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Effects of Varying Ball Bearing Cleaning Processes on Lubricant Life

20 January 1998

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Engineering and Technology Group

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Abstract

The processes used to clean ball bearings and other components in precision spacecraft mechanisms have undergone significant changes to eliminate the use of ozone depleting chemicals, such as Freon TF. This study was part of a larger NASA-funded program to assess the impact of the elimination of ozone-depleting chemicals on lubricant performance in space mechanisms previously qualified for 5 to 10 year lifetimes. The document reports the results of bearing life tests and surface analyses performed with components cleaned with three different methods: ultrasonic cleaning with Freon TF, ultrasonic cleaning with Vertrel XF (a hydrofluorocarbon), and cleaning with Brulin 815 GD (an aqueous detergent). The bearings were lubricated with Brayco 815Z, a perfluoropolyalkylether (PFPE) lubricant widely used in spacecraft applications that is susceptible to degradation under boundary lubrication conditions. The bearing tests were operated under boundary conditions, and the endurance of the lubricant was inversely correlated to the cleanliness of the bearing prior to lubrication. Specifically, parts cleaned with the Brulin detergent were shown to have less hydrocarbon residue prior to lubrication and experienced failure due to lubricant degradation in roughly half the time observed for parts cleaned with Freon TF. The Brulin process may also alter the steel-oxide layer structure, potentially impacting performance. Alternatively, parts cleaned with Vertrel XF retained a much greater amount of hydrocarbon contamination from the protective mineral oil than observed for the Freon parts, and subsequently ran approximately two times longer in our tests. The tests and analyses show that care must be taken to understand the impact of new cleaning processes on lubricant chemistry in mechanical systems.

Acknowledgment

The authors thank Sandra A. Jackson for performing the FTIR analyses, and Dr. Ann Bertrand for helpful discussions. This work was supported by NASA/GSFC through the SMC Contract No. F04701-93-C-0094 under an interagency agreement. We thank Dr. William Jones of NASA/Lewis, Dr. Roamer Predmore of NASA/Goddard, and Dr. Robert Thom of NASA/MSFC for this support and for helpful discussions. We also thank Daniel Mullville and Richard Weinstein of NASA/Headquarters for their financial support of this work.

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1. Introduction

The cleaning of precision mechanical components for spacecraft applications is a critical step in ensuring proper performance. Steel ball-bearing components are usually cleaned immediately prior to lubrication. Hence, the surface remaining after cleaning is the initial interface present to interact chemically with lubricants and additives. Historically, much of the cleaning of such components was performed with CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane), commonly called Freon TF, due to the numerous favorable properties of that solvent. Recent mandated changes in the use of ozone-depleting chemicals has forced bearing and mechanism manufacturers to develop new cleaning methods. This report covers accelerated performance tests of steel bearing components cleaned by different methods and lubricated with the perfluoropolyalkylether (PFPE) lubricant Brayco 815Z.

The cleaning methods used in this work include ultrasonic cleaning in Freon TF, ultrasonic cleaning in an alternative solvent, and cleaning with an aqueous detergent process. The test apparatus used was developed in house, and basically uses a modified thrust bearing run in an eccentric fashion to accentuate boundary lubrication conditions. The 815Z lubricant used in this program is one widely employed in spacecraft mechanisms and is known to break down under boundary contact.[1] The goal of the test program is to determine whether the different cleaning processes can affect the lubricant chemical breakdown, either accelerating or slowing the process relative to the baseline Freon TF-cleaned articles. Surface analyses of cleaned components are presented to assess the state of the surface prior to lubrication and determine whether an obvious link can be made between surface cleanliness and lubricant performance.

This work is part of a larger NASA program studying the impact of the elimination of cleaning processes using ozone-depleting chemicals on spacecraft mechanism performance.[2] The overall goal is the qualification of space mechanisms for 5 to 10 year missions. Since such life has been achieved with Freon TF-cleaned systems, it was hoped that new cleaning processes would produce no negative effects on lubricant life, enabling all mechanisms to remain qualified by similarity. Cleaning methods using alternative solvents, aqueous systems, supercritical carbon dioxide, and UV-ozone methods have been investigated in the larger program.[3]

2. Experimental

A bearing test fixture conceived of and built in-house was used to perform the tests. This fixture has been described in the literature.[4] Briefly, it uses modified INA Bearing Co. GT-1 size (1.25-in. diam) thrust bearings with the bottom race replaced by a polished steel flat. The rotation axes of the upper race and the rotating flat are intentionally misaligned to be non-coaxial, creating an eccentric path of the ball on the flat, and causing a significant amount of ball skidding and hence boundary conditions; i.e., the thickness of the lubricant film is less than the average surface roughness of the metal parts. This tester has been very useful in screening spacecraft lubricants based on their tendency to decompose under boundary contact and to evaporate in a vacuum, as well as to study the performance of boundary additives.[4] For this work, the steel flat was made of 440C stainless steel, as were the balls, which were substituted for the 52100 steel balls that were supplied in the stamped steel cage. The test fixture is contained in a turbomolecularly pumped vacuum chamber, and the tests were conducted in vacuum ranging from 10^{-6} to 10^{-7} Torr. The bearings were loaded with 180 N (41 lb), creating a mean contact stress of 1.2 GPa (180 ksi). The bearing speed was ramped slowly to 1800 rpm over the first 100,000 revolutions, and was maintained at 1800 rpm for the duration of the test. The tests were run until the steady-state torque increased by a factor of 2 above the nominal running torque. Without exception, the lubricant was significantly degraded at the end of the test.

The test articles were cleaned by three different methods prior to testing. After cleaning, the bearings were immediately lubricated with 30 μL of Castrol Brayco 815Z oil and installed into the test fixture. The major contaminant prior to cleaning was the protective mineral oil used on some of the components. The cleaning processes were: (1) ultrasonic cleaning with Freon TF; (2) heptane rinse followed by detergent cleaning with Brulin 815GD; and (3) ultrasonic cleaning with Vertrel XF, a hydrofluorocarbon (HFC 43-10) manufactured by DuPont and a possible Freon TF replacement. In the Freon TF process, three 5-min ultrasonic cleaning cycles were used, with 75–100 ml of fresh solvent used for each cleaning cycle. The detergent cleaning process was more complex and was modeled after the process used by a bearing manufacturer. The parts were briefly rinsed in heptane to remove gross organic contaminant. The parts were then cleaned ultrasonically at 65°C in 10% Brulin 815 GD detergent diluted with deionized (DI) water. The parts were then rinsed with warm DI water (38°C) and cleaned again in a fresh Brulin solution as described above. This wash was followed by three, 2-min rinses in room-temperature DI water, followed by immediate drying under flowing nitrogen gas. The parts were then placed in an oven at 90°C for 10 min. The final cleaning method consisted of several ultrasonic cleanings in the Vertrel XF. It was evident that this solvent was not very effective at removing the hydrocarbon oil, and cleaning cycles were performed until the solvent did not change its appearance (i.e., did not become cloudy) following a given cycle. Typically, this required five cleaning cycles of at least 10 min duration each, using 75–100 ml of solvent for each cycle. The product literature for Vertrel XF notes that the solubility of large hydrocarbon molecules can be improved by adding miscible esters and alcohols. We did not attempt to use any commercially available Vertrel mixtures or azeotropes to improve its effectiveness.

To determine the efficacy of the cleaning methods, cleaned bearing components were examined using Fourier Transform Infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). Balls stored in two different fashions prior to cleaning, both with and without a protective oil coating, were analyzed after cleaning. Samples of oil-stored balls after all three cleaning methods were examined with a Nicolet Magna 550 FTIR microscope. For the FTIR analyses, only one ultrasonic cleaning cycle was performed with the solvents, but the complete Brulin process was employed. Balls from both storage conditions cleaned with all three complete processes were examined with a Surface Science Instruments S-100 small-spot XPS instrument. The spot size used was 300 µm in diameter, with a 50-eV pass energy used to obtain high-resolution data on individual spectral features (C 1s, O 1s, Fe 2p and Cr 2p) and survey scans using 150-eV pass energy to look for any other contaminants. XPS-sputter profiles were also used to examine the oxide layer structure on selected balls. The balls were sputtered with 2-kV Ar ions at an approximate sputter rate of 2 Å/min.

3. Results and Analysis

Figure 1 shows the test fixture reaction torque trace for a typical test run in this program. After an initial run-in period characterized by decreasing reaction torque, the bearings typically operated at a relatively constant torque level until failure of the lubricant system. At that time, the test fixture either showed a rapid increase in the reaction torque or began to operate in an unstable mode where a negative reaction torque was recorded for a short period prior to increasing dramatically. In these tests, we have taken the onset of unstable behavior as failure and have verified that the lubricant has degraded at that juncture.

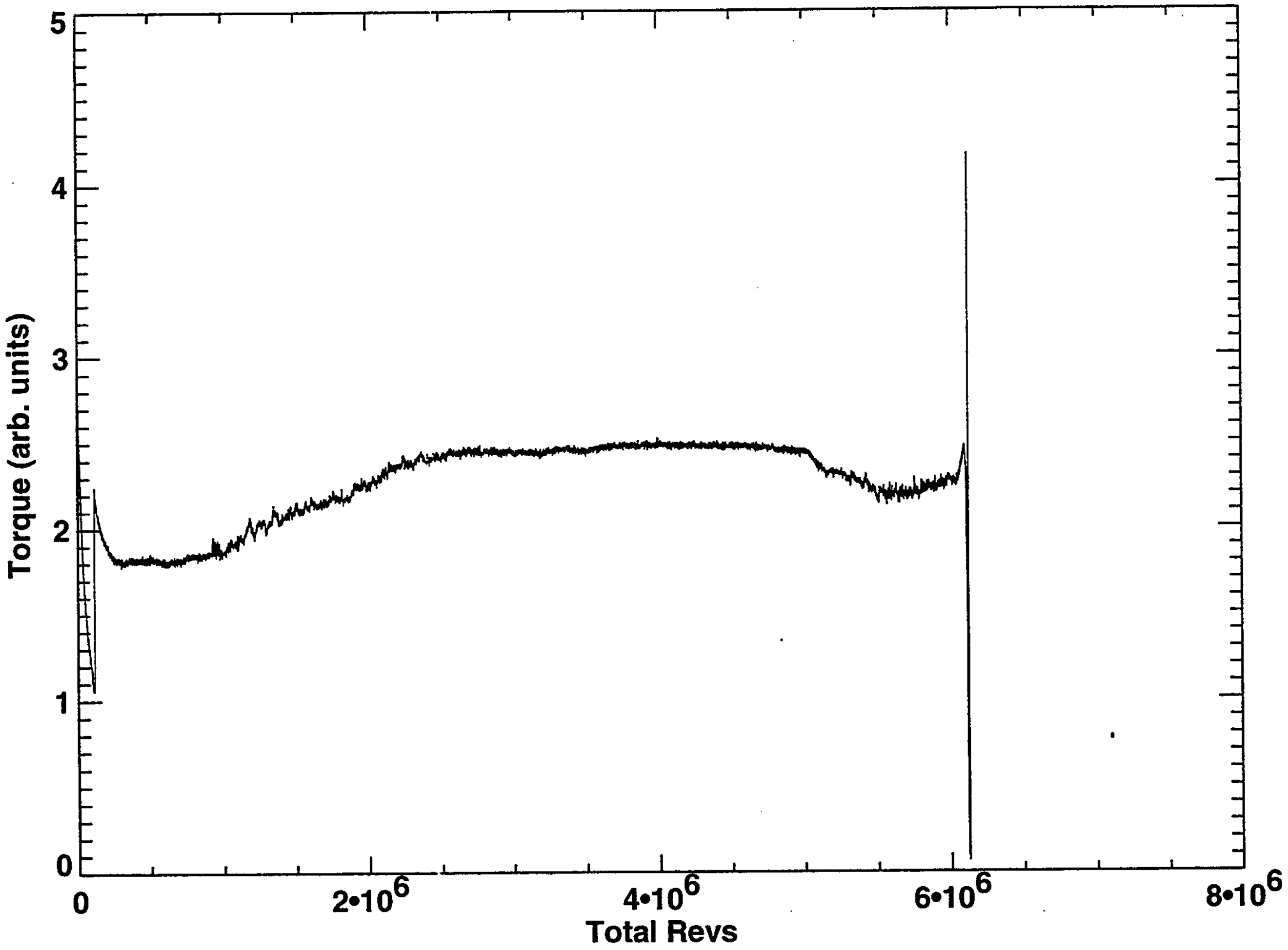

Figure 1. A reaction torque trace for a typical test run to failure in this program. This specific test was run on components cleaned with Vertrel XF. The discontinuity after 1 X 10^5 revolutions is caused by an adjustment to the zero level of the torque sensor.

Figure 2 presents photographs comparing new bearing components to those typically found following the termination of a test based on our failure criteria. The test bearing components are covered with a black residue that is characteristic of the degradation of a PFPE lubricant under boundary contact.

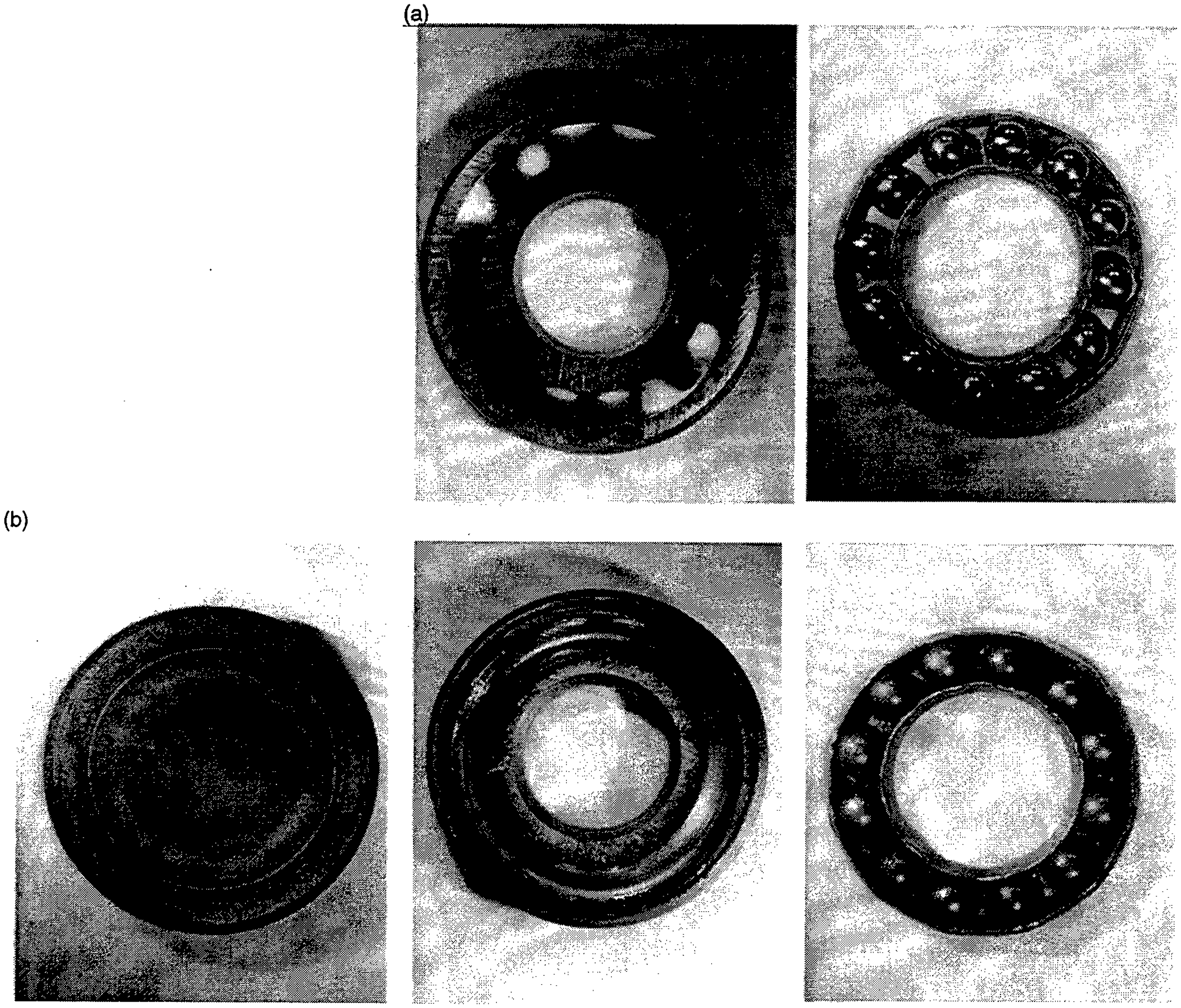

Figure 2. Photographs of bearing test components taken (a) before a test and (b) after test failure. The black residue is characteristic of the failure of PFPE lubricants. This test was conducted on components cleaned with the Vertrel XF.

Figure 3 provides a graphical representation of the endurance of all of the tests conducted with components cleaned with the three different processes. Each bar on the graph represents a test to failure, and the variation from run-to-run for a given set of conditions is fairly common for this fixture. The primary reason for this variation is likely the relatively poor quality of the bearing components being used, particularly the stamped steel cage, which can wear unpredictably and may be altered by the substitution of the 440C balls. Even with the variation, some obvious trends are present in our data. Specifically, components cleaned with the detergent process have a shorter operational life than those cleaned with Freon TF, while bearing items cleaned with the Vertrel XF solvent demonstrated a significantly longer life.

In comparing the detergent-cleaned results to the Freon TF results, only one Brulin test lasted as long as the shortest-lived Freon TF test. That particular detergent test was one of the longest of all of the tests, and should probably be discounted as an anomaly. The remainder of the detergent tests lasted for approximately 3 million or fewer revolutions, including two tests that were very short lived. All of the Freon TF-cleaned bearings lasted for at least 3.5 million revolutions and ranged up to 8.5 million (with most between 3.5 and 7 million). In contrast, all Vertrel- bearings lasted a minimum of 5 million, with one lasting as long as 13 million revolutions. Most of the Vertrel XF tests were in the range of 6 to 10 million.

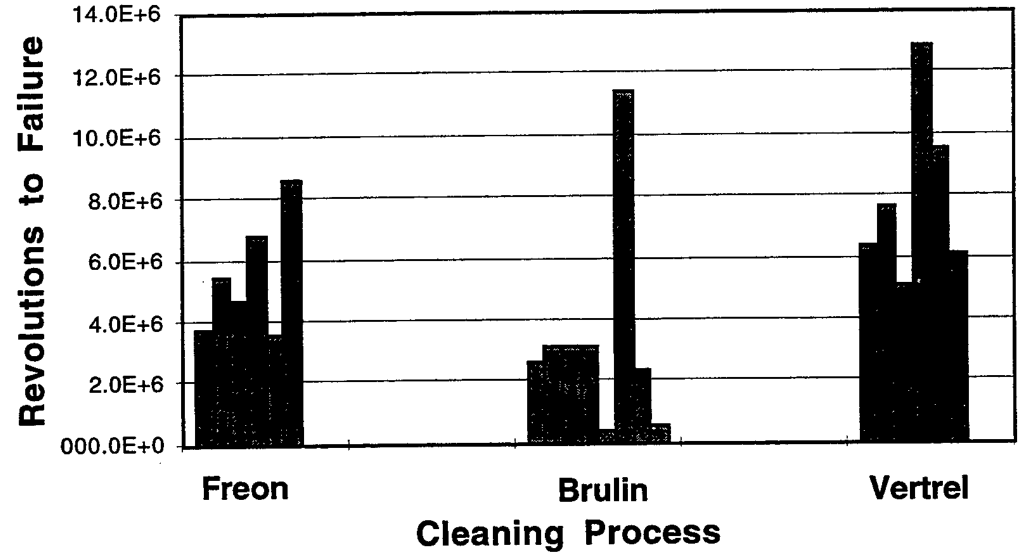

Figure 3. Graph showing the individual tests run to failure for each of the three cleaning processes. Each bar represents a single test, with the endurance given in the total number of revolutions.

Figure 4 presents the mean wear lives for the tests (omitting the one very long-lived detergent-cleaned bearing result) and the standard deviation for these results. These results show that, on average, the Freon TF-cleaned components lasted about 2.5 times longer than those cleaned with Brulin. The Vertrel XF-cleaned components last about 1.5 times longer than those cleaned with Freon TF. Overall, it is evident that the cleaning method could impact the lubricant life by nearly a factor of 4 when comparing the Vertrel XF-cleaned samples to those cleaned with detergent. However, the reasons for the variations must be assessed before the assumption of the superiority of one cleaning method based on the test results can be made.

As shown in Figure 2, the failure of these bearings results from the degradation of the 815Z lubricant. In previous work, analysis of this residue has shown it to contain polymerized PFPE mixed with iron wear particles and FeF_3, which is believed to catalyze the decomposition of the oil.[1,5] From these results, we conclude that the cleaning processes employed in our tests affect the rate at which the 815Z lubricant is degraded under mechanical contact. This degradation must be related to the surface chemical composition of the bearing components, implying that the different cleaning methods produce different surface chemistry. To determine possible reasons for this behavior, cleaned components were analyzed with FTIR and XPS to assess the chemical composition of the component surfaces.

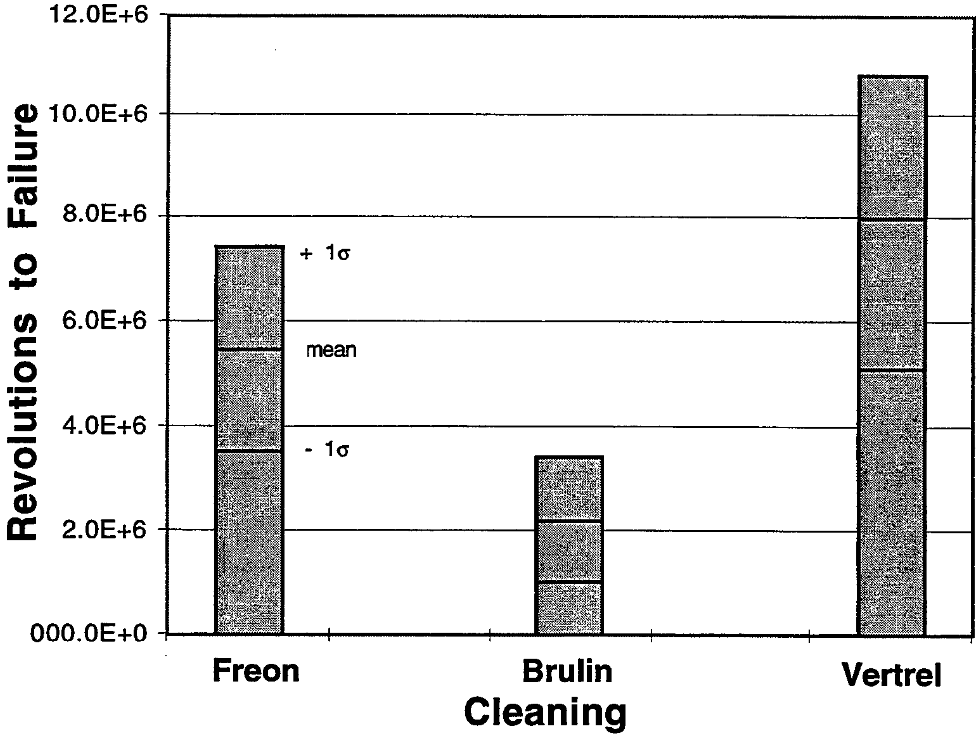

Figure 4. The mean endurance of the wear test data from Figure 3 for each of the cleaning processes. The mean value is given by the line indicated for the Freon data. The values of ±1 standard deviation are also provided on the graph. The Brulin data were averaged without the longest lived test.

Figure 5 compares the FTIR spectra obtained on balls processed through the limited cleaning procedures described in the experimental section. The most striking result is the obvious presence of carbon-hydrogen stretching vibrations near 3000 cm^{-1} on the ball cleaned with the Vertrel XF, and the absence of these features on the balls cleaned with Freon TF and Brulin. The features observed in the Freon TF and Brulin spectra were obtained at high sensitivity, and the resulting features are due to atmospheric gases that could not be completely purged from the system. These results are consistent with the observed difficulty in removing the protective mineral oil on the steel parts with the Vertrel XF solvent. The results also provide a possible explanation for the longer life of the components cleaned with the Vertrel XF since the thick residual hydrocarbon overlayer probably provided some boundary protection (especially if the oil contained boundary additives), delaying the degradation of the PFPE lubricant.[1] Although this cleaning process may have extended the life of the bearing, it did so by being an ineffective solvent and leaving behind a beneficial lubricating residue. It would be unwise to rely on such a process for assuring long life since ineffective cleaning is uncontrollable and assuredly not always beneficial.

In Figure 5, neither the Freon TF-cleaned nor the Brulin-cleaned ball had a detectable hydrocarbon signature in the FTIR, which is sensitive to films on the order of hundreds of Ångstroms[6] These cleaning processes, therefore, have effectively removed much of the hydrocarbon overlayer. More surface-sensitive probes must be used to determine whether the difference in the operational life of test bearings cleaned by these processes is due to a beneficial hydrocarbon residue left behind by Freon TF or some other change in surface chemistry caused by the detergent process. To address this issue, XPS analyses of balls cleaned by our processes were performed.

Figure 6 compares the XPS data obtained from oil-stored balls that were subjected to complete cleaning processes identical to those used to prepare bearings for test. These data show large differences in the composition of the near-surface region that depend sensitively on the cleaning process used. In particular, the intensity of the C 1s peak, centered at the characteristic binding energy for a hydrocarbon (284.6 eV), is very strong on the Vertrel-cleaned article (Fig. 6C), is much weaker on the Brulin-cleaned samples (Fig. 6B), and has an intermediate intensity on the Freon TF-cleaned samples (Fig. 6A). The intensities of spectral features from the substrate, particularly the Fe and Cr 2p peaks near 710 and 580 eV, respectively, also vary significantly with the cleaning process. A thick contaminant layer on the Vertrel-cleaned ball completely obscures the substrate features. On the Freon TF- and Brulin-cleaned balls, both substrate elements are evident, but they are clearly more intense for the Brulin ball, consistent with a thinner hydrocarbon contaminant layer, as expected from the lower carbon signal intensity. It should be noted that the sensitivity of XPS to the different elements varies greatly, and the relative concentrations of species can be determined using known elemental sensitivity factors as shown below. In addition, some trace elements were detected as indicated on the spectra. In particular, Na, Ba, and S were observed on the Freon TF- and Vertrel-cleaned balls, while a small amount of Si was detected on the Brulin-cleaned samples. We believe that the Na, Ba, and S contributions come from additives or impurities in the protective oil, while the Si is a residue of the Brulin process that has been observed before.[7]

Using the integrated peak intensities from high resolution-data (not presented) and the appropriate sensitivity factors, the concentrations of surface species detected after the cleaning processes are provided in Table 1. These data clearly show the differences among the surface cleaning techniques, with the Brulin sample obviously being the cleanest (least C, greatest Fe and Cr), and the Vertrel

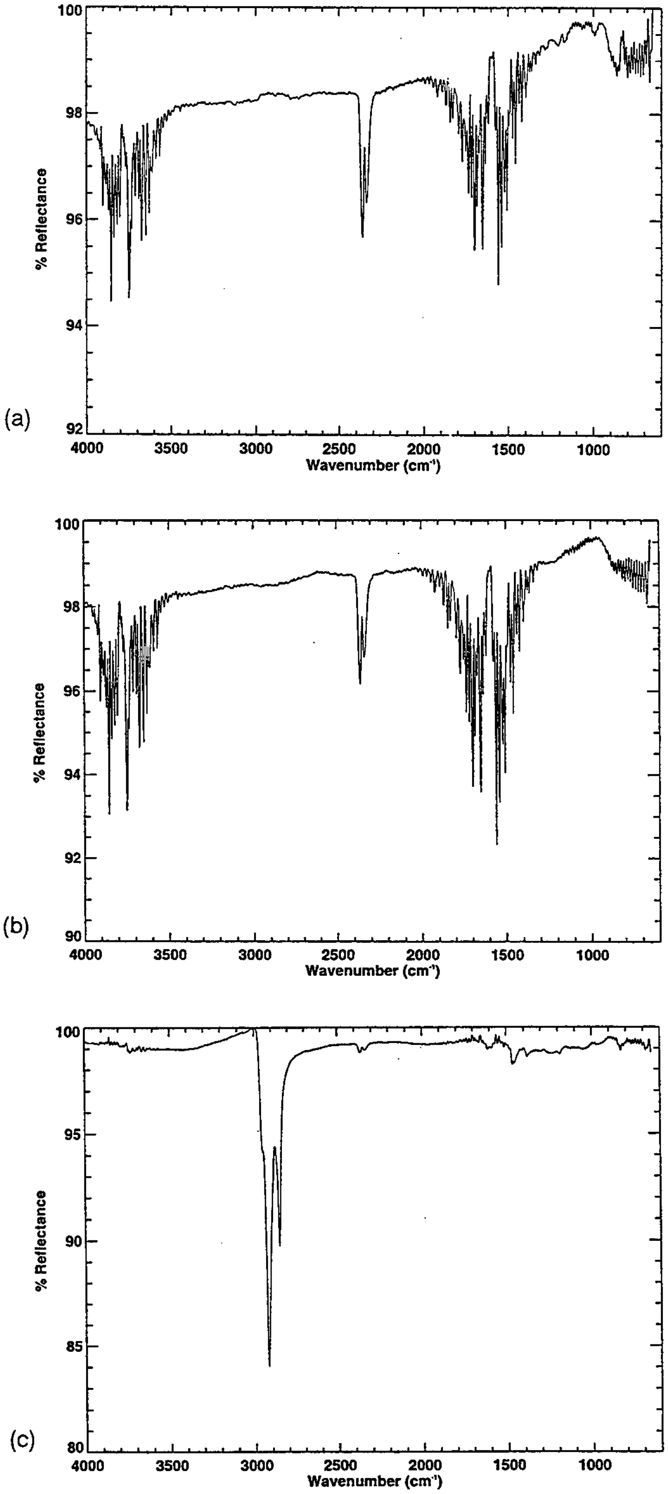

Figure 5. FTIR data obtained from bearing balls cleaned as described in the text with (a) Freon TF, (b) Brulin 815 GD, and (c) Vertrel XF.

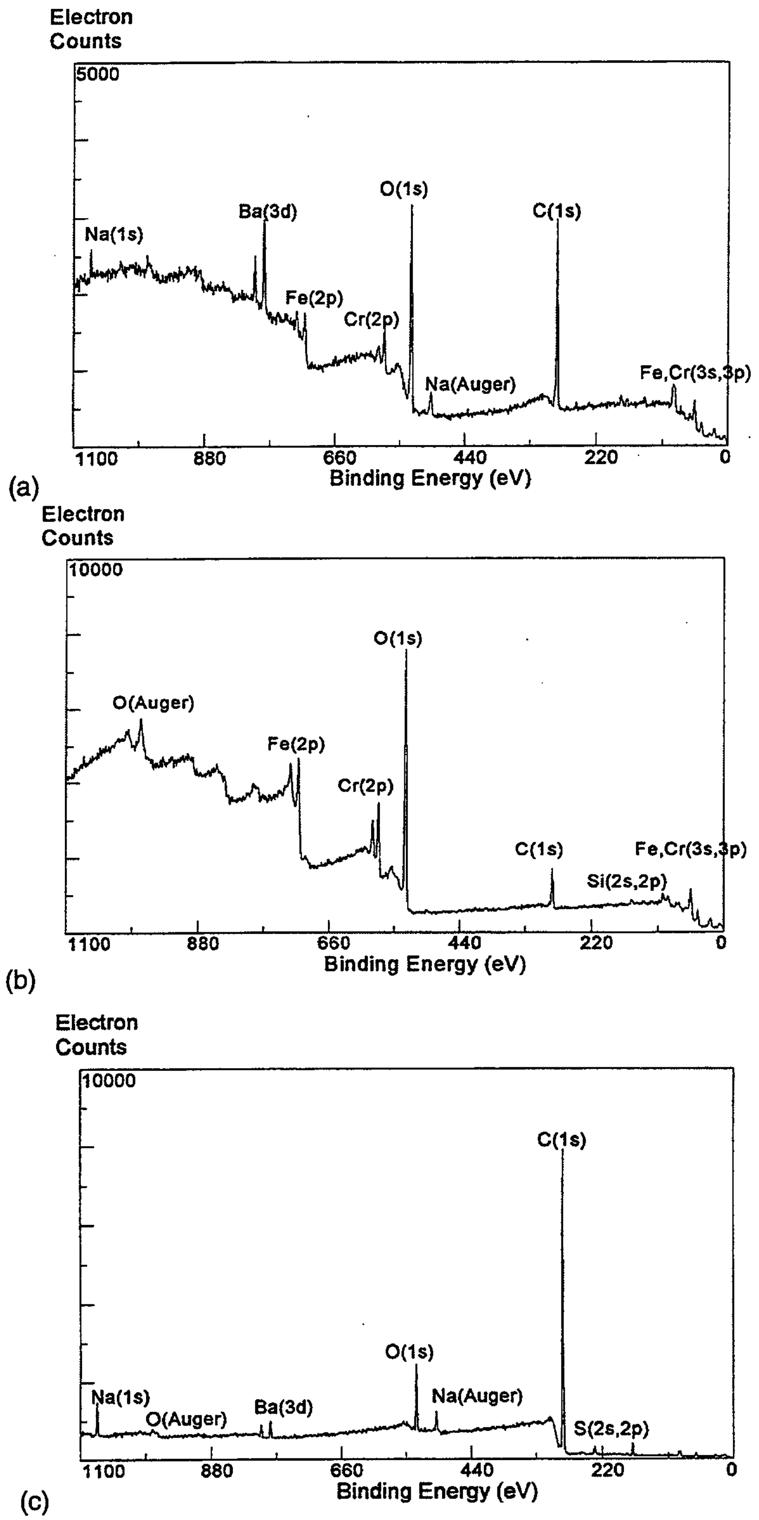

Figure 6. XPS survey scans obtained on bearing balls cleaned with (a) Freon TF, (b) Brulin 815 GD, and (c) Vertrel XF. Prior to cleaning, the balls had been stored with a protective mineral oil coating. The identities of the major peaks are provided on the spectra.

Table 1. XPS Determined Surface Chemical Composition (Atomic %) of 440C Balls Cleaned after Storage in Mineral Oil

Cleaning Method	% C	% O	% Fe	% Cr	% Si	% Other
Freon TF	54	38	3.1	3.2	0	2% Ba, 2% Na, trace S
Brulin	23	59	8.4	7.2	2.3	trace Na
Vertrel	86	9	0	0	0	2%Na, 2% S, trace Ba

sample having a thick hydrocarbon residue. On all samples, the carbon concentration is quite high while the substrate values are low because of the presence of a predominantly hydrocarbon contaminant overlayer on top of the steel substrates. The contaminant overlayer strongly attenuates substrate signals, and this attenuation will be used to provide relative estimates of contamination layer thickness below. The Vertrel-cleaned sample data show that the contaminant layer also contains almost 10% oxygen.

Figure 7 compares typical XPS survey scans taken from cleaned balls that were stored without the oil coating. The results from the Freon TF (Fig. 7A) and Vertrel XF (Fig. 7C) cleaning are very similar, and the main difference among the three spectra is the smaller amount of carbon and corresponding stronger substrate features always detected on Brulin-cleaned surfaces. The quantitative surface concentrations are presented in Table 2. As expected from Figure 7, the Freon TF- and Vertrel XF-cleaned samples have very similar chemical compositions, and the Brulin is again cleaner. None of the oil-related trace elements were detected on these balls, but a weak silicon signal was observed on the Brulin-cleaned surface. The amount of silicon detected was small, just above the detection limits for the technique, but its presence on all Brulin-cleaned balls indicates the potential for concern should inadequate rinsing become a process problem.

Table 2. XPS Determined Surface Chemical Composition of 440C Bearing Balls Cleaned by Various Processes—Balls Stored Without Oil Coating

Cleaning Method	% C	% O	% Fe	% Cr	% Si
Freon TF	49	42	3.8	4.7	0
Brulin	35	51	4.9	6.4	2.6
Vertrel	50	41	4.7	4.0	0

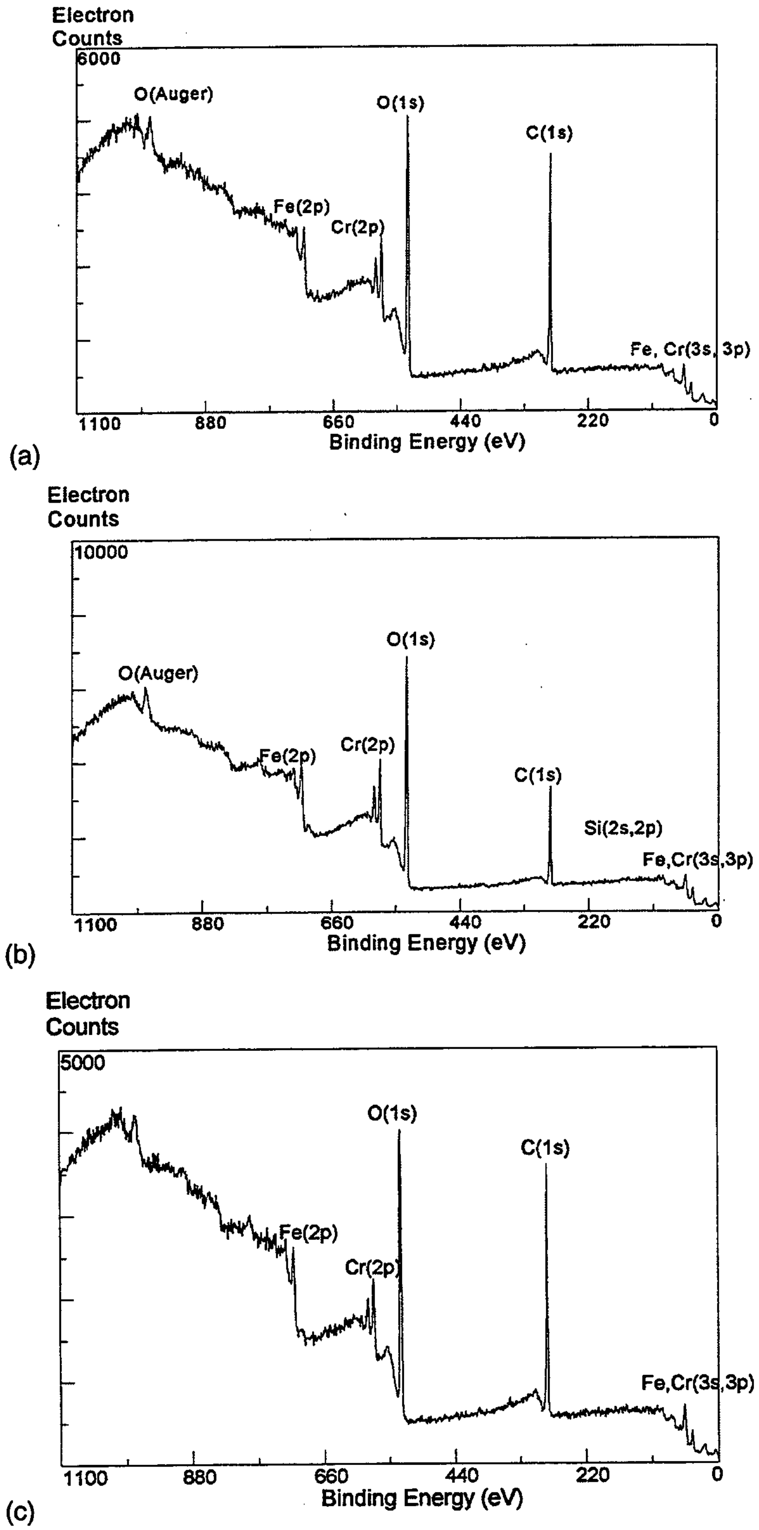

Figure 7. XPS survey scans obtained on bearing balls cleaned with (a) Freon TF, (b) Brulin 815 GD, and (c) Vertrel XF. Prior to cleaning, the balls were stored without any oil coating.

Since XPS is extremely surface sensitive and the analyses must take place under vacuum, one must be cognizant of the limitations of quantifying these cleaning results. If the signal from the steel substrate is detectable through the contaminant film, then the thickness of this overlayer must be less than approximately 100 Å. However, virtually every sample analyzed with XPS without any in-situ cleaning has a layer of adventitious carbon from hydrocarbons in the atmosphere that is thick enough to be detected (air exposure was limited to less than 10 min after cleaning). In addition, if some of the oil residue left behind after cleaning is somewhat volatile, it can evaporate off the surface upon introduction into the vacuum system. With these limitations in mind, it is still clear that there is a significant difference among the various cleaning techniques used. The XPS data can be used to estimate contaminant film thickness, as is outlined below.

Performing XPS analyses on the bearing balls after cleaning was convenient due to their small size relative to the flat and race. However, the curved ball surface and the large acceptance cone of electrons on our spectrometer analyzer make a quantitative determination of contaminant film thickness problematic. The attenuation of the intensity of a substrate feature by an overlayer in electron spectroscopy is generally treated as having an exponential dependence on the thickness of the overlayer:

$$I = I_0(e^{-d/\lambda\cos\theta}) \qquad (1)$$

In Eq (1), I is the measured peak intensity, I_0 is the intensity in the absence of the overlayer, d is the overlayer thickness, λ is the scattering length of the electron in the overlayer, and θ is the angle of the detector relative to the surface normal (nominally 60° in our system). The value of λ depends strongly on the kinetic energy of the emitted photoelectrons; it is longer for the higher kinetic energy C 1s electrons than for either the Fe or Cr 2p electrons. The value of λ also depends on the nature of the overlayer material through which the electrons pass. The intensity of the overlayer signal (which we will approximate using only the C 1s signal) is given in Eq (2), where I_0 is the expected intensity from an infinitely thick overlayer.

$$I = I_0[1 - (e^{-d/\lambda\cos\theta})] \qquad (2)$$

To determine whether the curvature of the ball is too great to enable this analysis to be performed, the spot size and electron energy analyzer acceptance angle must be considered. The X-ray spot used in these analyses is elliptical, with the smaller axis being approximately 300 µm across and lying in the same direction as the electron acceptance angle of the analyzer. With the balls for this analysis being 3/16 in. (4.76 mm) in diameter, the variance in the take-off angle over the extent of the spot size is approximately 7°. This is a significant variation, although much smaller than the angle defined by the acceptance cone of the analyzer (30°). The large acceptance angle also creates uncertainty for the actual value of θ (ranging from 45° to 75°), which we have approximated by using the angle to the center of the acceptance arc, which is 60°. This variation impacts the effective escape depth through the $\lambda\cos\theta$ term. However, the most difficult aspect of such an analysis is the actual positioning of the samples, which relies on aligning the sample with a microscope and following signal intensity as a function of position. On a flat, this is a straightforward procedure. On a curved surface, coordinating the maximization of the position optically along with the signal to noise is difficult. Thus, we cannot be sure that all samples were located in the exact focal point of the system to enable a comparison of their peak intensities. We will proceed, however, by using the relative peak intensities from samples prepared with the three cleaning processes to determine an approximate relative film thickness based on Eqs (1) and (2), and assuming that the surfaces are flat enough to enable such a comparison. With all of these limitations, the following estimates of relative contaminant thickness must be used with caution.

Analyses were performed by comparing XPS intensities of corresponding peaks from the cleaned balls. Specifically, iron and chromium $2p_{3/2}$ intensities from the substrates (a separate analysis for each element), and carbon intensities from the contaminant overlayer were compared. Starting with the balls that were stored in oil, the following conclusions can be reached. Since the Vertrel XF-cleaned ball had a contaminant layer that obscured all of the substrate peaks, one can use Eq (1), coupled to a detection limit of about 1%, to conclude that the thickness of the contaminant layer must be at least 2λ. It is difficult to provide an accurate value of λ through a disordered contaminant hydrocarbon overlayer, but a rough estimate for λ for an electron in the kinetic energy range of interest could be as large as 50Å,[8] meaning that the overlayer is at least 100Å thick. (Actually, this surface was sputter-etched for more than 30 min with argon ions with no reduction in C signal and no evidence of substrate peaks, proving that this layer is much thicker than 100Å, consistent with the FTIR results.) Furthermore, one can assume that the value of I_0 in Eq (2) can be taken from the result of the Vertrel-cleaned samples and then used to estimate the thickness of the contaminant layers on the Brulin- and Freon TF-cleaned surfaces from the intensities of their carbon peaks. Assuming a uniform layer, this results in the prediction of contaminant layers that are approximately 0.15λ (~7.5Å if λ = 50Å) thick on the Brulin-cleaned sample and 0.26λ (~13Å) thick on the Freon TF-cleaned sample. Since the Vertrel data indicate that the contaminant layer contains other species (approximately 86% C), then we can further correct the thickness values to 0.17λ and 0.31λ, respectively.

Moving back to Eq (1), the relative intensities of the Fe and Cr peaks from the Brulin- and Freon TF-cleaned samples can be used to derive relative contaminant thickness estimates to compare with those calculated from the carbon signal. It is important to note that the value of λ for these photoelectrons will be somewhat shorter than for the C 1s electrons due to their lower kinetic energies. In these analyses, the Fe and Cr data provide comparable results, and indicate that the contaminant layer on the Freon TF-cleaned surface is approximately 0.55λ thicker than that on the Brulin-cleaned surface, a value much larger than the carbon data difference (0.14λ) as expected for the smaller value of λ. These results confirm that a measurably thicker contaminant layer remains on Freon TF-cleaned surfaces than occurs with Brulin, consistent with the longer life of the Freon TF-cleaned bearings, which was perhaps enabled by the delay of lubricant breakdown.

Similar analyses were conducted on the cleaned balls that had not been stored with oil coatings. Using the same I_0 value for the analyses conducted above, Eq (2) predicts that the contaminant thickness based on the C 1s peak intensities are 0.26λ for Brulin, 0.37λ for Freon TF, and 0.35λ for the Vertrel sample. As expected from the raw data, the levels of contamination on the Freon TF- and Vertrel-cleaned balls are very similar. Completing the analyses with the Fe and Cr peak intensities, we calculate that the contaminant layer on the Freon TF-cleaned ball is 0.19λ thicker than that on the Brulin-cleaned ball, virtually the same result determined for the Vertrel-cleaned ball (0.20λ). These analyses predict that the value of λ for the Fe and Cr photoelectrons is approximately half that for the C 1s electrons. This is more reasonable than the factor of 3–4 that would have been predicted from the oil-coated balls, which indicates some inconsistency in that data set. In particular, the Freon TF-cleaned, oil-coated ball data look out of family since the concentrations from Table 1 would lead one to predict that the contaminant layer on these balls was really closer to 0.45λ to be more consistent.

Since many of the parts used in the bearing tests were coated with oil prior to cleaning, it seems reasonable that the longer life of the Vertrel bearings can be ascribed to the presence of a much thicker layer of contaminant film. The differences between the Freon TF- and Brulin-cleaned balls are more subtle, although it is clear that the detergent process created cleaner parts. The question of whether this difference in cleanliness was solely responsible for the observed difference in lubricant test life observed in this work is difficult to answer. In previous work, alkaline detergents have been observed to alter surface oxide layers on 440C.[9] To address the possibility that altered oxide layers may have impacted system performance, XPS sputter profiles were performed on Freon TF- and Brulin-cleaned balls to determine whether the oxide layers were affected by the cleaning processes.

Figure 8 compares the sputter profile obtained from a Freon TF-cleaned 440C ball to that from a Brulin-cleaned ball. Each profile has four distinct regions. The surface hydrocarbon overlayer is virtually removed after the first two sputter cycles, causing the large decrease in the carbon contribution and the significant increases of all the other constituents. (Hydrocarbon layers are easier to remove by sputtering than is the substrate, so one should not conclude that these layers are only 4–6 Å thick based on the assumed sputtering rate.) The three steel-related regions are approximately divided by the solid vertical lines on the two profiles. The first region is characterized by a slowly declining oxygen concentration coupled to approximately constant Fe and C, and slowing rising Cr concentrations. The detailed spectra obtained during this period clearly show a decreasing iron oxide signal, and previous work has concluded that an iron oxide overlayer exists on 440C; this overlayer is being sputtered away in this time frame.

With increasing sputter time, the next region is characterized by fairly dramatic changes. The oxygen signal falls steeply while the iron signal rises. The Cr concentration drops slightly while C increases. These changes coupled to the detailed data show that a chromium oxide underlayer is being sputtered away during this time period. The spectral changes differentiating this zone from the bulk steel are not sharp, and the line has been drawn to mark the times where the dramatic spectral changes become more gradual.

Comparing the two sputter profiles, three differences are evident, but they are subtle differences. First, the times required to sputter away the oxide layers on the Freon TF-cleaned ball are slightly longer than those required for the Brulin-cleaned ball. This difference is evident in both the iron oxide overlayer and the chromium oxide underlayer. The combined difference translates into a total oxide overlayer that was approximately 6Å thicker on the Freon TF-cleaned component. The second difference is that the boundaries between the regions seem more distinct on the Freon TF-cleaned ball. For example, it is much easier to distinguish the break between the iron oxide and chromium oxide layers in Figure 8A, perhaps indicating that these layers are better formed prior to the detergent cleaning. The final noted difference is the absolute carbon concentration, which is consistently higher in the surface region of the Brulin sample and has the characteristic binding energy of carbide species after the hydrocarbon is removed. Chromium carbides are known to oxidize more slowly than the metal,[10] and this may indicate that the oxide overlayers were significantly disrupted by the detergent cleaning process. All of these differences may be caused by sample variations, and a more exhaustive survey of these effects should be conducted.

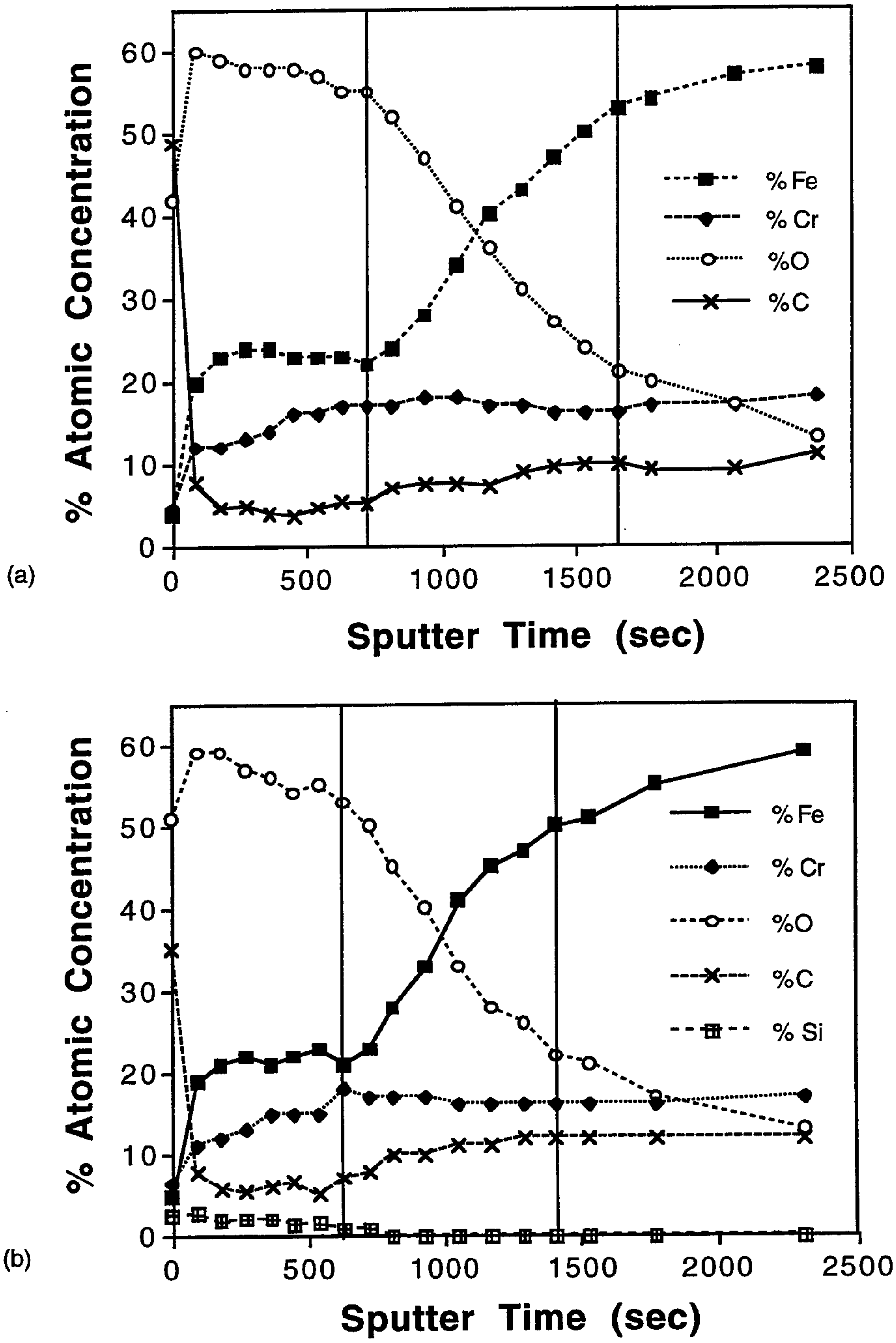

Figure 8. XPS sputter profile of a 440C bearing ball cleaned with (a) Freon TF and (b) Brulin 815 GD. The solid vertical lines indicate the approximate locations of interfaces described in the text.

4. Conclusions

This work has shown that a bearing cleaning process can affect the life of lubricated contacts in moving mechanical assemblies, particularly if lubricant life is limited by degradation in the contact. In the case of PFPE oils, degradation catalyzed by iron has been noted, and cleaning processes that either enhance or inhibit the exposure of the oil to bare metal can either shorten or lengthen the period of performance under boundary contact. This study has shown that a thick residual hydrocarbon residue left by relatively ineffective cleaning can extend the life of the PFPE, but in an uncontrolled and ultimately unreliable fashion. Alternatively, more aggressive cleaning processes such as aqueous detergents, can leave surfaces cleaner than traditional Freon TF processes, leading to earlier degradation and failure of the lubricant.

The precise cause of the shorter lifetime of the detergent-cleaned bearings has not been determined, but two possibilities are indicated by our surface analyses. First, there was clearly more residual hydrocarbon left on the Freon TF-cleaned components than observed on the detergent cleaned parts. In general, the contaminant films after both processes were fairly thin, and the difference between the processes was judged to be in the range of 5 to 10 Å, depending on the initial condition of the part. However, this analysis was complicated by the limitations of the technique used, and further investigations should be conducted to accurately quantify contamination levels. The second possible explanation for the performance difference is the slightly thinner and possibly less well ordered oxide layers present on the detergent-cleaned surface. These thinner layers would presumably wear away sooner than those of the Freon TF-cleaned bearing, exposing the lubricant to bare steel sooner, leading to earlier failure. The difference in oxide layer thickness was estimated to be less than 10 Å, with the Brulin oxide layer approximately 90% as thick as the Freon TF surface. On average, the Brulin tests lasted only 40% as long as the Freon TF-cleaned bearing tests, suggesting that some combination of the two effects may be ultimately responsible for the shorter lifetime of the detergent-cleaned system.

It is not the intent of this report to recommend any particular bearing cleaning process. Rather, since the industry is unlikely to converge upon a single cleaning method to replace Freon TF processes, this work serves as a caution to document and understand the surface composition of components cleaned by new processes, and to be aware of potential deleterious effects on lubricant performance that the new processes may cause. The impact of our results on the larger NASA program goal addressing the qualification of mechanisms cleaned by new processes is relatively clear. Our work indicates that these cleaning methods can significantly impact lubricant life, and thus mechanisms cleaned with new processes should not be considered equivalent to previously qualified Freon TF-cleaned systems without appropriate qualification testing.

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