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# Liquid Space Lubricants Examined by Vibrational Micro-Spectroscopy

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July 2008

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# Liquid Space Lubricants Examined by Vibrational Micro-Spectroscopy

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## Abstract

Considerable effort has been expended to develop liquid lubricants for satellites and space exploration vehicles. These lubricants must often perform under a range of harsh conditions such as vacuum, radiation, and temperature extremes while in orbit or in transit and in extremely dusty environments at destinations such as the Moon and Mars. Historically, oil development was guided by terrestrial application, which did not provide adequate space lubricants. Novel fluids such as the perfluorinated polyethers provided some relief but are far from ideal. With each new fluid proposed to solve one problem, other problems have arisen. Much of the work performed at the National Aeronautics and Space Administration (NASA) Glenn Research Center (GRC) in elucidating the mechanisms by which chemical degradation of space oils occur has been done by vibrational micro-spectroscopic techniques such as infrared and Raman, which this review details. Presented are fundamental lubrication studies as well as actual case studies in which vibrational spectroscopy has led to millions of dollars in savings and potentially prevented loss of mission.

## Introduction

The future of space exploration will include missions to the Moon and Mars. A typical scenario of a mission might include boosting exploration equipment into orbit, perhaps low earth orbit (LEO) for assembly, then continuing to a destination. Possible environmental exposure conditions while in LEO are summarized in table 1. These values were abstracted from the LEO exposure of the Hubble Space Telescope between April of 1990 and December of 1993 and represent typical values that might be encountered (de Groh, et al. 2001). Other exposure conditions and their effect on system failures have been documented (Fusaro and Khonsari 1992 and the databases referenced therein). Many of the values in table 1 are dependent on the direction in which the surface is exposed with respect to the positions of the Earth or the Sun. For transport from LEO, conditions progressively change toward conditions experienced on the Moon, with the possible exception of experiencing lower temperatures the further from the Sun. Conditions on the destinations, our Moon and Mars, are summarized in table 2. The effect of these environments on space lubricants used for designing future surface exploration vehicles is critical. A recent review by Jones and Jansen (Jones and Jansen 2005) presents an overview of the state-of-the-art in space lubricants through January of 2005.

TABLE 1.—POTENTIAL ENVIRONMENTAL  
CONDITIONS FOR LOW EARTH ORBIT

Exposure	Range	Units
Temperature	-100 to 50	°C
X-Ray fluence (1 to 8 Å)	40	J m <sup>-2</sup> yr <sup>-1</sup>
Other electromagnetic radiation	UV, Vis, IR	°
Electron fluence (>40 keV)	5.4×10 <sup>12</sup>	cm <sup>-2</sup> yr <sup>-1</sup>
Proton fluence (>40 keV)	2.2×10 <sup>9</sup>	cm <sup>-2</sup> yr <sup>-1</sup>
Atomic oxygen fluence (primarily in RAM direction)	8.6×10 <sup>19</sup>	cm <sup>-2</sup> yr <sup>-1</sup>

TABLE 2.—POTENTIAL ENVIRONMENTAL CONDITIONS FOR THE MOON AND MARS

Moon		
Exposure	Range	Units
Vacuum	$1 \times 10^{-11}$	torr
Temperature	-170 to 110 (day cycle)	°C
Dust	Magnetic	
Space radiations	X-Ray, $\gamma$ -Rays, UV, Vis, IR	
Day cycle	27.3	Day
Mars		
Exposure	Range	Units
Atmosphere (CO <sub>2</sub> )	0.01	Atm
Temperature	-143 (pole) to 27 (equator)	°C
Dust	electrostatic	
Dust size	50 to 100	micron
Day cycle	24.6	hr
Dust height above surface	10 to 20	cm
Wind velocity	up to 15	m/s
Permafrost depth ( $\pm 40^\circ$ from equator)	1	m
Space radiation	not evaluated	
Regolith oxidant components	peroxides and superoxides	

In the early days of satellites the lubricants were not the failure points and hence, the requirements for lubricating fluids were significantly less as the satellite typically failed for other reasons. With the development of more robust hardware, the need for better lubricants became imperative as failures were, and in many cases still are, caused by failure of lubricated moving mechanical assemblies.

The first Apollo missions including a vehicle Lunar Roving Vehicle (LRV) to transport the astronauts (Apollo 15 in 1971 and Apollo 17 in 1972) had specifications for operation in an environment of  $\pm 120^\circ\text{C}$  for as much as two years. In order to expedite the delivery schedule, these requirements were eventually reduced to operation in 0 to 100 °C for only a few hours. In order to provide adequate lubrication to the harmonic drive with lubricants available at the time, the traction drive assemblies (one per wheel each containing a harmonic drive, motor, etc.) were hermetically sealed with a nitrogen atmosphere at approximately 50 kPa (380 torr or 1/2 atmosphere) pressure. Two separate reports list the lubricant for the harmonic drive as either Krytox (Dupont) 143AZ oil (Jones and Nola 1971) or Krytox 143AC oil (Coward 1973), both of which are perfluorinated polyether, PFPE, oils. This author believes that Krytox 143AC was actually used. Other lubricating materials included Krytox 240AC grease in the traction drive assembly motors and steering motors as well as silicone based oil in the suspension damper. Dry lubrication was also employed. For comparison, from the data reported for Lunokhods 1 and 2, the Russian robotic lunar explorers, they were designed to provide 4 months of service. Two lubricants are listed: one characterized as an organo-silicon based fluid (Lunokhod 1 2007) and the other undocumented (Lunokhod 2 2007). The current specifications for lubrication of NASA rovers and other surface system moving mechanical assemblies include a five year lifetime which will not be met by any of the liquid

lubricants employed for the Apollo missions because the use of hermetically sealed chambers containing artificial atmospheres is impractical for this time span in the lunar environment. Further, the future missions will require longer traverses than a few miles (Morea 1993) in what is now known to be an abrasive environment created by fine particulate lunar regolith (Gaier 2007).

Simultaneous with the development of vacuum tribometers has been a parallel effort to develop better space lubricants. New fluids have been developed and employed like the Pennzanes (Royal Dutch Shell), multiply alkylated cyclopentanes (MACs). Other promising classes of oils that have been proposed and partially characterized include silahydrocarbons and ionic fluids. The ideal lubricant would perform under all of the extreme conditions outlined in tables 1 and 2; however, many mechanisms will not experience all of these conditions at the same time and some conditions may never be experienced at all. For example (1) A mechanism enclosed in a sealed housing may never experience high vacuum but on the Moon could definitely be exposed to the full range of temperature extremes. (2) For devices with labyrinth seals, the exposure to vacuum will either change with time or additional hardware to repressurize the compartment will add complexity to the component. It would be of great benefit to have a large number of qualified lubricants on the shelf for various space conditions during the early stages of design for exploratory vehicles and stationary systems. Further efforts to develop space qualified oils, additives and greases to fill the gaps in current generation lubricants is an area that must be actively pursued in order to provide a better selection of lubricants for designing systems that will be employed in space, on the Moon, and on Mars in the future.

### **Factors Influencing Choice of Lubricants**

The following section is included to provide some perspective to readers unfamiliar with the field of space tribology, the study of friction, wear and lubrication, particularly for use in space (Fusaro and Khonsari 1992).

Volatility is a primary cause of oil and additive loss under reduced pressure conditions. This property is directly related to the vapor pressure, a value tedious to measure for space oils and additives. The most rapid loss occurs when the atmosphere over the bulk oil is reduced to “zero”, or in other words, an ultra high vacuum for a given use temperature. Consequently, the vapor pressure of an oil versus temperature is a major consideration in choosing an appropriate oil for space lubrication, and generally the lower the vapor pressure, the more attractive a lubricant is. In practice, evaporation rate is the more useful information as it allows for direct determination of the amount of lubricant required over the lifetime of a given mission, though it is component geometry dependent.

Lubricant condensation may occur once molecules leave the site of application, redepositing themselves elsewhere. This can be a critical problem if the condensation occurs where it will damage or impede function of another component, for example, on lenses or optical windows.

Weightlessness is a contributor to lubricant selection in that conventional pumping systems for lubricant replenishment are not feasible. Under these conditions, lubrication systems traditionally rely on surface tension to distribute lubricant, hence, this is a property of base oils that is of importance in choosing an appropriate oil for a given application. In recent years several novel “pumping scenarios” have been proposed to deliver lubricant to starved mechanisms, although none have found widespread use (Glassow 1976; James 1977; Lowenthal et al. 1985; Marchetti et al. 2003). Greases are the primary choice for lubricating large mechanisms. On the Moon and other planets this is not an issue—the issue is added complexity and the consequential increased weight associated with oil transport mechanisms and reservoirs.

Thermal conductivity of the lubricant and tribocouple should also be considered. In vacuum, there is no gas convection mechanism for heat transport away from the site of lubrication, potentially leading to excessive heating which can degrade the lubricant. Lower viscosity provides some relief as it allows circulation to remove and redistribute the heat, but in general, circulation is not considered as a major pathway for cooling. Both lower viscosity, typically associated with lower molecular weight, and heating lead to undesirable higher vapor pressures.

Liquid lubricant viscosity and its variation with temperature are primary design considerations involving a number of trade-offs. In general, the higher the molecular weight, the greater is the viscosity, and the higher the temperature, the lower is the viscosity which is typically more of a concern. As viscosity decreases, creep increases providing both a higher surface area for evaporative losses and a direct pathway for liquid migration from the application site. In terms of tribology, higher viscosities are beneficial in that elastohydrodynamic lubrication can occur at lower velocities thus alleviating the lubricant thickness required for good boundary lubrication. On the other hand, higher viscosity leads to higher torque in the lubricated device resulting in higher power demand for operation.

Oxygen, readily available in air, serves as a reactant which enhances the friction and wear capabilities of various tribocouples by several mechanisms. First, oxygen reacts with many metals to form surface oxides which have better friction characteristics than the bare metal contact. Second, oxygen is known to be a direct participant in the functioning of additives. Lack of oxygen must be considered when choosing a lubricant where no oxygen will be available to assist the lubricant. As a reactant, oxygen may also serve to degrade carbon based lubricants during ground testing. Properties of lubricants for space considerations must be adequately evaluated for both atmospheric operation (ground testing) and space conditions (the actual application). Water is another reactant that is of considerable importance in the functioning of lubricants (Pepper 2005). The same considerations should be given to water when choosing a lubricant; however, the effect of moisture extending the lifetime of lubricants is as yet unexplained.

Radiation damage can be categorized by type of source, electromagnetic (photon) or particulate. On earth, the atmosphere shields some electromagnetic radiation such as ultraviolet but this shielding does not occur in space. Sources of electromagnetic radiation span the spectrum from ionizing high energy gamma rays through the visible into the Infrared (IR) region. Ionizing and ultraviolet radiation can promote direct degradation of lubricants through well established photochemical pathways. Absorption of IR radiation serves as a heat source resulting in thermal degradation pathways for the lubricant. Solar particulate radiation usually has a shallow penetration depth although these charged particles can do considerable damage to organic compounds. Most particulate radiation is easily shielded but is still a concern for exposed lubricants, and ultra-high energy particles, so-called Cosmic Rays, are nearly unshieldable without the thick atmospheric protective layer enjoyed on Earth.

General debris should have no impact on lubricant performance in space. However, for crew exploration vehicles and rovers, surface dust from the regolith, which is readily kicked up, often sticks tenaciously to all surfaces it contacts (Landis 1998; Gaier 2007). Certain components of the lunar regolith are magnetic and both lunar and Martian soils are readily charged. This puts an additional requirement on lubrication of exposed components in that the lubricant should not act as a getter of particulate matter, which would jam a contact or generate excessive abrasive wear. The surface dust on the Moon is composed of very fine structures (particles) from millennia of pulverization by impacts and, because there is no atmosphere or erosion mechanism for polishing, these dust particles also have sharp edges and points.

The chemistry of tribocouples, parts in relative moving contact, also greatly affects the performance of various lubricants. Certain elements, such as titanium in alloys, are notorious for decomposing perfluorinated polyether base fluids to form catalytic metal fluoride which further increases the decomposition rate. Hence, choice of both construction materials and lubricant must be carefully considered during the design stage. The reverse effect has also been demonstrated—coating metal surfaces with various solids and surface treatments has been shown to increase lubricant lifetime. Additives have generally proven ineffective for a number of reasons, but the majority fail because the vapor pressures of the additives are greater than the vapor pressure of the base oil.

To evaluate which lubricants and tribocouples are best suited for space application, traditional tribometers have been adapted for vacuum operation. Tribometers (for example the vacuum 4-ball tribometer, a modification of the American Society for Testing and Materials, International (ASTM) 4-ball method) typically give wear information, coefficient of friction, and relative lifetime information. These experiments do not provide direct information about the mechanism of lubricant failure which as a chemical process requires post mortem analysis of the tribocouples and lubricant residues. The use of surface analytical techniques has greatly enhanced the understanding of tribocouple chemistry and

lubricant degradation. X-ray photoelectron spectroscopy (XPS) has been used to look at bearings after failure to identify surface species which may have contributed to failure. Though XPS gives limited chemical structure information, it was used to identify metal fluoride formation during the degradation of PFPE lubricants. This analysis allowed researchers to test PFPE decomposition on metal fluorides to establish the catalytic behavior and degradation pathways associated with the metal fluorides. XPS does not provide enough molecular structural information for the examination of the carbon based liquid lubricants. The vibrational spectroscopic techniques; however, have long been used for organic chemical structural elucidation as spectral band locations and patterns provide unique identifies of functional groups. To this end, a great deal of research at GRC has been devoted to the use of vibrational spectroscopy (and in particular micro-spectroscopy) to determine degradation pathways of the base oils, which will be reviewed here.

## Experimental

For perspective, figures 1(a) to (c) are offered to show example rigs used to acquire tribological data. While many types of tribometer exist, at our facility we have developed and primarily use Spiral Orbit Tribometers (SOT), four-ball tribometers, and Pin on Disc (PoD), tribometers, figures 1(a) to (c) respectively, modified to work in high,  $<10^{-6}$  torr, to ultrahigh vacuum,  $10^{-8}$  torr or lower. It should be emphasized that there are many varieties of tribometers but not all are adapted to ultra high vacuum, a criteria for doing space tribology. Simple blanketing of the sample with even research grade inert gas has been brought into question due to trace contamination from water (Pepper 2005). Because of the ability to obtain relative lifetime data for lubricants in the SOT, we have moved away from PoD testing in recent years. The SOT, in which a ball rolls between a fixed plate and a rotating plate, simulates an angular contact ball bearing. The load, often chosen to provide a mean Hertz stress of 1.5 GPa, is applied through the fixed plate. The combination of high load, moderate speed, and small amount of lubricant (typically  $\sim 50 \mu\text{g}$ ) allows the system to always operate in the boundary lubrication regime where lubricant quickly degrades. The ball rolls and pivots in an ever increasing spiral, the track, and the orbit is reestablished by the guide plate. The force the ball exerts on the guide plate determines the friction coefficient, since the ball is sliding between the disks at the moment of measurement. The flat regions where the ball contacts both the guide plate and the stationary disc simultaneously are referred to as the scrub. From these figures it is obvious that the contact area where tribology occurs is very small. For example, the ball in the SOT is

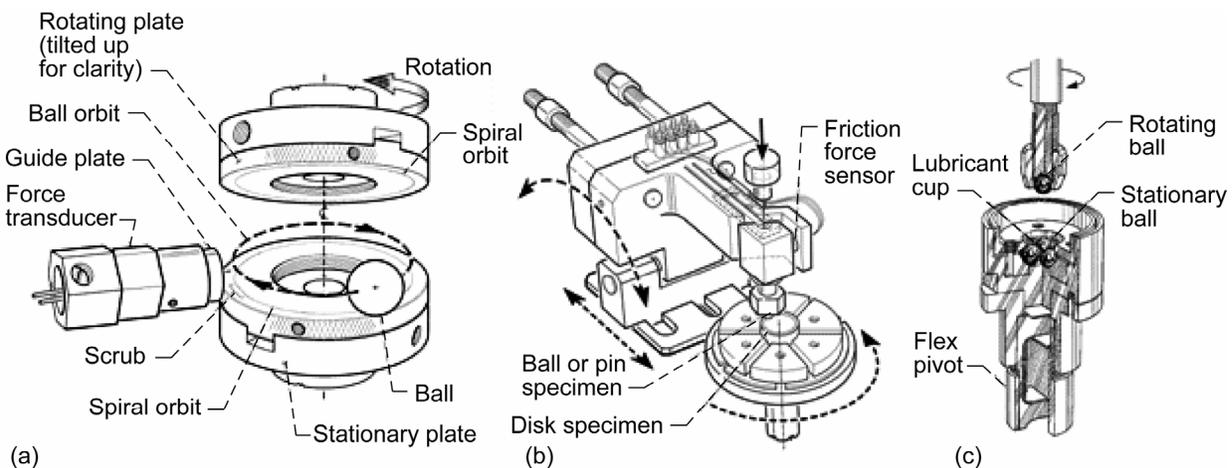


Figure 1.—Schematic diagrams of tribometers adapted to vacuum conditions. (a) Spiral Orbit Tribometer (SOT). (b) Pin on Disc tribometer (PoD). (c) Four ball wear tester.

typically 12.7 mm diameter (although smaller balls have been used) and in the PoD the pins are shaped to resemble a 6.35 mm diameter ball, both of which have contact regions of only a few tens of square micrometers. In the four-ball rig, all balls are held rigidly in position and the load is applied vertically while rotating the top ball. After a fixed number of rotations, the experiment is stopped to measure the wear scar dimensions on the balls. This process is repeated several times and the lost material is calculated for each step in the process. A plot of material loss versus the number of rotations allows computation of wear rate. In all of these experiments high quality tribocouples, metal tribological contacting surfaces often used in space bearings, are employed, such as 440 °C stainless steel hardened to 58–62 Rockwell C.

The use of conventional Fourier transform infrared (FTIR) and Raman spectrometers to characterize synthetic reaction products is a normal part of organic chemistry which will not be discussed, nor will their use for quality control quantification of additives to oils, another obvious use of these techniques. A more interesting use of the techniques is in the determination of reaction products after application of the oils, which is referred to as post mortem analysis. Because the surface area of interest in post mortem work is typically small, tracks on the order of 0.1 mm across, or the curved surface of a ball bearing, the techniques suited for small area analysis have gained popularity. In our lab we use micro-FTIR and micro-Raman which employ microscopes offering great advantage in analyzing small spot areas, with Raman particularly well suited. As a scattering technique, radiation is collected from almost any type of surface (curved or flat) with spot sizes down to the low micrometer dimension even though it does not provide the rich spectral data of IR. The FTIR microscope must either use a flat surface or the crown of a curved surface, as the radiation is directional and in addition must examine a much larger area, tens of micrometers diameter (Katon et al. 1980)—in our instrument the standard aperture interrogates an area of 100 mm in diameter. This means that flat surfaces or the crown of a curved surface must be oriented normal to the microscope axis. Since a large amount of information is obtained from balls, particular attention to orientation is important, especially if employing grazing angle objectives to enhance sensitivity (Pepper 1995).

### **Lubricant Quantification in Studies by FTIR**

In earlier studies, thin lubricant layers were applied to PoD and SOT discs and the thickness quantified by direct reflectance micro FTIR with grazing angle objectives to enhance sensitivity (Shogrin et al. 2003; Jones and Poslowski et al. 1999; Shogrin et al. 1995). Calibration was performed by establishing optical constants for Beer's law by measuring film thickness with ellipsometry in the visible wavelength range (Pepper 1995). This method of quantification of the amount of lubricant has several drawbacks for the intended tribological use. In these studies, the lubricant was applied as a thin uniform film to the discs. Consequently there was no method of quantifying the amount of lubricant consumed during the experiment. If the lubricant could be quantified then additional information about the relative lifetime of lubricants could be gained by normalizing the number of orbits at failure by the micrograms of lubricant consumed, or a normalized lifetime.

Therefore, a method of metering a known amount of lubricant to the ball was devised and the amount of lubricant was quantified by gravimetry, a tedious measurement for a few micrograms of oil on a ball itself often exceeding 10 g. In this method, the ball is magnetically held against a horizontally rotating shaft at one point, designated here as its north pole, and a measured volume of the lubricant solution diluted in solvent is applied to the rotating surface from a gas tight micro syringe. After the solvent evaporates, the weight gained by the ball is determined by a microbalance with a resolution of  $\pm 2 \mu\text{g}$ . The smallest weight of lubricant that can be reliably quantified in this manner is in the 10  $\mu\text{g}$  range.

A major limitation of infrared micro-spectroscopy arises where the coating thickness is not uniform over the surface and quantification is desired. Analysis thus requires spectral information from the entire surface or at least a statistically significant fraction thereof. However, to examine the surface of a 12.7 mm diameter ball bearing with a 100  $\mu\text{m}$  diameter viewing objective, over  $10^6$  spectra would be required and this is not feasible.

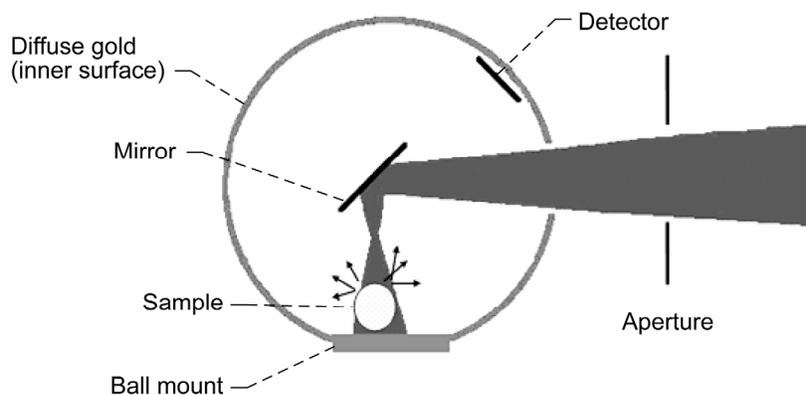


Figure 2.—Schematic of integration sphere technique for examining ball bearings.

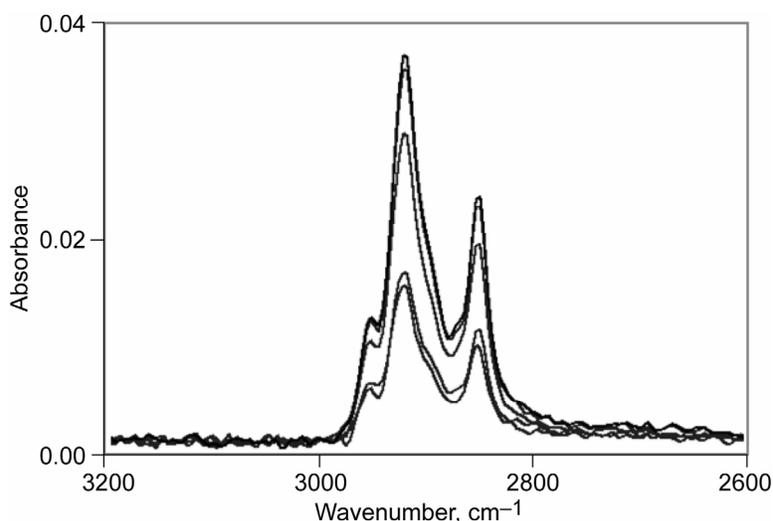


Figure 3.—Spectra acquired from 50  $\mu\text{g}$  of Pennzane on five different ball positions in an integrating sphere.

Integration spheres have long been available as attachments for FTIR spectrometers. Although they are used traditionally for scattering transmission or reflectance measurements from materials and surface coatings, it is also possible to mount objects having symmetrical geometry such as balls within integrating spheres and to obtain spectra from significant portions of the complete surface, thus averaging over local heterogeneity (Street and Pepper et al. 2007).

Figure 2 shows a simplified schematic of the integration sphere with ball bearing sample. The intensity of the incoming beam is not uniform, but is a complex function of the spectrometer aperture and beam steering optics within the FTIR bench. For a flat sample at the reflectance port, the beam converges on the center of the sample, but for three dimensional samples, the higher the sample, the further the center of the sample will be from the center of the beam such that the beam covers an estimated 20 to 50 percent of the surface of the ball. Coverage depends primarily on (1) the aperture setting, (2) the ball diameter, and (3) the positioning of the ball with respect to the center of the beam. Because of these uncertainties, five spectra, see figure 3, were obtained from each ball to provide information from the entire surface area. The positions investigated on the ball included the north and south pole and three evenly spaced positions about the equator. Optimization of other parameters is described in the paper. Figure 4 is a plot of the average absorbance for the C-H stretch bands at  $2923\text{ cm}^{-1}$  for the five positions where the spectra were taken on different 12.7 mm balls versus the lubricant charge. Using this methodology it was determined that the limit of detection was significantly lower than by the gravimetric

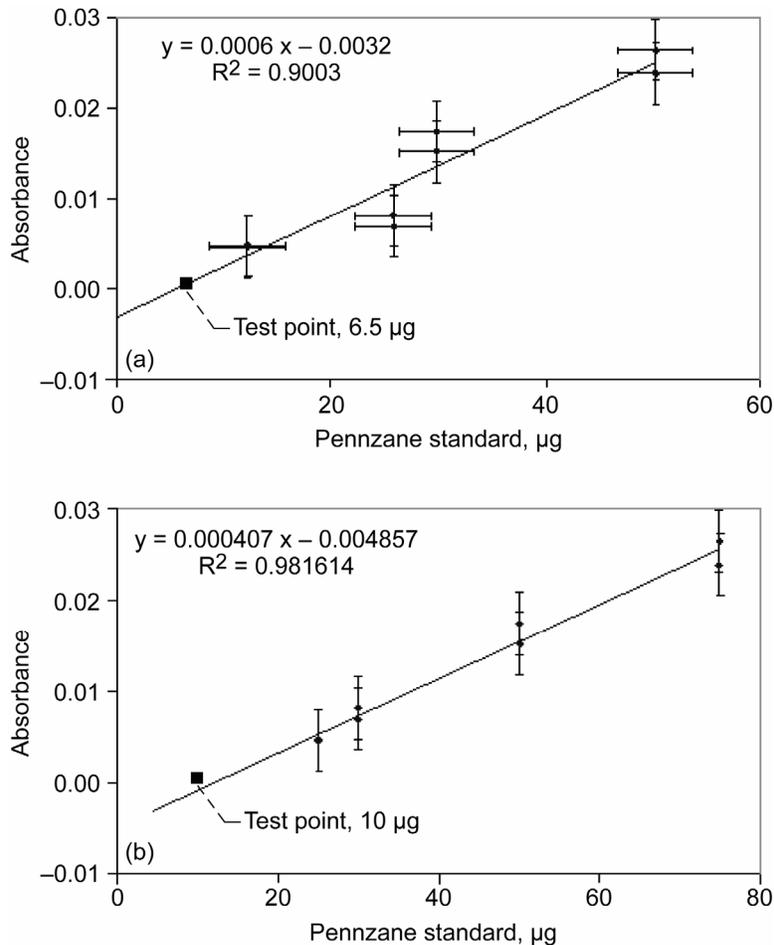


Figure 4.—Plot of average absorbance for the C-H stretch bands versus the lubricant charge. (a) lubricant charge in microgram. (b) lubricant charge in microliter of standard delivered.

method. Additional benefit is derived by the incident IR beam striking the ball at oblique angles similar to the enhancement observed in grazing angle spectrophotometry. Calculations indicate a five fold enhancement in absorbance over what would be predicted using two passes at normal incidence through the sample on the ball.

### Qualitative Information From Tribometer Studies

Microscopes, both Raman and IR, are the preferred method for examining small area on balls, discs and guide plates where residual used oil may be observed in droplets or for small damage features, etc. The microscopes also have the advantage that the interrogation area is often sufficient to examine the center of tracks on discs, residual material adjacent to tracks, and the scrub region of discs and guide plates. During the course of IR examination of balls it became evident that new techniques needed to be introduced to look at the condition of the entire ball rather than being biased by events occurring on small areas. The introduction of the integrating sphere technique as shown in figure 2 has greatly improved our ability to acquire information quickly. The technique originally developed to quantify lubricant coatings applied to balls prior to testing at loadings below those readily quantifiable by gravimetry has demonstrated utility in post mortem analysis. Figure 5 clearly shows a significant amount of material is left on a ball after failure. In this particular case the residual material was freely washed from the ball indicating that it was not polymerized during tribology and for some reason failure occurred prior to its consumption.

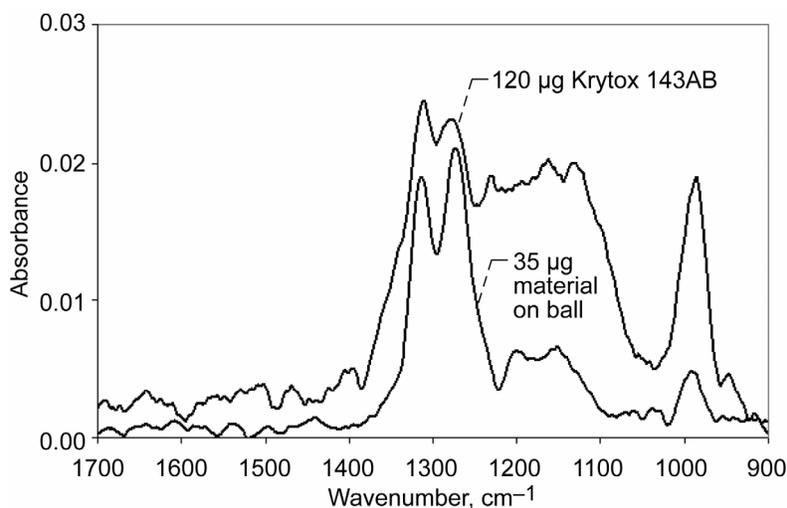


Figure 5.—Spectra of ball lubricated with Krytox 143AB and post mortem ball from SOT run with the same lubricant.

## Results and Discussion

### Properties of Ideal Lubricants

As a consequence of the above discussion, there are some desirable features that should be considered when choosing a lubricant for nonterrestrial applications. Aside from the obvious friction and wear properties of the lubricant and tribological surfaces combinations, the most important consideration is that the base oil survive launch, travel through space, and the destination site environment. Low vapor pressures are a primary consideration where prolonged exposure to vacuum is a part of the lifetime. The oil must remain liquid over a wide temperature range while providing adequate viscosity characteristics. At the low temperature extreme the ability of oil to perform is governed by its pour point, the temperature at which the oil will no longer flow, which is always higher than the melting point. Viscosity index, a measure of viscosity as a function of temperature, is used to rank performance, the higher index oils being preferred. It should be thermally stable and resistant to attack from oxygen, both molecular and atomic, and radiation tolerant. It should be a reasonable thermal transport medium. The oil should also be capable of being formulated with additives to provide good extreme pressure lubrication and for making of greases.

A large number of base oils have been developed over the past four decades including hydrocarbon (HC) and perfluoropolyalkylether (PFPE) materials as summarized in table 3. Mineral oil based fluids, esters and silicone oil are old technology materials still in use today for niche applications. Many of the mineral oil types are no longer manufactured and users have resorted to stockpiling to ensure future supplies. The earlier esters are no longer in production; however, a few low volatility neopentylpolyol esters are still marketed such as UC4 and UC9 (Nye Lubricants 2007), all of which contain trixylenyl phosphate additive which has a high vapor pressure. The silicone based materials are poor boundary lubricants and tend to degrade into abrasive by-products.

Additives require either solubility in the base oil or the ability to form a long term stable emulsion or dispersion. Additives are required for enhancing base oil properties, such as for extreme wear, oxidation, or poor boundary lubrication. For these specific purposes, the additive is best soluble in the base oil. To produce greases, soaps have been employed. These are soluble in the base oil and provide the desired degree of thickening to prevent creep and other problems associated with migration of the oil from the site of lubrication. Solid insoluble additives like Teflon have long been used to thicken the PFPE based greases. Solid additives need to disperse well and not separate from the base oil over time, while still releasing oil to the site of application to maintain lubrication.

TABLE 3.—BASE OILS FOR SPACE LUBRICATION

Base fluid	Benefits	Drawbacks	Examples
<i>Hydrocarbon based</i>			
Mineral oil	Good boundary lubricants, Easily formulated	Requires additives, High vapor pressure	Apeizon C
Esters	Good boundary lubricants	Modest vapor pressure	UC <sub>4</sub> , UC <sub>7</sub> , UC <sub>9</sub>
Polyalphaolefin	Good boundary lubricants	Modest vapor pressure	Oils 132, 182, and 186
Multiply Alkylated Cyclopentanes	Good Boundary lubricant, Easily formulated, Good Chemical stability	Higher vapor pressure than PFPE, Poorer viscosity than Silahydrocarbons at 20 °C	Pennzane
Ionic liquids	Low vapor pressures, Good friction coefficients	Not fully developed, Many are proprietary formulations	
<i>Silicon containing hydrocarbon based</i>			
Silicone oil	Low vapor pressure, Low pour point	Poor boundary lubrication, Abrasive decomposition products	Versilube F-50
Silahydrocarbons	Good boundary lubrication, Low volatility	Higher vapor pressure than PFPE	Tri-, tetra- and penta-silahydrocarbons
<i>Nonhydrocarbon based</i>			
Perfluoropolyether	Good chemical and thermal stability, High viscosity index, Low pour points	Poor Boundary lubrication, Traditional additives not soluble	Krytox, Fomblin, Demnum

Soluble hydrocarbon oil additives have been around for decades and are well established for terrestrial operation. Many of the conventional additives like tricresyl phosphate have been directly used in space lubricants with mixed success. These additives are readily soluble in the hydrocarbon space oils, but have significantly higher vapor pressures than the base oils. Consequently, they evaporate quickly in vacuum resulting in lubrication with the properties of the base oils. The hydrocarbon base oils tend to provide better boundary lubrication than the PFPE based oils, but they still require antioxidants, anticorrosion and antiwear additives yet to be discovered. In addition, environmental and toxicological concerns must be addressed where the additives have the potential to evaporate and redeposit themselves elsewhere.

### Base Oils

Each of the base oils summarized in table 3 has at least one significant shortcoming. PFPE have short lifetimes and decay into corrosive products; the HC have higher vapor pressures and pour points than desired; and conventional additives are even more volatile. The silicone based materials are poor boundary lubricants and tend to degrade into abrasive products. Newer hydrocarbon fluids, Pennzanes, also referred to as multiply alkylated cyclopentanes (MACs), have significantly improved properties such as friction coefficient, lifetime, vapor pressure and the ability to dissolve additives, and are now effectively replacing all old technology hydrocarbon fluids and some PFPE fluids. The PFPE base fluids have heritage and therefore are still used in spite of their poorer friction coefficient, lifetime and lack of additives. Their advantages remain their exceptionally low vapor pressures and wider useful temperature range. Ionic fluids show promise because of their extremely low vapor pressures, adequate friction coefficients and superior lifetimes to PFPEs. A final class of oils, the silahydrocarbons, has also demonstrated useful properties such as low vapor pressures, and adequate friction coefficients and lifetimes. All of the aforementioned hydrocarbon based materials are more attractive as space lubricants because additive development theory for HCs is better understood than additive theory for PFPEs.

## Post Mortem Analysis of Space Lubricants—Fundamental Investigations

### *Tribological Experiments on Base Oils and Greases*

Figure 6 is a typical plot of SOT data from which important tribological information is obtained. The plots of Coefficient of Friction (CoF) versus the number of orbits provide a ranking of the lubricants' ability to perform. Aside from the CoF information, the life—number of orbits to failure (with failure defined as a CoF above 0.2) divided by the amount of lubricant employed in micrograms—provides a normalized lifetime used to quantitatively rank the ability of the oil to provide adequate lubrication. For a good lubricant these SOT experiments may run for several weeks, hence the need for reliably measuring smaller and smaller amounts of initial lubricant on the ball. This data provides little information regarding mode of lubricant failure which typically progresses through several steps. During the initial phase (Region I) of the experiment the friction coefficient remains relatively constant as lubricant is consumed and during which time a “friction polymer” begins to form. Towards the end phase of lubricant life the friction coefficient begins to rise to  $>0.2$  (Region II—typically the last few hundred orbits) where degradation of the last of the original lubricant as well as the friction polymer occurs. During the final stage of the experiment (Region III) the friction coefficient rises to well over 0.3 due to metal on metal contact as the lubricant is exhausted.

Both mid-experiment and post-complete degradation examinations of balls and tracks in SOT experiments with PFPEs were made by various vibrational spectroscopic techniques (Herrera-Fierro et al. 2000). Due to the small track width FTIR microscopy is routinely employed. Direct reflection off the track or crown of the ball provides adequate sensitivity to see any residual unused lubricant which would exist in ridges directly adjacent to the wear track or in small patches on the surface of the ball. Our quantitative observations on patches of lubricant have consistently demonstrated little change in the IR signature (bands at 1310, 1270, 1127, and 990  $\text{cm}^{-1}$  for PFPE) from Region I indicating little structural change and that lubricant is distributed between ball and disc. In Region II, quantitative analysis of the lubricant in the track indicates near complete loss of material and thickness varies greatly. In Region III little lubricant is left in the wear track or on the ball and the IR spectrum of the remaining brown friction polymer on both disc and ball is quite different. Broad bands in the 3600 to 3000, 1669 and 1436  $\text{cm}^{-1}$  areas of figure 7 correlated well with other literature studies of polymeric fluorinated carboxylic acids (Carré and Markowitz 1985; Eapen et al. 1994; Xuan et al. 1993). The presence of a strong broad band at 3600 to 3000  $\text{cm}^{-1}$  suggests that some of the adsorbed carboxylate is hydrogen bonded. The strong carbonyl absorption band in a dimerized carboxylic acid typically found between 1700 to 1725  $\text{cm}^{-1}$  is not

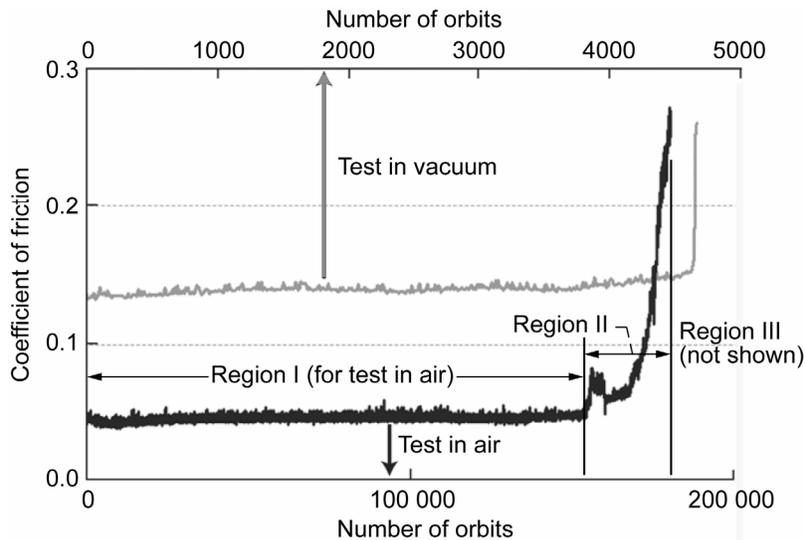


Figure 6.—SOT runs for Krytox 143AB in air and in vacuum.

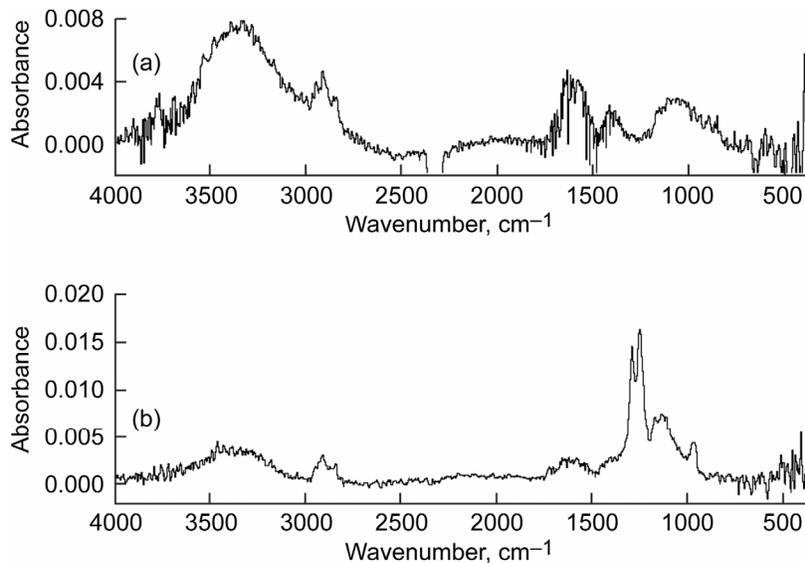


Figure 7.—Infrared spectra taken in integration sphere from post mortem balls of SOT runs with Krytox 143AB. (a) Ball run in air. (b) Ball run in vacuum.

apparent in the spectra. These IR spectra were indicative of sorbed metal ions, the two new peaks that appeared indicated the formation of the carboxylate ion. The carboxylate ion binds to metal ions and gives rise to an asymmetric stretching band between 1550 to 1650  $\text{cm}^{-1}$  and a symmetric stretching band near 1400  $\text{cm}^{-1}$  (for example see fig. 7(a)). The frequency of each of these two bands varies slightly depending on the metal ion involved (Nakamoto 1997; Tackett 1989).

Raman microspectroscopy is not often used as a quantitative technique but still provides very useful information in the post mortem analysis of oil degradation. The Raman signatures on all tribocouples tested no matter what the oil employed are quite similar. They exhibit two extremely broad bands, often on a highly sloping luminescent background (figs. 8(d) and (e)). All carbon materials yield unique Raman spectra, even with only subtle structural changes. Discrete molecules, such as the fullerenes, nanotubes, or nano-onions, figure 8(a), and well ordered  $\text{sp}^3$  material like diamond give rise to sharp spectra, unlike the broad peaks from post mortem analysis centered at 1604  $\text{cm}^{-1}$ , an  $\text{E}_{2g}$  band commonly referred to as the G band, and at 1364  $\text{cm}^{-1}$ , referred to as the disorder or D band, which are indicative of  $\text{sp}^2$  bonding in graphitized amorphous carbon, figure 8(b), or fluorinated amorphous carbon. These spectra appear on all tribocouple surfaces, more strongly in pits and crevices in the worn metal parts.

The spectroscopic evidence led to the proposed degradation pathway for all PFPE involving defluorination, chain scission and formation of carbonyl end groups as suggested in prior literature (Carré 1985; Eapen et al. 1994; Xuan et al. 1993). Carboxylic acid groups form quickly when the carbonyl groups react with humidity in the air which in turn react with surface metal ion species to form the carboxylates. The resulting Raman spectrum arises from a fluorine deficient network which is graphitic in nature. Neither the graphitic network nor the carboxylate species would be expected to be soluble in the Freon solvent used to wash the surfaces prior to spectroscopic analysis.

One drawback from using a SOT to perform tribological investigations is the lack of wear data obtained from these rigs. The standard “four-ball” ASTM method D4172-94(2004)E1 adapted for ultrahigh vacuum measurements was used to compare wear rates produced by various PFPE fluids (143AC, S-200 and Z-25) with three synthetic hydrocarbons, a MAC (2001a) a MAC formulated with antiwear and antioxidant additives (2001) and an unformulated PAO (PAO-100) as well as an unformulated silahydrocarbon (pentasilahydrocarbon) (Jones and Poslowski, et al. 1999). The wear rates determined in this investigation were ranked as follows:

PFPE Z-25>>PFPE S-200>>PFPE 143AC>PAO-100>MAC 2001a>  
MAC 2001(formulated)>pentasilahydrocarbon

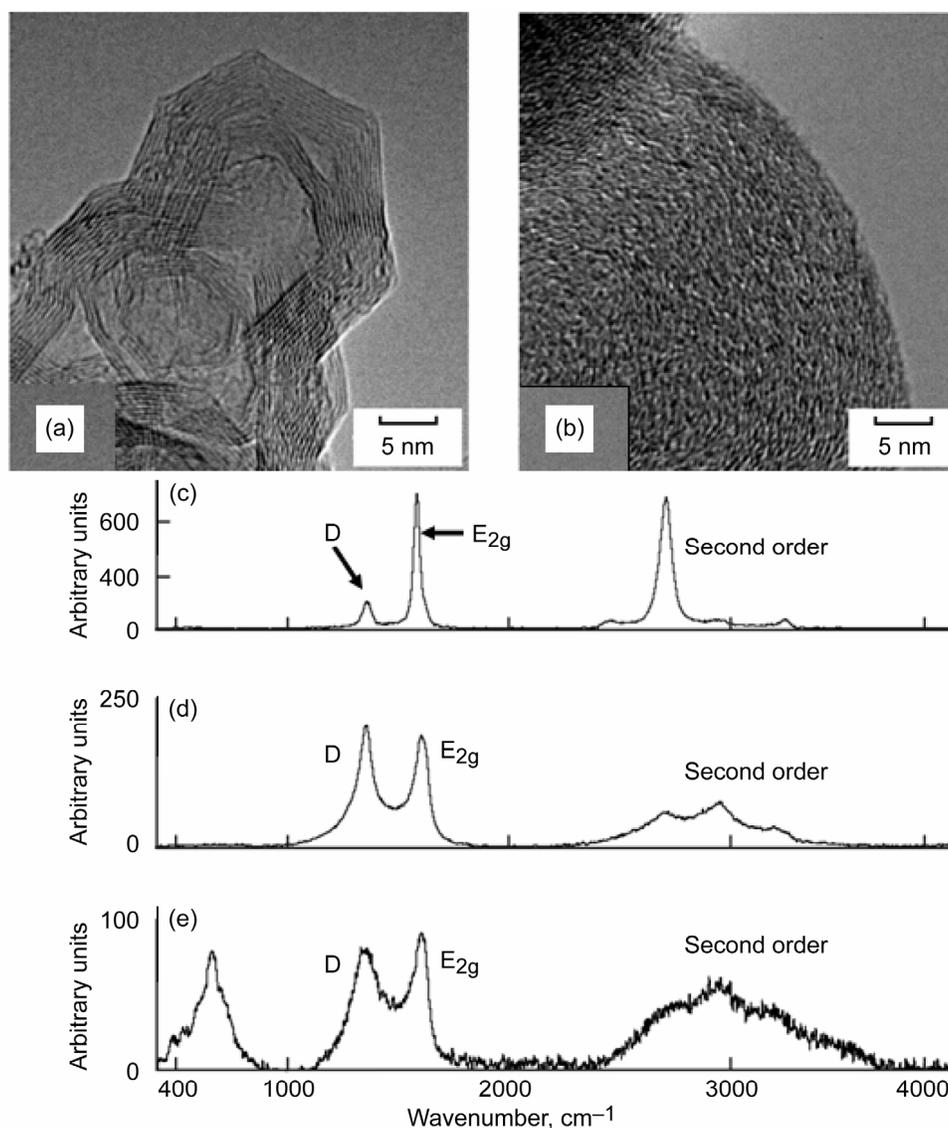


Figure 8.—Nanocarbon materials and their Raman spectra. (a) Carbon nano onions produced from (b) carbon black. (c) Raman spectrum of nano onions in (a). (d) Raman spectrum of post mortem SOT ball run with Krytox 143AB and nano onions in vacuum. (e) Raman spectrum of post mortem SOT ball run with Krytox 143AB and nano onions in air.

The last four of which are within statistical insignificance of each adjacent fluid. One stationary ball from the PFPE Z-25, PFPE S-200, PFPE 143AC, and MAC 2001a runs was washed with appropriate solvent, and on and off the wear scars were examined by FTIR and Raman micro-spectroscopies. From the IR spectra it was clear that the same decomposition mechanisms present in the prior investigation were present for the PFPEs in this study. Qualitatively, the quantity of the reaction products found as determined by IR spectral intensities correlated directly with the amount of wear for the PFPEs. The one HC lubricant examined showed little post wear material as determined by weak peaks in the 3000 to 2850 cm<sup>-1</sup> C-H stretch region of the spectrum. No other degradation signature was observed in the spectra for the MAC. Visual examination of balls from other lubricants showed negligible wear residue which is why these balls were not submitted for IR analysis. All Raman spectra revealed the same signature as previously detailed indicating that even the HC oil eventually decomposed into amorphous graphitic material.

Two commercially available ionic liquids (Covalent Associated, Inc., Corvallis, OR), referred to henceforth as IL-A and IL-B (for proprietary reasons) were used for vapor pressure determinations and tribological investigations (Street and Morales et al. 2007). Ionic liquids are salts, many of which are typically viscous fluids at room temperature characterized by negligible vapor pressures which led to study of their effectiveness as space lubricants. The vapor pressures were determined to be on the order of the best space liquid lubricants available and consequently the ionic liquids were tribologically evaluated in the SOT. Both fluids had better friction coefficients and better lifetimes than the PFPEs, but their lifetimes were distinctly less than MACs. Post mortem analysis of balls, guide plates and discs yielded information about the degradation mechanism for the ILs. Both ILs showed similar IR and Raman spectra for the wear areas. Broad IR peaks in the 1700 to 1600 and in the 3500 to 3100  $\text{cm}^{-1}$  regions are indicative of the build up of carbonaceous material. This trend is observed in the final stages of lubricant lifetime which is in line with all carbon based lubricants examined thus far. The broad Raman peaks centered near 1360 and 1580  $\text{cm}^{-1}$ , the D and G peaks respectively, are indicative of amorphous graphitic materials, the final stage of carbon based lubricants. Distinct lack of an identifiable second order peak in the 2500 to 3100  $\text{cm}^{-1}$  region of the Raman is another strong indicator of highly disordered graphitic material. Outside the wear areas, along the tracks in the discs and the scrub on the guide plate, droplets of unused or only slightly degraded ILs were identified from their IR signature. The amount of shed material was not quantifiable but presumably led to lower lifetimes being reported.

Greases are lubricant base oils thickened to semi solid form with either a soluble additive, for example, n-octadecylterephthalamate soap in the case of MACs, or with an inert insoluble material, PTFE Teflon in the case of PFPEs (Marchetti 2002). Because the greases are complex formulations, the method of lubricating the balls was changed to accommodate the presence of thickener prior to SOT testing. Grease was applied directly to a ball which was then rolled between two plastic membranes for distribution and removal of excess grease. The membrane process was repeated until approximately the correct amount of lubricant remained on the ball. In this investigation, it was important to confirm that a representative amount of thickener, especially in the case of the PTFE thickener, was applied to the balls along with the base oil. Infrared spectroscopy was used to measure the ratios of oil to thickener peaks to ensure that the composition of the grease was approximately preserved during lubrication. The IR spectra of the decomposition products in post wear testing were similar to those described previously.

Because the PFPE fluids have no soluble thickening agents, a study was undertaken to use nanostructured carbon material—carbon nano-onions shown in figure 8(a), which we have synthesized from amorphous carbon spheres shown in figure 8(b)—as thickener. This would also act as an auxiliary lubricant in the boundary lubrication regime. The lubrication role of solid particles introduced in a fluid lubricant, generally in greases, depends on the size of particle, on the number of particles, and on the geometry of the contact. The introduction of small particles is beneficial in boundary lubrication, when the ratio of film thickness to surface roughness is below 0.3 on the Stribeck lubrication curve, i.e., the lubricant film is not separating the surfaces in contact. The particles present in the lubricant have to be of small size to allow good fluid circulation within the contact and to not “jam” it. The amount of particles is generally low, a few percent in volume, and up to 10 percent for graphite. Under severe conditions, very small graphite particles can produce a layer which helps to protect the surfaces; however, it is the edge sites present at the graphitic lamella that promote decomposition of graphite lubricant. As an alternative to graphite we have evaluated the ability of graphitic nano-onions, 20 percent by weight, to make the oil into a thick grease while simultaneously improving the lubricating lifetime of the oil, Krytox 143AB, in SOT testing (Street et al. 2004). The anticipated advantage of the nanostructured carbon is that the particles are small and contain few reactive edge sites. Tests were conducted at room temperature in ambient air and ultrahigh vacuum. Examples of friction traces and the lifetime obtained are given in figure 6. The use of nano-onions did not improve the lifetime, nor did it change the friction coefficient of this PFPE oil run in vacuum: however, tests in air resulted in a very low friction coefficient (0.04 to 0.05) with a lifetime eight times greater than that of the original oil. Furthermore, the failure is more “progressive” compared to the one observed in vacuum. This is consistent with the behavior of graphite which requires traces of water to perform effectively.

Infrared analysis was also performed postmortem on the balls (fig. 7). Both types of balls showed peaks in the 2960 to 2850  $\text{cm}^{-1}$  range and a broad band in the 3360  $\text{cm}^{-1}$  range. These bands correspond to hydrocarbon impurities and possibly the PFPE degradation products respectively. Weak peaks in the 1600 and 1400  $\text{cm}^{-1}$  range indicative of carboxylate functional groups were found in both spectra. The ball run in vacuum (fig. 5 and 7(b)) revealed traces of material resembling the original Krytox 143AB having bands in the 1346 to 970  $\text{cm}^{-1}$  region of the spectrum. This result is unexpected since all the lubricant is typically consumed during a SOT experiment. The material from figure 5 freely washed from the ball and 35  $\mu\text{g}$  of Krytox 143AB would not have caused a failure indicating that the material was not the original lubricant. Further interpretation of the spectra is complicated by the fact that the ratio of band intensities as a function of concentration is not a constant for the Krytox fluids. The observed IR spectra are a complex function of the extinction coefficient ( $k$ ) and the refractive index ( $n$ ). In most cases, the band intensity ratio as a function of concentration is a constant but in the case of this PFPE, the refractive index contribution to the observed spectrum causes the shape of the spectra to vary considerably as a function of concentration (Pepper 1995). Raman analysis on the balls run in vacuum (fig. 8(d)) indicated the presence of a large quantity of graphitic material having well defined D (1341  $\text{cm}^{-1}$ ) and G (1592  $\text{cm}^{-1}$ ) peaks as well as multiple small peaks in the second order peak region (2520 to 3300  $\text{cm}^{-1}$ ). These spectra are not similar to those of the applied nano-onions (fig. 8(c)) but resemble conventionally degraded lubricants. It should be noted that we have evidence the nano-onions degrade to produce similar spectra, so it is not possible to distinguish the source of the degraded material. The ball run in air (fig. 8(e)) had similar spectral features but at much lower concentrations. Additionally, a moderate, broad unidentified peak occurred at 694  $\text{cm}^{-1}$  in all spectra for the balls run in air.

### ***PFPE Additive Investigations***

A major problem with the PFPEs is that they all have very short lifetimes relative to the hydrocarbon based fluids and PFPE decomposition products, being corrosive, attack the bearing metal. Over the years considerable effort has been expended developing soluble additives for these oils which will improve their performance. Because these lubricants decompose into corrosive products in the boundary lubrication regime, additive efforts have focused on enhancing performance under extreme pressure. In one study (Shogrin 1999) several organic functional groups were modified with long chain pendant perfluoropolyether moieties to increase their molecular weight (lowering vapor pressure) and to promote solubility in the base oils. Because only 1 percent additive was incorporated into the formulations no distinguishable change in the IR spectra was observed prior to four-ball wear testing these formulations. After rinsing the wear scars with appropriate solvents, the IR and Raman peaks of degradation products previously discussed became apparent. The amount of friction polymer in the residue, as determined by the intensity of the IR spectra, directly correlated to wear as in previous investigations. In a second study (Morales 1997), a conventional silane coupling agent, 3-aminopropyltriethoxysilane, was both added to a PFPE oil and used to pretreat the tribologically contacting surfaces. The silane was not soluble in the PFPE, hence the 1 percent mixture was sonicated to a milky color which was stable for two months. In space tribology, emulsions are not considered an ideal solution to the problem since the lubricated mechanism is launched into space for typically a five year mission with no relubrication. Emulsions must be stable for the mission duration for them to be successful.

Another method for improving the lifetime of PFPE fluids is to alter the tribocouples. In these investigations, the PFPE with additive was tested against both unmodified and silane treated tribocouples (Morales 1997). The surface treatment produced a 3  $\mu\text{m}$  thick coating with IR peaks at 3367 and 3298  $\text{cm}^{-1}$  (N-H antisymmetric and symmetric stretching vibrations, respectively), 2932 and 2840  $\text{cm}^{-1}$  (C-H stretching vibrations), 1100 and 930  $\text{cm}^{-1}$  (Si-O-CH<sub>2</sub> vibrations) and other characteristic peaks associated with this type of compound. In short duration PoD sliding experiments, the surfaces of the washed tribocouples appeared smoother and had lower wear than without silane added to the process, and the wear surface retained the IR signature of the silane treatment but did not show any signature of PFPE decomposition products. Examination of an uncoated pin run against a silane treated disc showed the IR

signature of the silane as a transfer film. In long duration experiments the wear scars lacked the IR signature of the silane but showed the signature typical of the PFPE degradation products.

### ***Tribocouple Modification as a Means of Improving PFPE Performance***

As stated previously, the major degradation pathway for PFPE lubricants involves production of corrosive end products. These corrosive products attack the metal bearing parts to produce metal fluorides which themselves are soft and lubricious, but ironically serve as catalysts to accelerate further decomposition (Carré 1985; Eapen et al. 1994). In the prior section additives were employed in attempts to react with the surface and prevent the degradation reaction. An alternate manner of accomplishing the same effect is to alter the chemistry of the tribocouples through surface alteration. Conventional surface treatments for bearings include acid passivation of the surface by chromic acid bath and phosphating by tricresyl phosphate soak which have been tested to see if they would improve PFPE lubrication (Shogrin et al. 2003). Only marginal improvement was observed. In another study (Jones et al. 2000), the balls employed were coated with a thin layer of TiC yielding somewhat improved performance. In both of these studies IR micro-spectroscopy was used to examine the degradation products, which were identical to degradation products of prior studies.

### **Post Mortem Analysis of Space Lubricants—Case Studies**

In prior sections we have mostly discussed studies performed under accelerated conditions in tribometers that simplify and therefore only simulate bearings. In order to fully understand how an actual tribological system will behave, component (i.e., an actual bearing) testing is performed. In these tests more realistic conditions are employed such as using a more representative load on a bearing which is fully lubricated. Under these conditions the test can last many months to years and run through millions of cycles. One such test was performed in order to evaluate the duplex bearing pair of the Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the Terra, EOS AM-1, satellite (VanDyk et al. 2002). The MODIS mission is to view Earth's entire surface, gathering data to better understand the global dynamics and processes occurring on land, in the oceans, and in the lower atmosphere. All observations are made through an extremely high resolution, optically and mechanically precise, scan-mirror motor/encoder assembly. The reliable performance of this assembly depends on two duplex bearing pairs lubricated with Pennzane SHF-X-2000, formulated with lead naphthenate. Upon disassembly, some lubricant discoloration was observed, but none of the bearings had visible damage. The bearings surfaces and oil were analyzed by a large variety of techniques including XPS, Scanning Electron Microscopy (SEM), Size Exclusion Chromatography (SEC), and Raman and FTIR micro-spectroscopy. Raman and IR analyses of the lubricant indicated the standard signature for non-degraded Pennzane. Based on the suite of analyses and because of the design similarities between the engineering model and life test unit, and the flight scanners, it was concluded that the flight scanners had sufficient margin for the five-year mission even though the SEC data indicated that some polymerization of the oil had occurred.

In late 2001, a pre-launch Geo-stationary Operational Environmental Satellite (GOES) instrument bearing failure occurred. A pre-qualified bearing seized resulting in a hold on the launch of two more units, one of which was on the launch pad in countdown at that time and could not be launched until the root cause for bearing failure was determined. The disassembled bearing was submitted to the author and IR spectroscopy was used to perform analysis of the failed bearing components. What little lubricant was detected on the balls and in the contact region of the inner race of the bearing appeared normal. From the IR data it was determined that an insufficient lubricant charge had been applied by the instrument manufacturer resulting in premature failure, a determination which allowed timely launch of the other two properly lubricated satellites.

To give perspective on the advantage of FTIR micro-spectroscopy, the entire IR analysis took less than half a day. The diagnosis was later confirmed by gravimetric analysis of the residual lubricant in the

bearing, a tedious process which required approximately three weeks. Extreme cost is involved with launch delays which include maintenance of launch readiness. Costs incurred by teardown, inspection and recertification of two satellites would be in the millions of dollars range, not to mention the loss of revenue associated with failure to generate data.

Each of the space shuttle body flaps contains four actuators to drive it (Street and Sovinski 2005). Four similar actuators in the tail drive the rudder/speed brake. These actuators are deemed as Critical 1 components where failure means loss of vehicle and crew. These components are connected in series; hence failure of one actuator in a section of the craft causes complete loss of function in that section. To date many actuators have seen service and have been disassembled for maintenance and refurbishment. Only one bearing from all the actuators examined thus far has the unique appearance of “black balls,” best described as black mirrors. The as received balls (both the black balls from the space shuttle Discovery body flap actuator and used balls from a similar body flap actuator on the space shuttle Atlantis) had been cleaned with Fluoroclean (Dupont) solvent. No further details were provided on the black balls and the used balls. Unfortunately, none of the extract was maintained for chemical analysis which might have indicated degradation of the lubricant itself. These bearings were previously lubricated with grease which contained a PFPE base oil. The IR signature of the black balls was extremely weak, possibly due to the aggressive sonication employed during the cleaning effort. Still, the classic IR signature of decomposed PFPE was evident in the 3600 to 3100  $\text{cm}^{-1}$  range as well as at 1732, 1534, and 1438  $\text{cm}^{-1}$ . The peak at 1732  $\text{cm}^{-1}$  is ascribed to unreacted carbonyls associated with the broad peak in the 3600 to 3100  $\text{cm}^{-1}$  range, and the peaks at 1543 and 1438  $\text{cm}^{-1}$  are carbonyls associated with metal ions. In the Raman, the classic D and G band signature was observed. An XPS analysis of the black balls indicated the presence of iron fluoride and iron oxides. The color of iron fluoride is dependent on the oxidation state and state of hydration and ranges from white to yellow to green. Iron fluoride has been shown to catalyze the decomposition of PFPE lubricants, which could have been accelerated by high temperatures experienced by the bearing during reentry. Under normal conditions iron fluoride is stable; however, under the conditions these balls were exposed to, it is likely that the iron fluoride hydrolyzed into iron oxides and hydrogen fluoride. Some iron oxides and mixed hydroxy-oxides are typically black which may have contributed to the black appearance of the balls. From the combination of XPS, IR and Raman spectroscopic results it was concluded (1) that this particular bearing had experienced extreme heat leading to both lubricant degradation and bearing condition and (2) that this was a singular event.

## Conclusions

Infrared and Raman micro-spectroscopies have been used to great advantage in tribological investigations, both fundamental and in actual case studies. In fundamental investigations IR spectroscopy can be used to provide quantitative information about the lubricant load employed in tests either by micro-spectroscopy or by using the integration sphere technique. Qualitatively the use of IR signature intensity has been correlated directly to wear behavior and to the elucidation of lubricant decay mechanisms. The decay mechanisms are confirmed by Raman micro-spectroscopy which is complementary to the IR in that the IR provides useful information on functional groups attached to the lubricant carbon backbone while the Raman provides information on the structure of the degraded backbone. In case studies, not only are failure mechanisms elucidated but the vibrational micro-spectroscopic techniques allow for large parts to be easily examined intact, facilitating diagnosis.

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<b>14. ABSTRACT</b> Considerable effort has been expended to develop liquid lubricants for satellites and space exploration vehicles. These lubricants must often perform under a range of harsh conditions such as vacuum, radiation, and temperature extremes while in orbit or in transit and in extremely dusty environments at destinations such as the Moon and Mars. Historically, oil development was guided by terrestrial application, which did not provide adequate space lubricants. Novel fluids such as the perfluorinated polyethers provided some relief but are far from ideal. With each new fluid proposed to solve one problem, other problems have arisen. Much of the work performed at the National Aeronautics and Space Administration (NASA) Glenn Research Center (GRC) in elucidating the mechanisms by which chemical degradation of space oils occur has been done by vibrational micro-spectroscopic techniques such as infrared and Raman, which this review details. Presented are fundamental lubrication studies as well as actual case studies in which vibrational spectroscopy has led to millions of dollars in savings and potentially prevented loss of mission.					
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