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Performance and Analysis of Perfluoropolyalkyl Ether Grease Used on Space Shuttle Actuators—A Case Study

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This Revised Copy includes the following changes: Report title has been changed. Tables have been reorganized and new data added. Figures 1 and 2 were replaced with two new figures to clarify the text. Text has been extensively expanded and now includes a more in-depth introductory discussion; some new results and improved interpretation thereof; several new references; and an Epilogue.

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Abstract

Actuators used on the United States space shuttle fleet are lubricated with unspecified amounts of Braycote 601 (Castrol Braycote) grease consisting of a perfluoropolyalkyl ether (PFPAE) base oil thickened with a polytetrafluoroethylene (PTFE) filler. Each shuttle has four body flap actuators (BFAs) (two on each wing) on a common segmented shaft and four rudder speed brake (RSB) actuators. The actuators were designed to operate for 10 years and 100 flights without periodic relubrication. Visible inspection of two partially disassembled RSB actuators in continuous use for 19 years raised concerns over possible grease degradation due to discoloration of the grease on several places on the surfaces of the gears. Inspection revealed fretting, micropitting, wear and corrosion of the bearings and gears. A small amount of oil dripped from the disassembled actuators. Whereas new grease is beige in appearance, the discolored grease consisted of both grey and reddish colors. Grease samples taken from the actuators together with representative off-the-shelf new and unused grease samples were analyzed by gravimetry for oil content; by inductively coupled plasma spectroscopy (ICP) for metals content; Fourier transform infrared (FTIR) spectroscopy for base oil decomposition; and by size exclusion chromatography (SEC) for determination of the molecular weight distributions of the grease oil. The Braycote 601 grease was stable after 19 years of continuous use in the sealed RSB actuators and was fit for its intended purpose. There were no significant chemical differences between the used grease samples and new and unused samples. Base oil separation was not significant within the sealed actuators. No corrosive effect in the form of iron fluoride was detected. The grey color of grease samples was due to metallic iron. The red color was due to oxidation of the metallic wear particles from the gears and the bearings comprising the actuators.

Introduction

The United States space shuttle fleet was originally intended to have a life of 100 flights for each vehicle, over a ten year period, with minimum scheduled maintenance or inspection. The first space shuttle flight was that of the Space Shuttle *Columbia* launched April 12, 1981. The disaster that destroyed the *Columbia* occurred on its 28th flight, February 1, 2003, nearly twenty-two years after first being launched. At that time as well as today, the Space Shuttle *Discovery* had the most flights. The 30th flight of the *Discovery* occurred August 10, 2001. This was approximately 17 years after its first flight launched August 30, 1984. As a result of the *Columbia* accident, concern was raised in July 2003 over possible grease degradation and wear of body flap actuators (BFAs) and Rudder/Speed Brake (RSB) Actuators rolling-element bearings made from AISI 52100 steel and gears made from AISI 9310. Visible inspection of partially disassembled *Discovery* RSB actuators was made September 16, 2003.

Each shuttle has four BFAs (two on each wing) on a common segmented shaft and four Rudder/Speed Brake (RSB) Actuators. The BFA comprises a single planetary gear set. The RSB comprises two planetary gear sets. The BFAs control the position of the large body flap that controls the attitude of the shuttle. The rudder speed brake (RSB) actuators act to extend the sides of the rudder to slow the shuttle on descent into the earth's atmosphere. The sealed actuators are lubricated with space qualified Grade 2 perfluoropolyalkyl ether (PFPAE) grease and were designed to operate for life without periodic relubrication and maintenance (Ref. 1).

Many of these actuators were without maintenance in excess of 20 years. During actuator refurbishment and inspection, there were external signs of corrosion on one of the RSB actuators. Pitted gears and discolored grease were observed inside. The grease-lubricated ball bearings and gears making up the actuators exhibited various degrees of wear. Both the bearings and gears operated under a dithering (rotation reversal) motion in the actuators when these systems were powered during ground operations (Ref. 1). Grease samples taken from the disassembled actuators ranged in color from beige taken from one actuator to grey and red taken from the second actuator. Beige is the original grease color. In addition, a small amount of oil dripped from one of the disassembled actuators.

Two studies were conducted by Oswald et al. (Ref. 1) and Krantz et al. (Ref. 2) to experimentally duplicate the operating conditions of the space shuttle actuator gears and input shaft ball bearings and determine their usable life. The results were compared to field data from the space shuttle fleet to establish actuator life and reliability.

The disassembled actuators presented a unique opportunity to assess the condition of the Grade 2 PFPAE grease that had been in use for at least 20 years lubricating the bearings and gears inside these actuators. One primary area of concern was the extent of base oil separation from the grease thickener leading to less than adequate lubrication. The other area of concern was base oil degradation and its effect on the condition of the grease and its ability to provide effective lubrication.

A search of the literature reveals a large amount of qualitative wear data that has been generated on an assortment of laboratory testers over a period of decades. Equations and analysis exist together with friction and wear data to allow for calculating lubricant film thickness, lubrication operating regime, and the qualitative severity of the wear (Refs. 3 to 5). However, there is no definitive analysis that allows an engineer to predict, with any degree of engineering certainty, the quantity of wear or the applicable usable life of a specific lubricant (grease) that can occur in a specific application. Quantitative results need to be obtained experimentally for specific applications (Ref. 1).

Ohno et al. (Ref. 6) tested two greases used for space applications and their respective base oils. All tests were done under ambient laboratory temperature and air atmosphere. One of the greases was the same or similar PFPAE grease to that used for the space shuttle actuators. Tests were performed in order to characterize the rheological base oil behavior of each grease versus pressure and temperature. Longer ball bearing fatigue life was obtained with the PFPAE grease than with the PFPAE base oil (Ref. 6).

Analysis showed that the viscosity of the PFPAE base oil, containing perfluoromethyl- and perfluoroethyl- ether groups (-(CF_2)O-) and (-$(CF_2)_2$O-), was lowered by the high shear rates in the elastohydrodynamic (EHD) Hertzian contact. Ohno et al. (Ref. 6) concluded that the PFPAE base oil decomposes, generating acid fluoride which then hydrolyzes to hydrogen fluoride by reacting with water moisture. As a result, the formation of the hydrogen fluoride shortens bearing life by forming metal fluorides when run with only the base oil. However, for the PFPAE grease, viscosity loss of the base oil did not occur (i.e., no base oil decomposition) resulting in longer bearing life (Ref. 6).

In a continuation of the research reported in Reference 6, Ohno et al. (Ref. 7) performed bearing fatigue tests of the PFPAE base (815Z) oil and multiply alkylated cyclopentane (MAC 2001A) base oil in air and vacuum environments. The test oils were analyzed to determine whether changes occurred as a result of operating in air and in a vacuum. In vacuum, the PFPAE base (815Z) oil had a longer fatigue life than the MAC 2001A oil. However, in an air environment, the MAC 2001A had a longer fatigue life than the PFPAE base (815Z) oil.

In the study by Krantz et al. (Ref. 2), spur gear pairs made from AISI 9310 steel, the same material used for the actuator gears without surface coatings, were lubricated with the Grade 2 PFPAE grease. The gear pairs were loaded to a maximum Hertz stress of 1.1 GPa (160 ksi) and operated under a dithering motion at ambient (room) temperature and atmosphere. The gears were run from 20,000 to 80,000 total dithering cycles. The wear rate for these spur gears “was on the order of 600 times greater than referenced data for oil lubricated gears” using six different polyol esters and one polyalkylene glycol based oil (Ref. 2). In a related study, Krantz et al. (Ref. 8) lubricated spur gear pairs with PFPAE grease and ran them under different atmospheres. The tests conducted under ambient air or dry air produced reddish colored debris in the PFPAE grease, whereas tests conducted in dry nitrogen (N_2) produced grey colored debris in the grease. Neither the reddish nor the grey colored debris were chemically identified.

In view of the aforementioned, the objectives of the work reported herein were to: (a) determine long term stability of Grade 2 PFPAE grease in the space shuttle actuators; (b) quantify base oil separation from the actuator grease samples; (c) identify base oil degradation in order to assess actuator grease performance; and (d) identify the grey and reddish colored materials in the grease samples taken from the actuators.

Apparatus, Specimens and Procedure

Rudder/Speed Brake (RSB) Actuator

The Rudder/Speed Brake (RSB) Actuator system is contained in the Space Shuttle Orbiter tail section shown in Figure 1. The RSB actuator system comprises a Power Drive Unit and 4 RSB actuators. The system controls the rudder/speed brake panels through the four actuators that are driven by the single Power Drive Unit (PDU).

A schematic of the RSB actuator is shown in Figure 2. The actuators are designed to provide both rudder and speed brake (S/B) functions by a split design in the vertical tail section shown in Figure 1 in which two input shafts enter the actuator – one at each end. By rotating the shafts in the same direction, the panels are moved concurrently for rudder function. When the input shafts rotate in opposite directions, the panels move apart for S/B function. Both rudder and S/B functions can be used simultaneously.

The gears comprising the actuators were manufactured from AISI 9310 steel. Typical chemical content for the AISI 9310 steel is as follows: 3.0 to 3.5 percent Ni; 0.45 to 0.65 percent Mn; 1.0 to 1.4 percent Cr; 0.08 to 0.15 percent Mo; and the balance, Fe. Most, if not all, of the AISI 9310 gears were coated with manganese phosphate.

Manganese phosphate coatings were introduced in the 1940s as an anti rust process. It forms a crystalline coating on the steel surface by taking advantage of the surface pH while etching the steel surface (Ref. 9). Recently, it was reported by Chen et al. (Ref. 9) that the coating decreases wear and increases the contact fatigue life of steel gears.

The actuators' rolling-element bearings were manufactured from AISI 52100 steel. Typical chemical content for AISI 52100 steel is: 0.95 to 1.1 percent C; 0.2 to 0.5 percent Mn; ≤ 0.35 percent Si; ≤ 0.025 percent S; nil Ni; 1.3 to 1.6 percent Cr; and the balance, Fe. Coatings were not applied to the AISI 52100 rolling-element bearings.

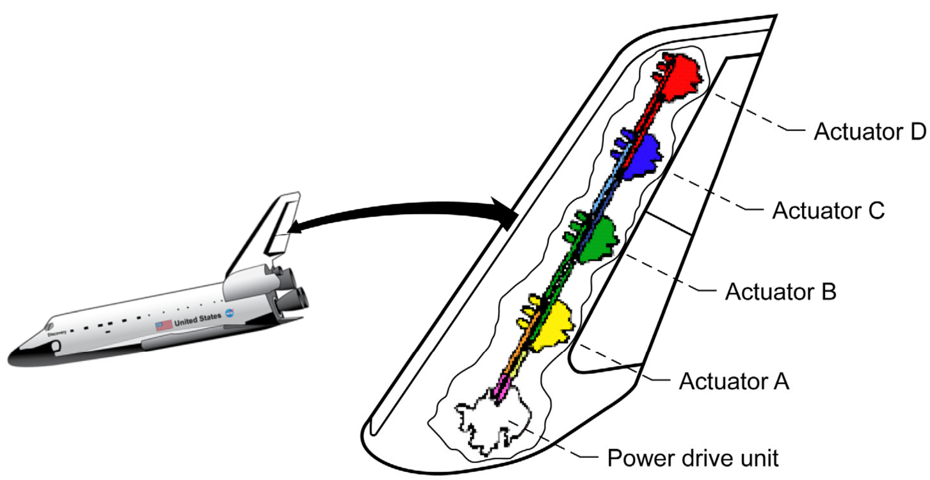


Figure 1.—Rudder/Speed Brake actuation components.

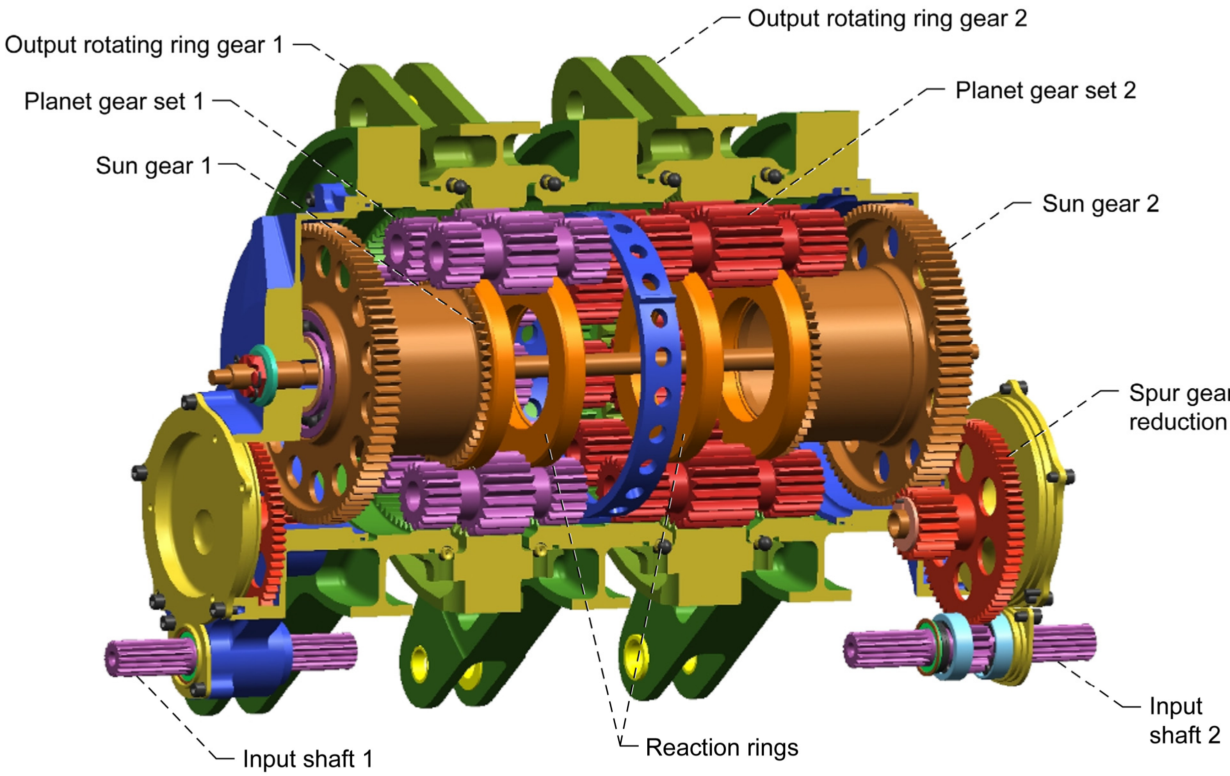


Figure 2.—Schematic of space shuttle Rudder Speed/Brake (RSB) actuator.

Lubricant

The mechanical actuators used on the space shuttle are lubricated by Braycote 601, a space-rated, Grade 2 grease containing a perfluoropolyalkyl ether (PFPAE) base oil, a Z-type fluid, with small polytetrafluoroethylene (PTFE) particles as a thickener, and sodium nitrite and dimethyloctyldecylbenzyl ammonium bentonite as rust and corrosion inhibitors. It is formulated to a buttery smooth consistency of Grade 2 grease, hence the ratio of oil to PTFE thickener may vary slightly from lot-to-lot due to the thickening ability of the variations in PTFE. The grease manufacturer does not have data on the particle size range or shape of the PTFE telomeres used for thickening.

The PFPAE base oil itself is a low molecular weight polymeric liquid having an average molecular weight of 9400 atomic mass units (amu). The grease has a wide operating temperature range: –80 to 200 °C (–112 to 400 °F). The viscosity of the lubricant base oil at the three temperatures used for this test program, 24, 60, and 74 °C (75, 140, and 165 °F), is approximately 4,750, 128, and 77 cSt, respectively. Gschwender and Snyder (Ref. 10) provide an excellent overview of the properties of this and other PFPAE base oils. The grease does not contain reactive extreme pressure additives that are typically added to hydrocarbon grease because these additives will not dissolve in the base oil (Ref. 11). Although considerable advances in PFPAE-soluble additives have been made since the grease in question was formulated in the early 1980’s, none are in use to date.

New (unused) grease has a beige color. Grease samples removed from two of the four disassembled actuators ranged in color from beige to grey (taken from RSB-403), and red (taken from RSB-405). In addition, a small amount of oil dripped from the disassembled actuators. These samples of grease along with representative virgin grease samples were analyzed for base oil content, for metals content, and for signs of base oil decomposition.

Gravimetric Analysis

Gravimetric analysis was performed on various grease samples to determine the amount of base oil and solid filler material in the grease samples. A fluorinated solvent, 1,1,2-trichlorotrifluoroethane (TCTF), was used to dissolve and extract the base oil from pre-weighed grease samples leaving behind solid residue. The solid residue was dried and weighed and this weight was then subtracted from the original grease weight resulting in the weight of the base oil. Both the residue (for the grey and reddish greases, the residue weight was corrected for the wear metal content as described later) and base oil weights were converted to percentages. This procedure was performed on used grease samples taken from the shuttle actuators as well as unused PFPAE grease samples manufactured in the years 1987, 1988, 1994, and 2004.

Insoluble Fraction Analysis

The weighed residue from the fluorinated solvent extraction was transferred to a PTFE beaker. This residue was then heated to just below boiling with 3 ml of 6 molar hydrochloric acid, followed by 3 ml of 6 molar nitric acid and finally with 3 ml of 6 molar hydrofluoric acid. The solutions were not boiled to prevent loss of volatiles such as SiF_4. The sample was then filtered through a pre-weighed PTFE filter. The filter was dried and weighed to obtain the acid soluble content by difference in the weight. The acid soluble sample filtrate was then subjected to Inductively Coupled Plasma (ICP) analysis for the metals contained in AISI 9310 gear steel, sodium (from sodium nitrite additive in the grease formulation), aluminum and silicon (from the bentonite additive in the grease formulation), and phosphorus from the manganese phosphate coatings on the AISI 9310 gears.

Fourier Transform Infrared (FTIR) Spectroscopy Analysis

Infrared spectra were collected with a FTIR spectrometer equipped with a standard deuteratedtriglycine sulfate (DTGS) detector. Spectra were acquired over the range of 650 to 4000 cm^{-1} at 4 cm^{-1} wavenumber resolution in transmittance mode through samples of neat grease pressed between potassium chloride (KCl) windows to the appropriate thickness. Typically, between 100 and 250 scans were averaged, converted from transmittance to absorbance and corrected to remove baseline curvature and water vapor and carbon dioxide absorption bands where necessary.

Size Exclusion Chromatography Analysis

Size exclusion chromatography (SEC), a molecular separation technique, was performed on both unused and used grease samples. A weighed amount of grease, 10 mg, was added to 3 ml of TCTF in a 5 ml sample bottle with a PTFE lined cap. After shaking the bottle until all the grease disintegrated, the contents were filtered through a 0.5 µm PTFE filter, collected and a 100 µl aliquot was injected in the SEC unit. The SEC unit utilized the fluorinated solvent as the mobile phase running at 1.0 ml per minute through one 500 Å and one 100 Å size exclusion columns in series and then through a refractive index detector where the separated molecules were detected and recorded as peaks.

Results and Discussion

The United States space shuttle fleet was originally intended to have a life of 100 flights for each vehicle, over a ten year period, with minimum scheduled maintenance or inspection. The first space shuttle flight was that of the Space Shuttle *Columbia* launched April 12, 1981. The disaster that destroyed the *Columbia* occurred on its 28th flight, February 1, 2003, nearly twenty-two years after first being launched. At that time as well as today, the Space Shuttle *Discovery* had the most flights. The 30th flight of the *Discovery* occurred August 10, 2001. This was approximately 17 years after its first flight launched August 30, 1984.

Each shuttle has four BFAs (two on each wing) on a common segmented shaft and four RSB actuators shown in Figures 1 and 2. The actuators are lubricated with Braycote 601 grease consisting of perfluoropolyalkyl ether (PFPAE) base oil thickened with a polytetrafluoroethylene (PTFE) filler. The actuators were designed to operate for their design life (10 years) without periodic relubrication. However, some had been in continuous use for over twenty years without inspection and relubrication. This was in contrast to commercial aircraft actuators that are refurbished every 2 $^{1}/_{2}$ to 3 years. Even for light duty, it is good engineering practice to replenish the grease in a system on a periodic basis and not for a period longer than 5 years. This is because, with time, the liquid (oil) separates from the grease (thickener). When approximately 50 percent of the liquid is lost, the grease is referred to as "dead grease" and is generally no longer effective in providing reliable lubrication (Ref. 12).

In July 2003, as a result of the *Columbia* accident, concern was raised over possible grease degradation and wear of *Discovery* RSB actuators. Inspection of the actuators revealed fretting, micropitting, wear and corrosion of the bearings and gears. The condition of these components suggested the need to replace the *Discovery* RSB actuators before its return to flight.

For the remaining actuators in the space shuttle fleet, work performed under simulated operating conditions by Oswald et al. (Ref. 1) and Krantz et al. (Ref. 2) established with reasonable engineering and statistical certainty the life and reliability of the space shuttle actuator gears and input shaft ball bearings. However, concerns remained over possible grease degradation due to discoloration of the grease on several places on the surfaces of the gears. New (unused) grease has a beige color. Grease samples removed from two of the four disassembled actuators ranged in color from beige to grey taken from one actuator, and red taken from the second actuator. In addition, a small amount of oil dripped from the disassembled actuators. How long can the Braycote 601 grease remain in-situ in the actuators and still be fit for its intended purpose? The answer to this question would, together with the results from References 1 and 2, determine whether some or all of the actuators on the remaining space shuttles would be replaced and/or refurbished before being returned to space.

In order to answer the question regarding the long term viability of the grease, grease samples were taken from the *Discovery* actuators, a Hamilton Sundstrand qualification unit, and representative off-the-shelf virgin grease. These samples were analyzed by: gravimetry for oil content; inductively coupled plasma spectroscopy (ICP) for metals content; Fourier transform infrared (FTIR) spectroscopy for signatures of base oil decomposition; and size exclusion chromatography (SEC) for determination of the molecular weight distributions of the grease oil.

Gravimetric Analysis

A gravimetric analysis of the unused grease samples was performed and is summarized in Table 1. Referring to Table 1, the weight percent oil for the unused grease samples ranged from 70.7 to 77.3 percent. Duplicate analysis of the 1994 grease sample yielded good precision for this analysis. This suggests that the variation in the results for these unused greases is correct and that the variation is likely associated with the grease formulation. The grease manufacturer indicated that the grease formulation process has not changed over the years; however, the oil to thickener ratio may vary slightly as discussed previously. The only used beige grease falling outside this range was from the HS Qual Unit with unknown history. The RSB-403 grey samples fell within this range although the grey and red samples from RSB-405 did not as these results are skewed by the presence of large amounts of metal (especially iron) in the residue detected by ICP metal analysis described and discussed below.

Taking the metal content for the RSB-405 reddish grease into account from Table 2 (Cr, Fe (calculated as Fe or Fe_2O_3 – see below), Mn, and Ni), all components of 9310 steel as well as P (calculated as PO_4) from the phosphating revises the total residue weight from 20.3 mg to possibly as low as 6.1 mg (based on Fe as Fe_2O_3) or 9.9 mg (Based on Fe as elemental Fe). The Cu is not part of the 9310 or 52100 steel but is also not a component of the virgin grease, hence it too was subtracted from the TCTF insoluble residue weight. This would revise the oil content to 89 or 84 percent base oil,

TABLE 1.—GRAVIMETRIC DETERMINATION OF SOLIDS IN USED AND UNUSED PFPAE GREASE TAKEN FROM SPACE SHUTTLE ACTUATORS

Grease	2004 unused	1994 unused	1994 unused	1988 unused	1987 unused	(Beige)	(Brown)	(Beige)	(Grey)	(Grey)	(Beige)	(Grey)	(Red)
Description	Braycote	Braycote	Braycote	Braycote	Braycote	HS Qual Unit	HS Qual Unit	RSB-403	RSB-403	RSB-403	RSB-405	RSB-405	RSB-405
Sample		Sample A	Sample B			Sample A	Sample B	Sample A	Sample B	Sample C	Sample A	Sample B	Sample C
Wt grease, (g)	1.0428	0.3088	0.3154	0.3224	0.3022	0.3208	0.1772	0.5089	0.4091	0.1088	0.5966	0.3033	0.0713
Total Wt residue, (g)	0.3052	0.0721	0.0716	0.0802	0.0710	0.0665	0.0375	0.1215	0.0874	0.0213	0.1536	0.0789	0.0203
Wt% residue, (%)	29.3	23.3	22.7	24.9	23.5	20.7	21.2	23.9	21.4	19.6	25.7	26.0	28.5
Wt acid solubles, (mg)	19.7	6.2	6.7	7.6	6.4	5.0	4.2	14.4	9.9	2.1	------------	-----------	6.8
Wt% acid solubles, (%)	1.9	2.0	2.1	2.4	2.1	1.6	2.4	2.8	2.4	1.9			9.5
Wt% oil, (%)	70.7	76.7	77.3	75.1	76.5	79.3	78.8	76.1	78.6	80.4	74.3	74.0	71.5

TABLE 2.—INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPIC ANALYSIS OF ACID SOLUBLES FROM EXTRACT RESIDUE

Sample	2004 unused	199 unused	1994 unused	1988 unused	1987 unused	(Beige)	(Brown)	(Beige)	(Gray)	(Gray)	(Red)
Description	Braycote	Braycote	Braycote	Braycote	Braycote	HS Qual Unit	HS Qual Unit	RSB-403	RSB-403	RSB-403	RSB-405
		Sample A	Sample B			Sample A	Sample B	Sample A	Sample B	Sample C	Sample C
Element	Wt% of Acid Soluble Materials[a]										
	AISI 9310 and 52100 metal elements (Iron, a contaminant of Braycote, is included here as the major element of steels)										
Fe	1.73	2.1	2.2	1.8	1.6	1.3	8.8	1.8	10	8.2	43
Cr	-----	-----	-----	-----	-----	-----	0.21		0.7	1.0	1.1
Ni	-----	0.10	-----	-----	0.40	-----	0.42	0.10	0.70	1.0	2.0
Cu	-----	-----	-----	-----	-----	-----	-----	-----	0.12	0.18	0.15
	Grease component elements										
Al	6.11	5.7	5.3	5.9	5.4	3.9	2.4	4.5	3.3	4.7	1.0
Si	18.3	20	21	18	17	12	7.7	14.9	13	15	3.2
Na	12.1	12	12	10	11	11	4.0	9.5	7.7	9.2	1.9
	Phosphating elements (Manganese, a component of 9310 and 52100 steel is included here as the high amounts are likely from phosphating)										
P	-----	-----	-----	-----	-----	-----	-----	-----	4.1	4.0	3.0
Mn	-----	-----	-----	-----	-----	-----	-----	-----	5.2	2.8	3.7
	Miscellaneous uncharacterized elements										
Mo						0.02	0.04	0.01	0.05	0.06	0.09
Mg	0.80	0.68	0.51	0.83	0.76	0.41	0.23	0.46	0.44	0.78	0.20
Zn	-----	-----	1.3	0.14	-----	0.18	-----	-----	0.11	0.17	0.23

[a]Any values not listed are <0.1 percent.

respectively. These high percentage oil numbers are perhaps the result of only a small sample being available for analysis, but from this we can conclude that calculations of the amount (percentage) of oil loss by determining filler content can lead to potentially large errors in the direction of oil loss if not corrected for wear metal content. No information was available to determine if correction should be based on Fe as the metal or as oxide other than color. Small amounts of the oxide may have colored over the grey which would have been present if some of the Fe was as metal. The grey grease is unambiguously elemental Fe contaminant and when a similar correction is applied, the grey grease oil content from RSB-403 becomes 82 and 84 percent which would be in line with the red grease if most of the Fe in it was as elemental Fe. For reference, if we apply a similar correction to the unused greases which also have normal iron contaminant, it raises their oil content by a percent or two as well. Removal of the Fe from the unused grease is incorrect since virgin grease also contains iron, thus begging the question "exactly how much of the Fe in the used colored greases is original grease contaminant and how much is wear metal?" The amount of Fe in the grey and red grease clearly requires correction but because there is no way of telling the Fe sources apart, the corrections applied above are overcompensations on the order of a few percent more oil. To provide perspective, for a grease initially containing 75 percent oil to be "dead" as previously defined, the percent insoluble fraction from the grease alone would be 40 percent plus any content from wear metals. The results of gravimetric tests for red or grey grease show that base oil depletion through tribological destruction was not significant for over two decades of use. Further, separation of oil from the beige actuator grease was not significant after two decades within the sealed actuators.

ICP Metal Analysis

Unused PFPAE grease was analyzed for metal content and is summarized in Table 2. The analysis yielded several percent of the original TCTF insoluble residue as acid soluble (Table 2). Very small amounts of iron were found which may be a contaminant of another component in the grease such as the bentonite mineral. The majority of the residuals were sodium (from the sodium nitrite) and aluminum and silicon from the bentonite, $Al_2Si_4O_{12}H_2 \cdot xH_2O$ (Ref. 13).

The analysis of the grey grease sample (Table 2) contained substantial amounts of Na, Al and Si as compared to iron. This would suggest that a small amount of wear metal contamination relative to the grease additive materials is in this grey grease sample supporting the above discussion. The red grease sample (Table 2) contained significant amounts of iron plus traces of other components of AISI 9310 steel, including Ni, indicating that a large fraction of the acid soluble material contained wear metal. The 52100 steel used in the bearings has negligible Ni content implying that the metallic debris is gear material. The amounts of Na, Al and Si were considerably lower than the amount of iron in this sample although Na, Al and Si were still in the same relative ratio with respect to each other as in the unused grease residue and the grey grease residue, again supporting the gravimetric analysis discussion. Analysis of the undissolved solids from RSB-403 (beige) ad the HS Qual Unit (beige) showed negligible iron (1.8 and 1.3 percent, respectively of the residue weight) and amounts of Na, Al and Si similar to the unused grease samples.

The virgin grease, used as a comparative baseline, had Na, Al, and Si, the last two being in correct additive ratios. The grey and brown colored grease from the actuators in addition to Na, Al, and Si, had around 8 to 10 percent Fe, 5.3 percent Mn and 4.1 percent P. In this grease the Fe and Mn are not in correct ratio for 9310 steel but are more likely attributed to the gear phosphating process leaving a surface manganese phosphate rich layer which was removed prior to disintegration of the gear metal. The actuators with the red grease in addition to Na, Al, and Si, had 43 percent Fe, 2 percent Ni, 3.7 percent Mn and 3 percent P which are explained similarly to the grey grease above. Nickel is not a component of AISI 52100 steel although it cannot be concluded that all the wear debris came from the AISI 9310 gears.

It was concluded that the grey color in the grease sample was due to metallic iron and that the red color was due to oxidation of the wear particles from the gears and the bearings comprising the actuators. Small amounts of the wear metals were submitted to x-ray diffraction to see if metal oxides or fluorides could be detected. Some iron oxides and no metal fluorides were detected although the samples were too small for rigorous analysis.

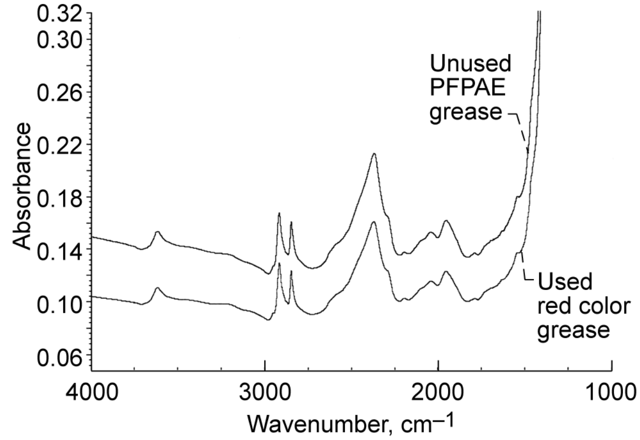


Figure 3.—Fourier Transform Infared (FTIR) spectra of unused PFPAE grease and used red colored PFPAE grease removed from space shuttle actuator.

FTIR Spectroscopy

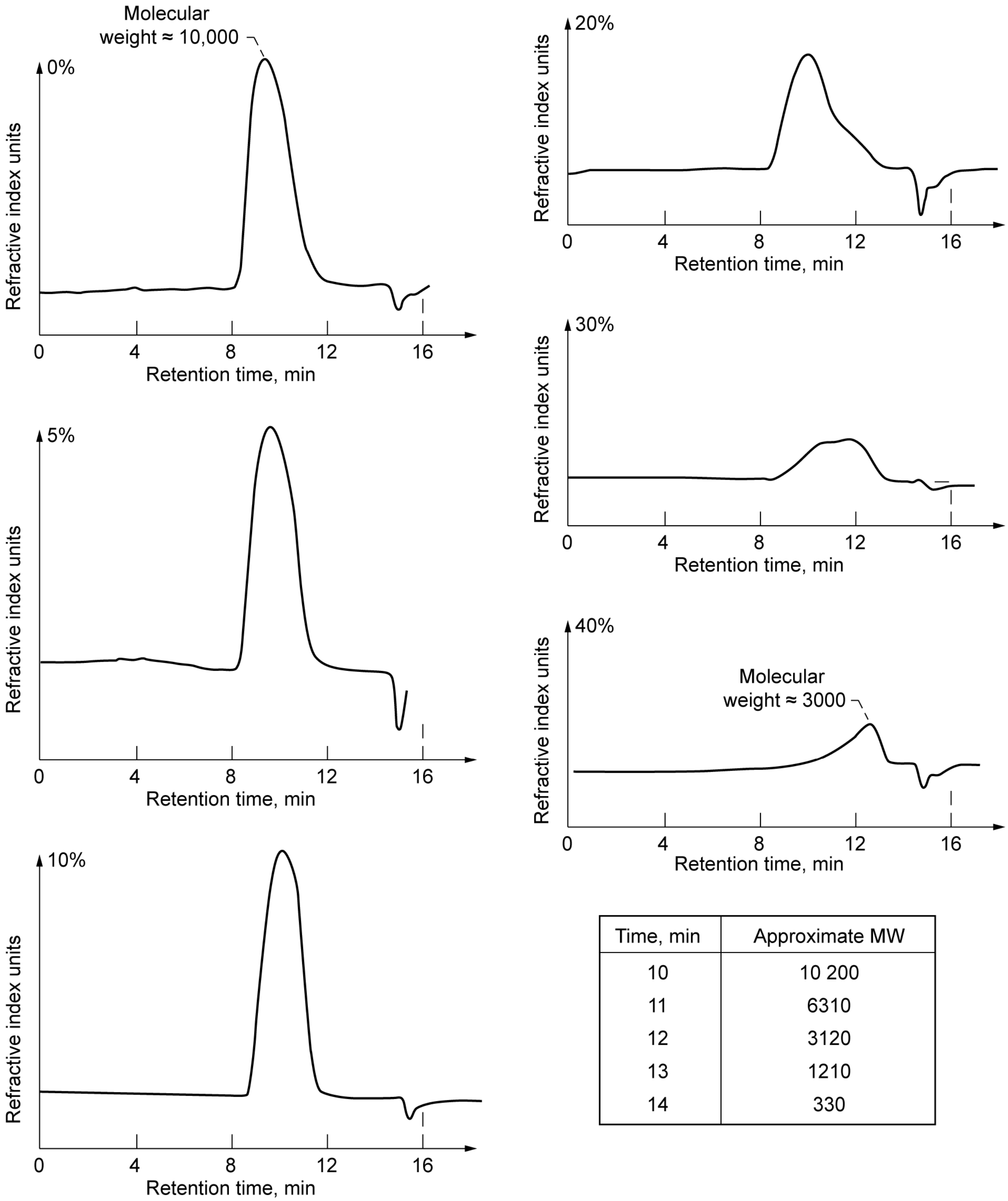
Figure 3 is the FTIR spectra of virgin and used grease. In these spectra we examine the regions between 1900 to 1700 cm^{-1} and between 3700 to 3400 cm^{-1}. The peak in the 1800 cm^{-1} range would be indicative of the carbonyl band formation due to oxidation of a carbon backbone in a lubricant or the formation of acid fluorides, both degradation products associated with the PFPAE based greases. The peaks found between 3700 to 3400 cm^{-1} would be indicative of the acid fluoride formation. While the acid fluorides are quite volatile, they are also quite reactive to both water and metals. Direct attack of the acid fluorides with metals in the absence of water would yield less volatile organo-metallic compounds readily observable in the 1550 to 1650 cm^{-1} and near 1400 cm^{-1} regions of the IR (Refs. 14 and 15).

No difference was observed between the used and unused greases in these locations of the IR spectra, suggesting little or no degradation by these pathways was observed over the decades of operation in the actuators. Unfortunately, these compounds may not have survived in the grease if the grease was exposed to vacuum prior to reaction with metals so degradation still could have occurred. As previously stated, no evidence of the more stable metal fluorides was found. If there was degradation of the grease, it would have occurred in the Hertzian contact areas of the bearings and gears. Unfortunately, we were not able to retrieve grease samples from these contact areas.

Size Exclusion Chromatography (SEC)

In SEC analysis, various substances dissolved in the mobile phase solvent are physically separated from each other based on their molecular size (or weight). Larger molecules are eluted first from the separatory column followed by medium and then smaller molecules. The set of columns used in this study were capable of separating six different standard substances ranging in molecular weight from >2 million to 92 amu.

SEC analysis has been successfully used to show PFPAE base oil decomposition. Figure 4 shows the results of a study (Ref. 16) where a new PFPAE base oil sample was catalytically decomposed by aluminum oxide at elevated temperatures. The changing patterns in the chromatograms indicate decomposition of the PFPAE base oil to smaller molecular weight products. The x axis (retention time in minutes) is approximately related to the logarithm (base 10) of the molecular weight, with higher molecular weight compounds having shorter retention times. The y-axis (refractive index, RI, units) indicates the approximate concentration of the compound. In other words, the SEC plot reveals the molecular weight distribution and concentration of individual polymer components comprising the sample material as all chromatograms were run on the same RI scale.



Time, min	Approximate MW
10	10 200
11	6310
12	3120
13	1210
14	330

Figure 4.—SEC chromatograms of 0, 5, 10, 20, 30, and 40 percent PFPAE Z-type fluid decomposition on gamma alumina.

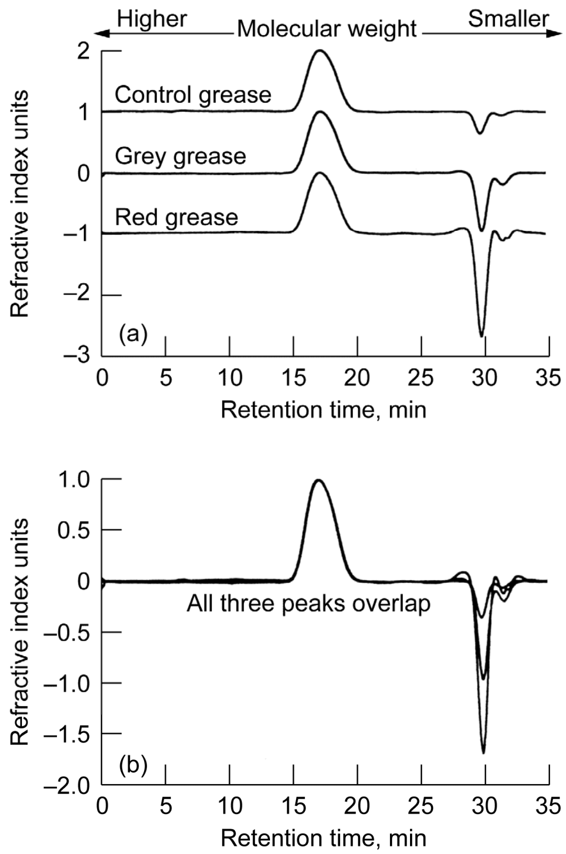


Figure 5.—SEC analysis of oil degradation in shuttle grease samples. (a) Individual offset chromatograms. (b) Chromatograms from (a) overlapped.

Figure 5 shows the SEC chromatograms of the oil from the actuator RSB-403 grey and RSB-405 red grease samples in addition to a PFPAE control sample, 2004 unused Braycote grease. All three chromatograms, when normalized to the chromatographic peak, completely overlap at all locations. No noticeable degradation of the base oil occurred in the samples analyzed. Lighter degradation fragments from end group cleavage (Ref. 10) may have volatilized off during vacuum exposure leaving slightly lower molecular weight fragments having very low volatility. The remarkable correspondence in these chromatograms gives great confidence that no degradation occurred. Degradation would have skewed these chromatograms toward slightly lower molecular weights resulting from the end group cleavage pathway which would not have volatilized and would be readily apparent in the chromatographic overlays.

Summary of Results

The United States space shuttle fleet was originally intended to have a life of 100 flights for each vehicle, over a ten year period, with minimum scheduled maintenance or inspection. Each shuttle has four body flap actuators (BFAs) (two on each wing) on a common segmented shaft and four rudder speed brake (RSB) actuators. The actuators are lubricated with Braycote 601 grease consisting of perfluoropolyalkyl ether (PFPAE) base oil thickened with a polytetrafluoroethylene (PTFE) filler. The actuators were designed to operate for their design life of 10 years and 100 flights without periodic relubrication or inspection. Some actuators had been in continuous use for over twenty years. Visible inspection of two partially disassembled RSB actuators, however, raised concerns over possible grease degradation due to discoloration of the grease on several places on the surfaces of the gears. Inspection also revealed fretting, micropitting, wear and corrosion of the bearings and gears. The objectives of the work reported were to determine long term stability of Grade 2 PFPAE grease in the space shuttle actuators; quantify base oil separation from the actuator grease samples; identify base oil degradation in order to assess actuator grease performance; and identify the grey and reddish colored materials in the grease samples taken from the actuators. The following results and conclusions were obtained:

(1) The Braycote 601 grease consisting of perfluoropolyalkyl ether (PFPAE) base oil thickened with a polytetrafluoroethylene (PTFE) filler was stable after 19 years in the sealed RSB actuators and was fit for its intended purpose.

(2) Both FTIR and SEC analyses show no significant chemical differences between the used grease samples taken from the sealed RSB actuators after 19 years of use and new, unused samples of the same grease.

(3) Gravimetric tests from the actuator PFPAE grease show that neither base oil consumption nor separation was significant within the sealed actuators.

(4) The grey color of grease samples taken from the shuttle actuators was due to metallic iron. The red color was due to oxidation of the metallic wear particles from the gears and the bearings comprising the actuators.

Epilogue

The body flap actuators (BFAs) on all remaining space shuttles were limited to 12 flights each before refurbishment. The remaining two rudder speed brake (RSB) actuators were removed from the Space Shuttle *Discovery*. All four of the removed RSB actuators were replaced with four actuators that had been subjected to three flights and had been removed from a sister space shuttle. On July 26, 2005, the *Discovery* returned to flight on a mission to the International Space Station (ISS), the first space shuttle to fly since the Space Shuttle *Columbia* disaster on February 1, 2003. This was the 31st mission and flight of the *Discovery*. On July 4, 2006, the 32nd flight of the *Discovery* occurred on a mission to the ISS. This was the second consecutive return to flight since the *Columbia* disaster. The *Discovery* was flown seven more times to the ISS without incident for a total of 39 flights. After the 39th mission on March 9, 2011, the Space Shuttle *Discovery* was retired from service and will be placed on permanent display in the Smithsonian Air and Space Museum, Washington, DC. The BFAs and the RSB actuators functioned as intended without incident. The RSB actuators in the *Discovery* at the time of its retirement had a total of 12 flights, 9 flights from those in the *Discovery* and 3 previous flights before being removed from the Space Shuttle *Endeavor*.

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14. ABSTRACT
Actuators used on the United States space shuttle fleet are lubricated with unspecified amounts of Braycote 601 (Castrol Braycote) grease consisting of a perfluoropolyalkyl ether (PFPAE) base oil thickened with a polytetrafluoroethylene (PTFE) filler. Each shuttle has four body flap actuators (BFAs) (two on each wing) on a common segmented shaft and four rudder speed brake (RSB) actuators. The actuators were designed to operate for 10 years and 100 flights without periodic relubrication. Visible inspection of two partially disassembled RSB actuators in continuous use for 19 years raised concerns over possible grease degradation due to discoloration of the grease on several places on the surfaces of the gears. Inspection revealed fretting, micropitting, wear and corrosion of the bearings and gears. A small amount of oil dripped from the disassembled actuators. Whereas new grease is beige in appearance, the discolored grease consisted of both grey and reddish colors. Grease samples taken from the actuators together with representative off-the-shelf new and unused grease samples were analyzed by gravimetry for oil content; by inductively coupled plasma spectroscopy (ICP) for metals content; Fourier transform infrared (FTIR) spectroscopy for base oil decomposition; and by size exclusion chromatography (SEC) for determination of the molecular weight distributions of the grease oil. The Braycote 601 grease was stable after 19 years of continuous use in the sealed RSB actuators and was fit for its intended purpose. There were no significant chemical differences between the used grease samples and new and unused samples. Base oil separation was not significant within the sealed actuators. No corrosive effect in the form of iron fluoride was detected. The grey color of grease samples was due to metallic iron. The red color was due to oxidation of the metallic wear particles from the gears and the bearings comprising the actuators.

15. SUBJECT TERMS
Greases; perfluoropolyalkyl ether (PFPAE); Gears; Infrared spectroscopy; Gravimetry; Liquid chromatography; Space shuttle

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