Preventing the “Brown Sugar” Lubricant Phenomenon: The Relationship Between PFPE Chemical Compositions and their Susceptibility to Lewis Acid-Catalyzed Degradation

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Abstract

Lubricants play a critical role in ensuring that mechanisms perform reliably under the demanding operating conditions found in space. Known for their chemical inertness, broad operating temperature range, and low volatility, perfluoropolyethers (PFPEs) are attractive lubricants for space applications. The one Achilles Heel of PFPEs is their susceptability to Lewis acid-catalyzed degradation, also known as the “Brown Sugar” effect, which can negatively impact the wear life of a lubricant.

However, not all PFPEs have the same chemical structure, making some PFPEs more susceptible to Lewis acid-catalyzed degradation than others. In this study, two greases were examined, the legacy Braycote® 601EF and the recently launched NyeTorr® 6350EL, as well as their respective base oils. The greases and oils were subjected to thermal treatments in both the absence and presence of Lewis acids found in space applications.

Samples were monitored for thermal degradation via Thermogravimetric Analysis (TGA) during treatment, and grease samples were subjected to antiwear testing on the SRV® test system and Vacuum 4 Ball Wear Tribometer after treatment. These results provide fundamental insight into the impacts that Lewis acid exposure has on the performance of different PFPE chemistries.

Our preliminary findings suggest that products made with PFPEs classified as “Z fluids”, like Braycote® 601EF, are inherently susceptible to Lewis acid-catalyzed degradation. Z fluids also exhibit inferior wear performance after exposure to Lewis acids at high temperatures when compared to PFPEs of different chemical structures. The data collected demonstrates the cause of the Brown Sugar effect and enables engineers to make informed decisions when selecting lubricants for space mechanisms.

Introduction

<u>Background</u>

PFPE-based oils and greases have been go-to solutions for lubrication in space applications for over fifty years [1]. The inherent properties of these fluids make them a good fit for the space environment; their attributes include low vapor pressures and outgassing, broad operating temperature range, and chemical inertness. Their broad operating temperature range is especially important for lubricants in space, not only due to extreme sweeps in ambient temperature conditions, but also due to limited opportunities for heat transfer and dissipation in a vacuum environment. PFPEs offer the highest thermal stability of available base oils and thus are best equipped to withstand the localized high temperatures generated at frictional contacts [1–3].

While PFPE fluids check many of the “must-have” boxes when selecting lubricants for space applications, there are some areas where they fall short. In particular, despite representing some of the most inert lubricants available, in the presence of Lewis acids PFPEs are subject to degradation. When this failure-inducing phenomenon occurs, it is sometimes referred to as the “Brown Sugar” effect due to the resulting residue resembling the color and texture of brown sugar. This phenomenon has been well documented and

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studied. At this point, our understanding of the conditions that cause the brown sugar phenomenon is quite good; we know that it is caused by the Lewis acid sites that exist on metal surfaces and that it is more likely to occur under boundary lubrication conditions – presumably due to a combination of elevated localized temperatures at asperity contacts and wear debris that are generated. It is also known that the degradation reaction products exacerbate the problem and promote even more rapid degradation of the fluid [2,4–10]. Available mitigation strategies on the other hand, are more limited. Beyond avoiding conditions that are known increase the chance of degradation occuring, by using ceramic coated balls in bearings for example, it hasn't been possible to prevent Lewis acid-catalyzed degradation of PFPE fluids.

To better understand this problem, we need to look at what is happening on a molecular level. All PFPE fluids are polymers; they are long chain molecules that are made up of repeating units called "monomers" that are chemically linked together. All PFPE monomers are fully fluorinated (no hydrogen atoms – this is what imparts their incredible inertness) and the monomers are linked together by oxygen atoms. The identity of the monomers largely dictates the fluid properties; there are a variety of different PFPE fluids commercially available in varying viscosities. For the purposes of this discussion it should be noted that some fluids contain acetal linkages (-O-CF_2-O-), and others do not. Figure 1 depicts the structures of four different commercially available PFPE fluids; Fomblin® Z, Fomblin® Y, Krytox®, and Demnum™. Shown in red, Fomblin® Y and Fomblin® Z both contain acetal linkages in their structures, with the Fomblin® Z fluid containing the much higher proportion of acetal linkages between the two. In contrast, the Krytox® and Demnum™ fluids do not have any acetal linkages in their structures at all. There is evidence that acetal linkages in PFPEs are especially susceptible to Lewis acid-catalyzed degradation; wih Fomblin® Z fluids known to be the most degradation-prone fluids [10]. Despite this shortcoming, Fomblin® Z fluids are still a popular lubricant selection due to their unrivalled high viscosity index, low evaporative loss, and wear protection.

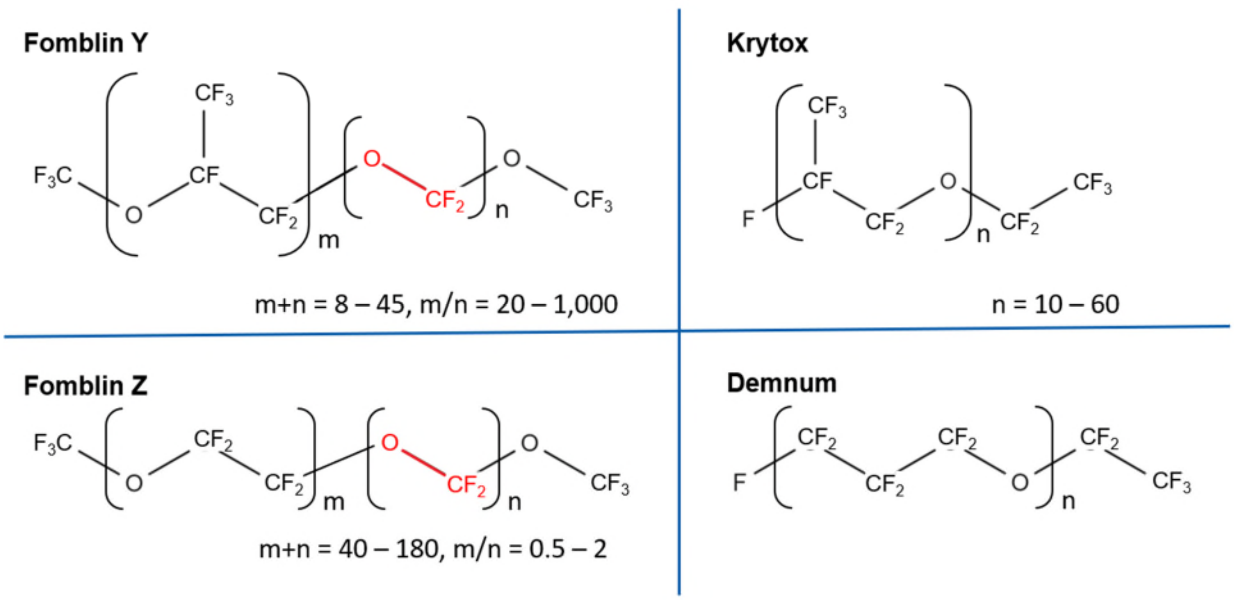

Figure 1. Representation of different PFPE fluid structures

A "Lewis acid" is broadly defined as a species that can accept electrons [11]. In space lubricant applications, a relevant example of a Lewis acid is iron (III) oxide (Fe_2O_3), which is found on stainless steel surfaces. The iron (III) oxide plays a fleeting role in the PFPE degradation process; it temporarily accepts some electron density from the polymer chain, enabling a fluorine atom to transfer from one -CF_2- unit to another, ultimately causing the chain to break in two, as shown in Figure 2. In PFPEs containing acetal units, this transfer is especially easy to do, making them among the most susceptible fluids. Some of the by-products from PFPE chain destruction are highly reactive species such as carbonyl fluoride (COF_2) that can interact with iron (III) oxide and convert it to iron (III) fluoride (FeF_3), an even stronger Lewis acid.

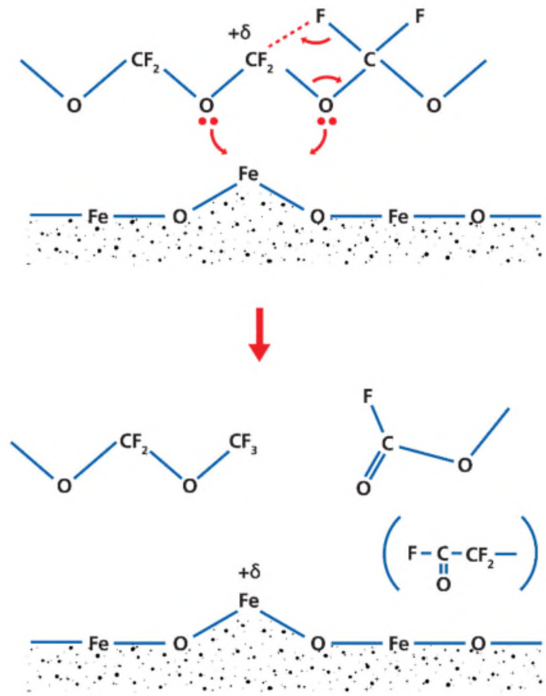

Figure 2. Depiction of a Lewis acid site interacting with an acetal group in a PFPE chain, resulting in chain scission. Adapted from Kasai et. al.[10]

In this work, the heritage space lubricant Braycote® 601EF, which is based on a Fomblin® Z fluid [3], is compared to NyeTorr® 6350EL, which utilizes a proprietary blend of PFPE fluids in its formulation. Both greases and their respective base oils (Brayco® 815Z, NyeTorr® 6351) were subjected to thermal treatments in the presence and absence of the Lewis acids Fe_2O_3 and FeF_3. Additionally, a "booster" additive was added to NyeTorr® 6350EL experimentally to enhance its Lewis acid-catalyzed degradation resistance. Sample masses were monitored during treatment as an indicator of degradation, and after treatment samples were subjected to wear testing on the SRV and Vacuum 4 Ball Tribometer.

Sample Preparation

Neat samples of commercial lubricants were used as received. Lewis acids used in this study were Iron(III) Oxide, (Strem, Hematite, 99.8% Fe) and anhydrous Iron(III) Fluoride (Strem, 99%+). For TGA testing, Lewis acid spiked samples were prepared by combining 9 grams of lubricant with 1 gram of the specified Lewis acid and speedmixing to ensure homogeneity. Spiked samples were prepared immediately before testing to limit the amount of degradation allowed to occur at room temperature prior to starting the TGA test. For wear tribometer tests, Lewis acid spiked samples were prepared by combining 2.7 grams of lubricant with 0.3 gram of the specified Lewis acid. Samples were mixed with a spatula in a Petri dish and placed in an oven at 200°C for 24 hours. Samples were allowed to cool to room temperature prior to testing. Heat treated samples were prepared in a similar manner, without the addition of Lewis acid.

Experimental Methods

Using a TA Instruments TGA Q50 Thermogravimetric Analyzer, thermal stability testing was performed in an air-filled environment. In the method utilized the temperature was ramped at a rate of 100°C/min to 230°C and then held there for 24 hours. Using the precise balance built into the instrument, the weight of the sample was monitored as the temperature was held. The amount of mass loss the sample exhibited was used as an indicator of degradation; samples that demonstrated greater mass losses are considered more prone to degradation.

Wear testing on the SRV® was used to determine a lubricant's ability to protect against wear when subjected to high-frequency, linear oscillation motion. In this work, conditions included a 52100 steel ball on disc contact, a test load of 100 N (yielding a contact pressure of 2.1 GPa), a frequency of 50 Hz, a stroke amplitude of 1.00 mm, a duration of 1 h and a temperature of 50°C. Specimens used were of hardness Rockwell C60, and met surface roughness and topography criteria as specified in ASTM D 5707 (Standard Test Method for Measuring Friction and Wear Properties of Lubricating Grease Using a High-Frequency, Linear-Oscillation (SRV) Test Machine) section 7.1-7.2. To protect the instrument, a maximum coefficient of friction cutoff was set where the test was terminated if it was exceeded. After the conclusion of a test, the total distance travelled by the specimens was calculated and the wear volume of the scar on the disc was measured using a Taylor Hobson 3D Optical Profilometer. With this information a wear rate was calculated and expressed in $\mu m^3/mm$; this method of data analysis enables the evaluation of even samples that are unable to complete the entire test method, allowing for greater resolution when ranking relative sample performance.

Wear testing on the Vacuum 4 Ball Tribometer (a custom built rig controlled with a LabView DAQ system) was used to evaluate lubricants' performance under conditions more closely resembling the environment in space. In the test method used for this work, a vacuum level of 6.7×10^{-4} Pa was achieved before initiating the test, typically by the end of the test the vacuum level had further dropped to 1.3×10^{-4} Pa. Selection of other parameters was based off of ASTM D2266 (Standard Test Method for Wear Preventive Characteristics of Lubricating Grease) with some modifications, largely made to reduce the amount of sample needed to a volume of 4 mL. For specimens, 7.9375 mm (5/16 inch) 52100 Alloy Steel balls were used with a hardness of Rockwell C60. An applied load of 290 N was used for testing, resulting in an initial contact pressure of 4.2 GPa. The test was run for one hour at room temperature and a speed of 600 rpm. After completion of the test, wear scar diameters on the lower three balls were measured using a microscope and the average reported. Each sample was run in triplicate.

Results and Discussion

In thermal degradation testing, each commercial base oil and its spiked samples were heated to 230°C and held at that temperature on the TGA, with the total mass loss of the sample after 24 hours of treatment recorded. Each sample was run in duplicate, the average mass losses are displayed in Table 1. Both the NyeTorr® 6351 and Brayco® 815Z exhibited minimal mass loss when run as neat oils, both less than 5% loss but with NyeTorr® 6351 exhibiting the least mass loss with only a 0.12% reduction over the course of 24 hours. When mixed with a Lewis acid prior to heating, both oils exhibited mass loss, which is an indicator of degradation. For each oil the identity of the Lewis acid (Fe_2O_3 vs. FeF_3) didn't have a significant impact on the extent of degradation. The two oils did differ in the extent of mass loss demonstrated, the Brayco® 815Z exhibited a 90% mass loss in each of its runs. Given that 10% of the sample size was the spiked Lewis acid that was not expected to volatilize at this temperature even if degraded, it can be assumed that 100% of the oil in the sample was broken down and volatilized. In contrast, NyeTorr® 6351 only exhibited about 45% mass loss in the presence of Lewis acids; presumably some oil was left intact and hadn't degraded (Figure 3). It is worth noting that for both Brayco® 815Z and NyeTorr® 6351 nearly all degradation occurred within the first 45 minutes of the experiment, the change in mass from hour 1 to hour 24 of the test was negligible. While the identity of the Lewis acid didn't significantly impact the amount of degradation, the identity did impact how long it took for degradation to begin; samples treated with Fe_2O_3 typically didn't have degradation onset until approxiamtely 30 minutes into the run, whereas samples treated with FeF_3 exhibited onset of degradation within the first 15 minutes of the run. This observation is consistent with other experiments reported in the literature where it was found that Fe_2O_3 was converted to FeF_3 during PFPE degradation, and that FeF_3 is an even stronger Lewis acid catalyst [2].

An additional experiment was performed to test the efficacy of a new additive hypothesized to impart resistance to Lewis acid-catalyzed degradation on susceptible base oils. For this experiment pure Fomblin®

Z25 was studied, which is known to degrade rapidly in the presence of Lewis acids at elevated temperatures [5,10]. Consistent with the literature, neat Fomblin® Z25 exhibited minimal mass loss when heat treated (4.44%) but when heat treated in the presence of FeF_3 it underwent complete and rapid degradation. A sample spiked with the "booster" additive at a 1% treat rate was prepared and subjected to the same heat treatment in the presence of FeF_3. Indeed, this sample exhibited stability comparable to that of the neat base oil, with only a 5.12% mass loss over the course of the 24 hour test, in contrast to the 90.36% mass loss exhibited by Fomblin® Z25 in the presence of FeF_3 without the booster additive (Figure 4).

Table 1. Total Mass Loss of Oil Samples Test on TGA

Lubricant	Lewis Acid	Total Mass Loss (wt%)*
Brayco® 815Z	--	3.12%
Brayco® 815Z	Fe_2O_3	89.11%
Brayco® 815Z	FeF_3	90.59%
NyeTorr® 6351	--	0.12%
NyeTorr® 6351	Fe_2O_3	45.19%
NyeTorr® 6351	FeF_3	45.40%
Fomblin® Z25	--	4.44%
Fomblin® Z25	FeF_3	90.36%
Fomblin® Z25**	FeF_3	5.12%

*average of 2 runs
** spiked with booster additive

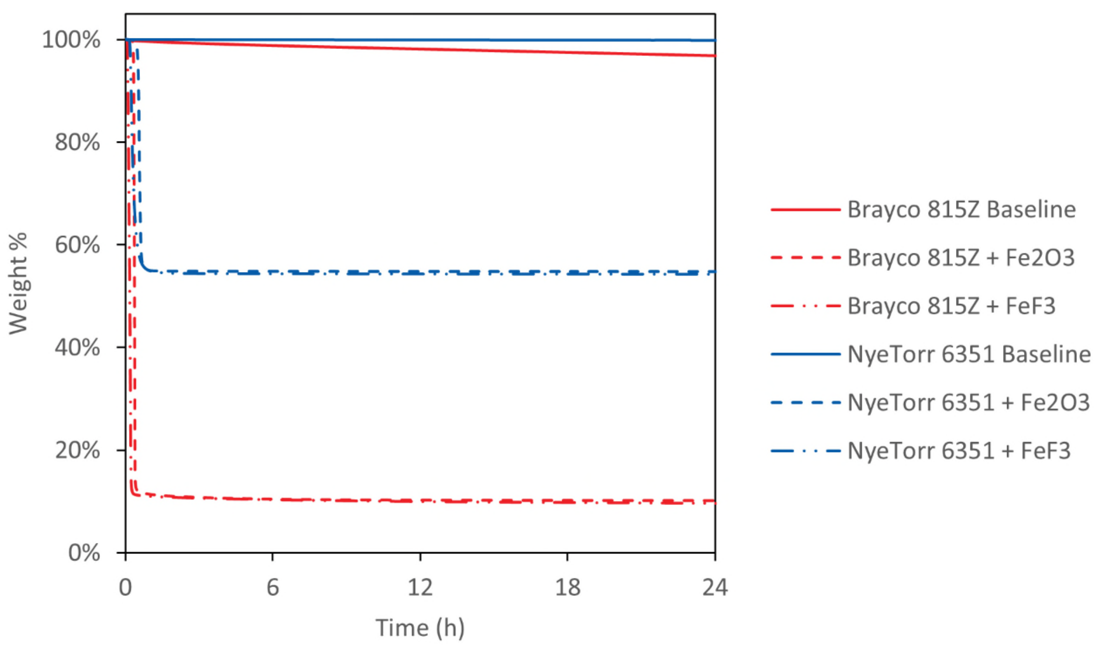

Figure 3. TGA traces of commercial oils in the presence and absence of Lewis acids

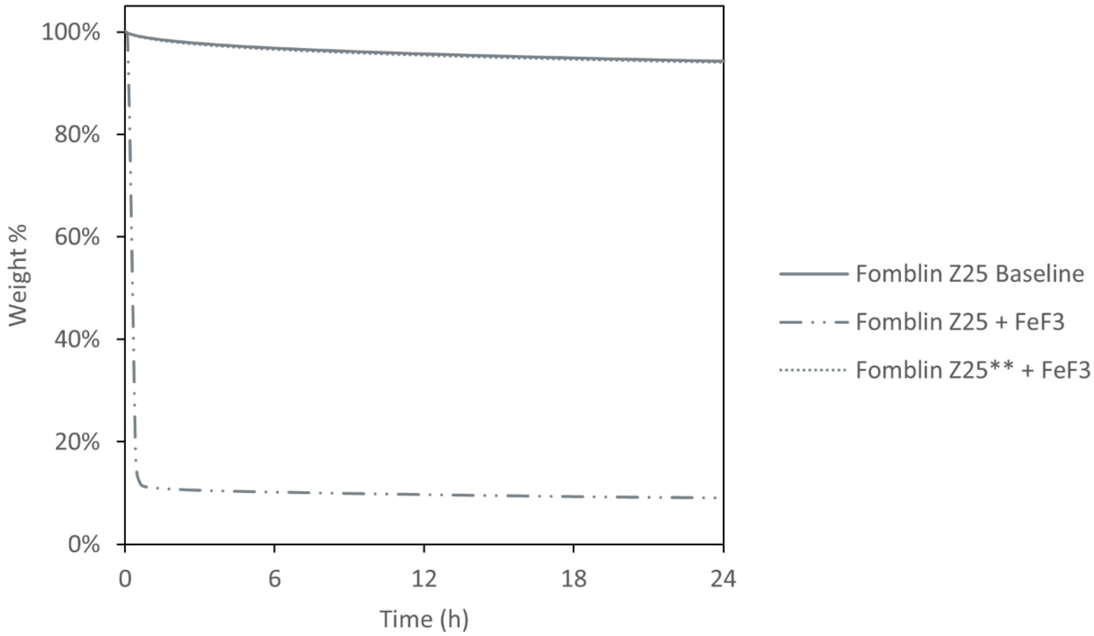

Figure 4. TGA traces of Fomblin® Z25 in the presence and absence of Lewis acids and booster additive

Grease samples were treated in a manner similar to oils on the TGA, results are displayed in Table 2. For both Braycote® 601EF and NyeTorr® 6350EL, mass loss exhibited by the neat greases was minimal, comparable to what was observed for their neat base oils. In the presence of Lewis acids, the story becomes more convoluted. This is perhaps due in part to the fact that greases are more complex formulations with a greater number of components than typically seen in oils, perhaps the most impactful of which is the thickening system. In the neat oils it is feasible that some mixing of the sample and interaction with the Lewis acid would occcur *via* convection currents; with the presence of the thickener network in greases, mixing would be inhibited – this could cause greater variability in performance. In the case of Braycote® 601EF, exposure to Fe_2O_3 resulted in an average mass loss of 11.42%, while exposure to FeF_3 had a more drastic impact with an average mass loss of 30.80%. In contrast, NyeTorr® 6350EL was less affected by the presence of Lewis acids, with merely an average 1.55% mass loss in the presence of Fe_2O_3 and 3.51% mass loss average in the presence of FeF_3 (Figure 5). The improved resistance to degradation in NyeTorr® 6350EL is likely due to the greater inherent resistance demonstrated by its base oil, NyeTorr® 6351 discussed above, as well as impacts from the thickener and other components in its formulation. Inspired by the results of our experimentation with Fomblin® Z25 and the booster additive, an experimental sample of NyeTorr® 6350EL was prepared with this booster (referred to as NyeTorr® 6350EL Plus) to see if its performance could be enhanced even further. As expected, the NyeTorr® 6350EL Plus demonstrated baseline performance comparable to that of NyeTorr® 6350EL, and in the presence of Lewis acids its mass losses were the lowest observed in the study, all less than 1.5% (Figure 6).

Table 2. Total Mass Loss of Grease Samples Tested on the TGA

Lubricant	Lewis Acid	Total Mass Loss (wt%)*
Braycote® 601EF	--	3.60%
Braycote® 601EF	Fe_2O_3	11.42%
Braycote® 601EF	FeF_3	30.80%
NyeTorr® 6350EL	--	0.52%
NyeTorr® 6350EL	Fe_2O_3	1.55%
NyeTorr® 6350EL	FeF_3	3.51%
NyeTorr® 6350EL Plus	--	0.83%
NyeTorr® 6350EL Plus	Fe_2O_3	0.78%
NyeTorr® 6350EL Plus	FeF_3	1.07%

*average of 2 runs

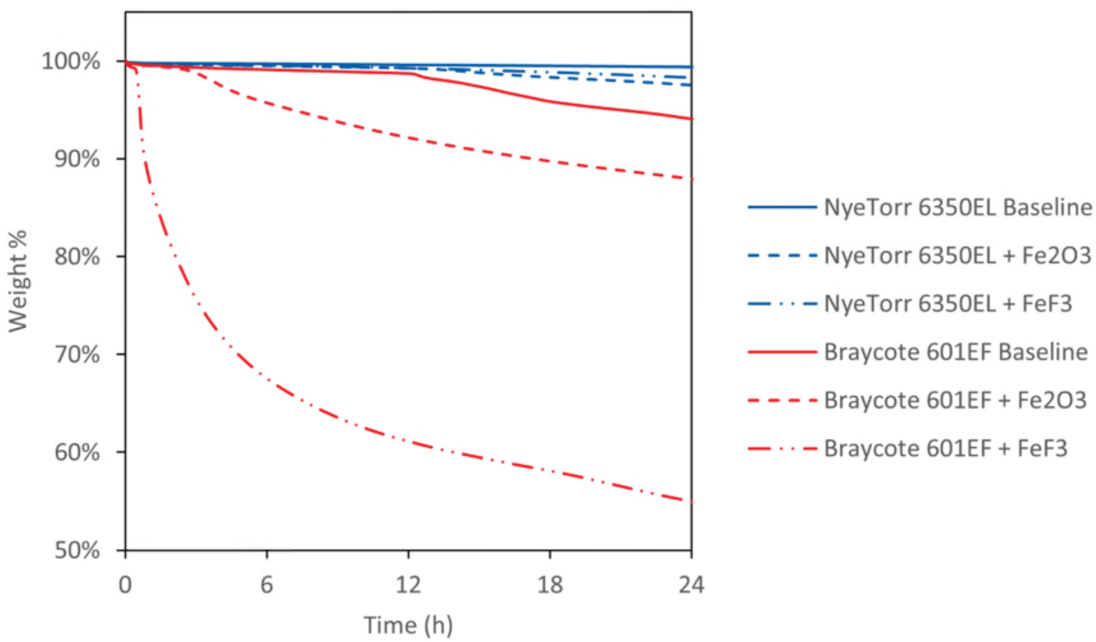

Figure 5. TGA traces of commercial greases in the presence and absence of Lewis acids

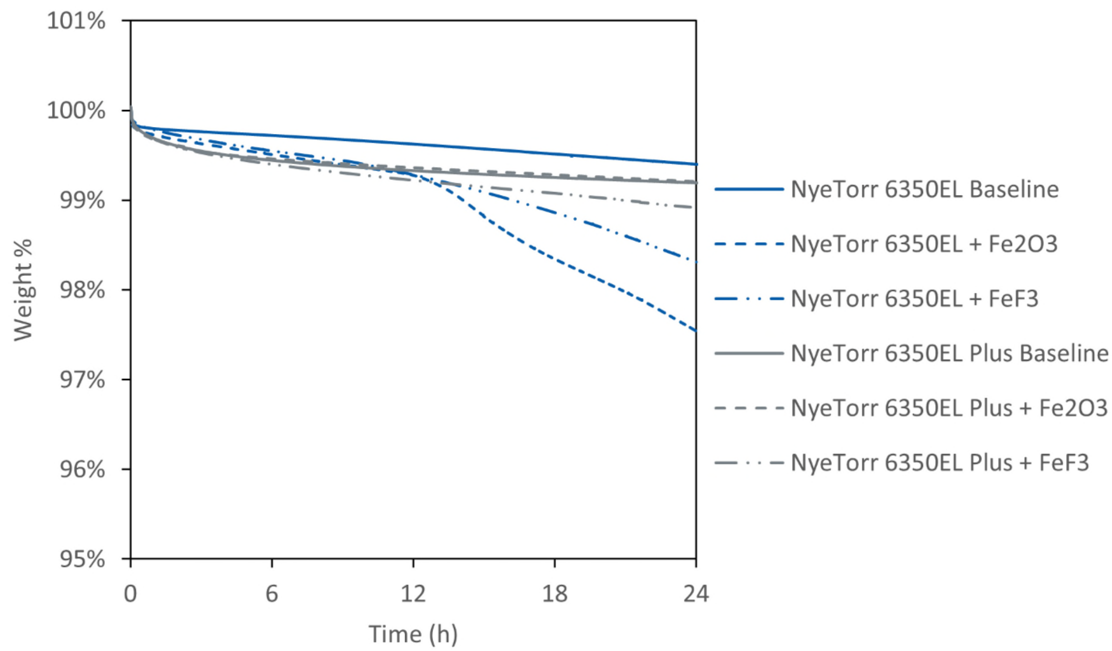

Figure 6. TGA traces of NyeTorr® 6350EL and the experimental NyeTorr® 6350EL Plus in the presence and absence of Lewis acids

Grease samples that were treated with Lewis acids and then heated in an oven were tested on the SRV to evaluate their wear performance. Additional controls were performed including neat, untreated samples as well as greases subjected to heat alone without Lewis acids present. Figures 7-9 show images of Braycote® 601EF, NyeTorr® 6350EL, and the experimental NyeTorr® 6350EL Plus samples as they appeared before and after heat treatment in the presence and absence of Lewis acids. Note that all greases appeared more brown or orange after being heated in the presence of FeF_3, which is likely due to the FeF_3 reacting with the air to form other inorganic, oxidized compounds – reactions happening alongside and in addition to any interactions with the PFPE fluid.

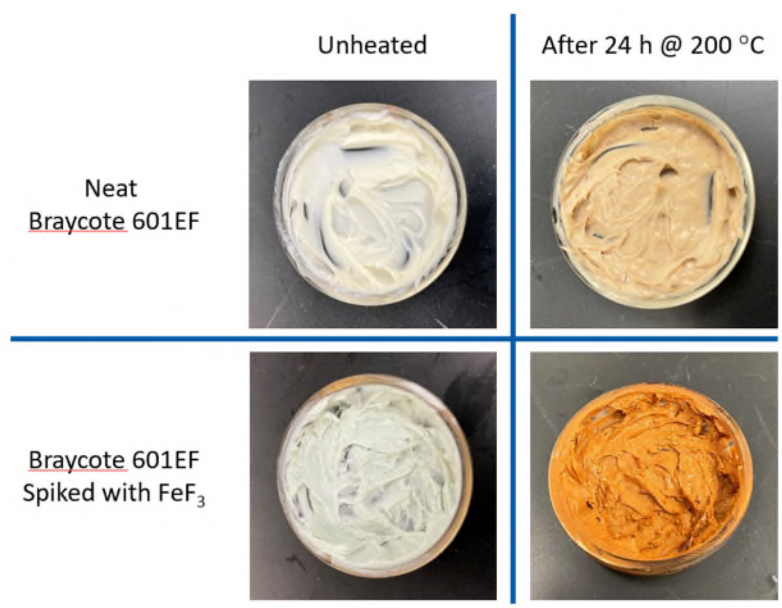

Figure 7. Images of Braycote® 601EF under different treatment conditions

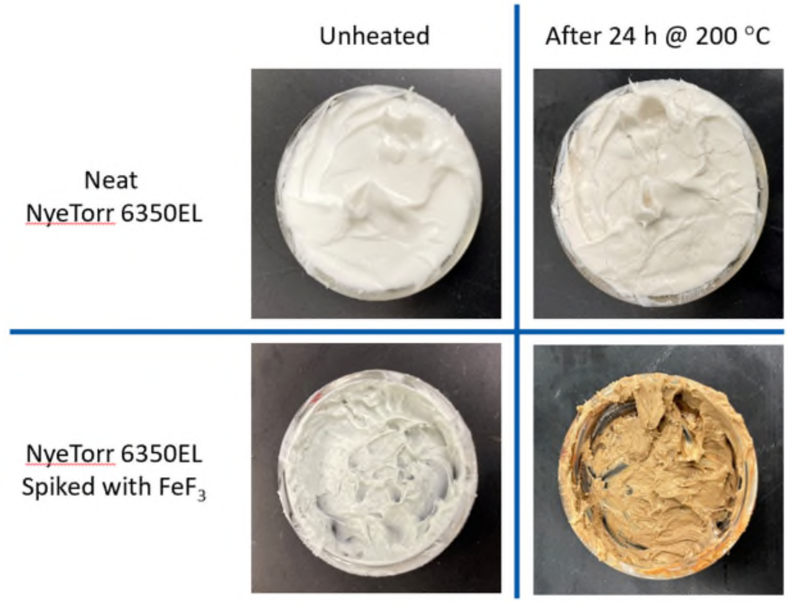

Figure 8. Images of NyeTorr® 6350EL under different treatment conditions

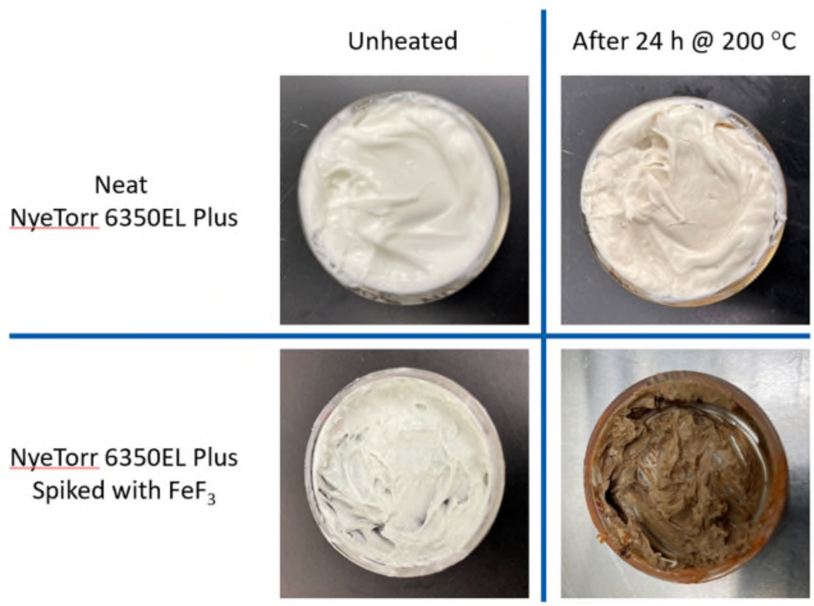

Figure 9. Images of NyeTorr® 6350EL Plus under different treatment conditions

Since none of the samples evaluated on the SRV ran to completion, wear rates were calculated and reported for each so that fair comparisons could be made, these results are displayed in Figure 10. Predictably, each grease had the best performance (lowest wear rate) when not subjected to heat or Lewis acid exposure. Heat treatment resulted in slightly higher wear rates, but the highest wear rates observed were after exposure to Lewis acids. Braycote® 601EF and NyeTorr® 6350EL performed comparably; after exposure to Fe_2O_3 NyeTorr® 6350EL performed better than Braycote® 601EF, but after exposure to FeF_3 the Braycote® 601EF offered the slightly lower wear rate when compared to NyeTorr® 6350EL. Of note, wear rates were higher for both greases after exposure to Fe_2O_3 than they were after exposure to FeF_3. This is potentially due to the fact that FeF_3 is itself a good lubricant – one of the things that make PFPEs effective lubricants is a minor amount of breakdown resulting in FeF_3 formation on the metal surface, which itself functions as an excellent solid lubricant [12] It is possible that the Fe_2O_3 spiked samples had artificially inflated wear rates due to the Fe_2O_3 particles present, which are not effective solid lubricants. Perhaps of greatest note, the NyeTorr® 6350EL Plus sample (containing booster additive) offered superior wear protection even in the presence of Lewis acids. After treatment with either Fe_2O_3 or FeF_3, NyeTorr® 6350EL Plus offered wear rates nearly half of those observed for Braycote® 601EF and NyeTorr® 6350EL. While NyeTorr® 6350EL Plus is still an experimental sample, it appears that it could be an excellent solution for applications where wear protection in the presence of Lewis acids is essential.

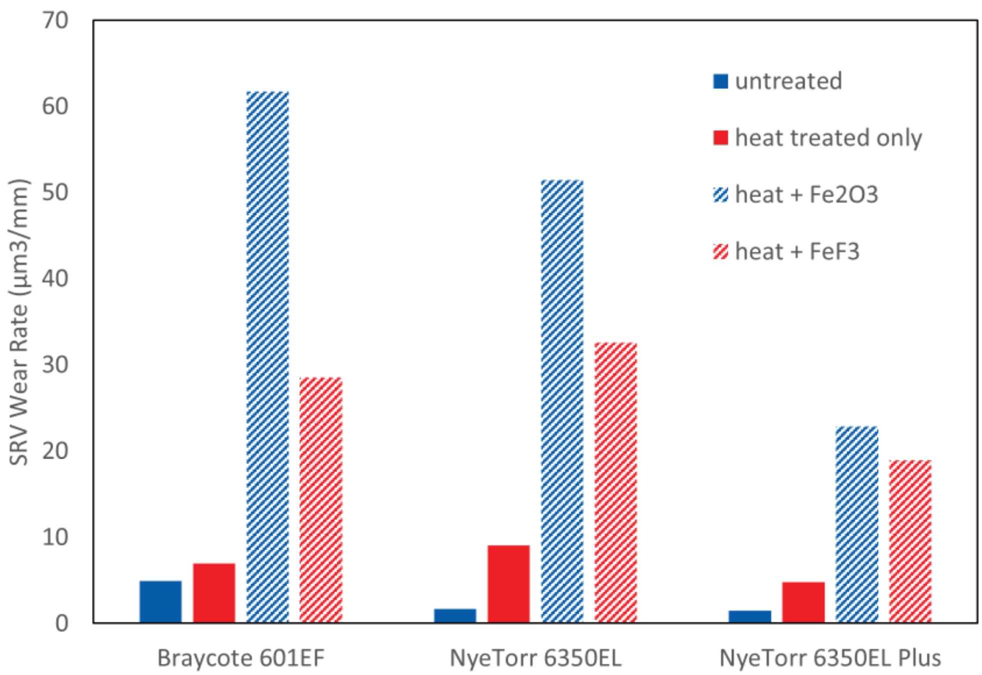

Figure 10. SRV® wear rates for greases subjected to Lewis acid exposure

To evaluate greases' performance in an environment more closely resembling those found in space applications, the Vacuum 4 Ball Wear Tribometer was employed. Similar to the data collected on the SRV, samples were heated in an oven while in the presence of Lewis acids. This testing is still ongoing; currently average wear scar diameters for commercial greases neat and untreated can be reported as a baseline, as well as commercial greases after being subjected to heat in the presence of FeF_3. Preliminary data displayed in Figure 11 indicates comparable performance of Braycote® 601EF and NyeTorr® 6350EL, with Lewis acid treatment having little impact on wear performance. This is in contrast to what was observed in the SRV® testing, where exposure to Lewis acids resulted in significant increases in wear rate of the samples. That being said, it could be that the test conditions used were not harsh enough for us to obtain good resolution in relative performance between the samples studied. This work is ongoing, as performance in a vacuum environment is a critical evaluation for lubricants used in space applications.

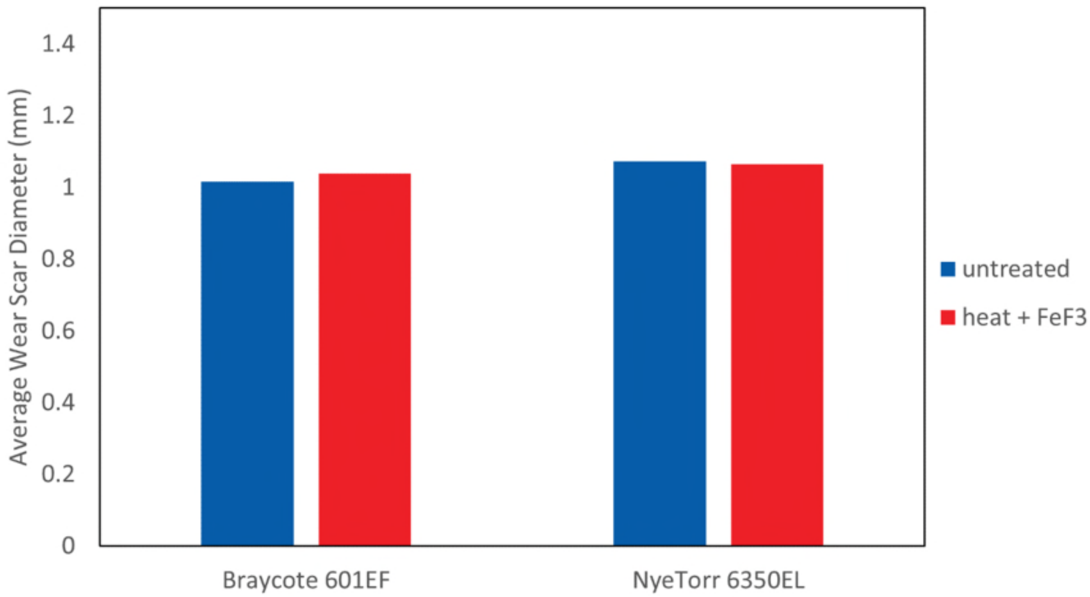

Figure 11. Vacuum 4 Ball Wear average scar diameters for greases before and after Lewis acid exposure

Conclusions

Formulating with raw materials that are inherently resistant to Lewis acid-catalyzed degradation results in lubricants with greater resistance to the phenomenon. NyeTorr® 6351 and NyeTorr® 6350EL offer greater resistance to Lewis acid-catalyzed degradation in thermal studies when compared to heritage products used for space applications. Base oils lacking inherent resistance to Lewis acid degradation can gain resistance with the addition of a “booster” additive; its properites are effective in greases as well as in oils. SRV® wear data after heat treating grease samples in the presence of Lewis acids indicated comparable performance of Braycote® 601EF and NyeTorr® 6350EL. A standout performer was the experimental grease NyeTorr® 6350EL Plus, demonstrating nearly half of the wear rates observed for the commercial products tested. Vacuum 4 Ball Wear Tribometer data indicates that both Braycote® 601EF and NyeTorr® 6350EL offer comparable wear protection in a vacuum environment, regardless of whether treated with Lewis acids or not – this testing will be further refined to gain a better understanding of the impact of Lewis acids on lubrication in the vacuum environment.

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