. Samples were analysed for weight changes and for their visual appearance (Figure 11). The metal samples did not change in weight after all the grease was removed. Visually, no signs of corrosion could be detected.

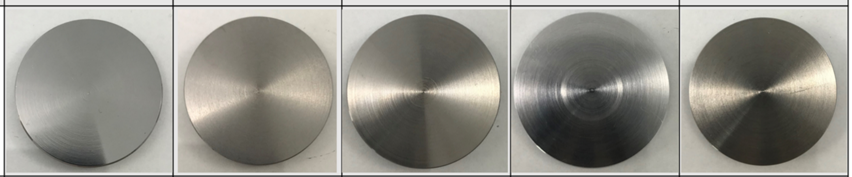
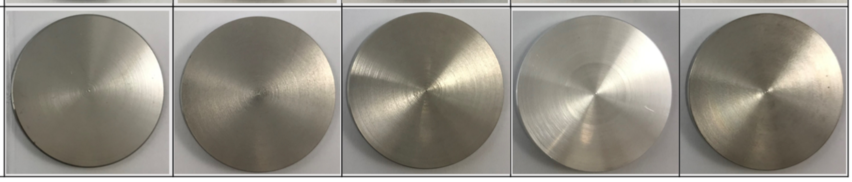
	1.3505	1.4125	1.4542	3.7075 (Al)	3.1765 (Ti Gr. 5)
weight change [mg]	0.1	-0.1	0.1	0	0.3
before					
after					

Figure 11. Visual inspection of metal samples before and after corrosion tests (2 weeks at 80 °C and 60% relative humidity) with formulation-4. The metal samples are discs of 27 mm diameter.

When larger volumes of lubricants are applied, migration is a likely phenomenon because the mass of the fluid body is high compared to the retaining viscous forces and substrate oil–film surface energetics. Such migration may impact the subsequent flight lifetime of the affected mechanism if the oil is able to exit the bearing envelope. During on-ground storage, creep is primarily driven by surface energy differences and can be minimised partly by control of the surface features and by the appropriate application of anti-creep coatings which have a lower surface energy than the lubricating fluid. Oil migrations with the creep barriers Acota EGC 2708 and Dr. Tillwich Antispread E2 Concentrate were performed on a tilted steel plate. After 24 h of testing, the oil spread over the substrate due to the tilting, but it was not possible to pass the creep barriers. This could confirm the compatibility and usability of the base oil with the tested creep barriers to mitigate lubricant creep risks.

Compatibility with the porous phenolic resin Krütex 100P was tested to investigate the oil saturation of phenolic bearing cage materials. Such phenolic cages are typically vacuum impregnated with an appropriate oil prior to assembly, and it is a known difficulty to achieve a full saturation of cages with oil. It is an LTS concern that these cages have a capacity to take up more free oil from the bearing during months or years in storage, reducing the free oil quantity in a lubricant and even leading to an insufficient supply of lubricant present on balls and raceways to permit proper lubrication. In order to address this concern, a multistep impregnation procedure with the base oil of LTS grease was performed. Weight change was observed for the detection of a saturation limit and visual inspection was performed to detect potential incompatibilities. After three impregnation cycles, a saturation could be achieved. Furthermore, visual observations showed neither discolorations nor signs of swelling, which indicates that no interaction between the materials occurred. Therefore, formulation-4 is suitable for phenolic cages impregnation up to saturation.

4. Conclusions

The successful development of a space grease with optimization towards resistance to LTS was described. Different properties of the developed formulation were investigated to demonstrate compliance with essential space lubricant requirements. The main benefits of our formulation were low outgassing parameters, low oil separation, and high tribological lifetimes.

In upcoming activities, the confidence in resistance to LTS shall be increased by long-term testing, and additional tribological qualifications shall follow in accordance with the ESR's guidelines. For space application, this means qualification tests on the mechanism or component levels according to ECSS-E-ST-33-01C [1].

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/lubricants12030072/s1, Table S1: Technical info on tested PTFE powders provided by suppliers; Figure S1: Internal arrangement of SOT, showing arrangement of sample set; Figure S2: SOT flat & guide plate (before testing); Figure S3: Lubrication of a ball with grease through rolling; Table S2: Typical outgassing species identified in Fomblin Z25 (according to ESA-ESTL-TM-0102 01-'Characterisation of Degradation of PFPE Based Lubricants'); Table S3: Outgassing species identified in Formulation-4.

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