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Experience With Synthetic Fluorinated Fluid Lubricants

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Abstract

Since the late 1970's, the wet lubricant of choice for space mechanisms has been one of the family of synthetic perfluoropolyalkylether (PFPE) compounds, namely Fomblin Z-25 (Bray-815Z) or Dupont's Krytox 143xx series. While offering the advantages of extremely low vapor pressures and wide temperature ranges, these oils and derived greases have a complex chemistry compared to the more familiar natural and synthetic hydrocarbons. Many aerospace companies have conducted test programs to characterize the behavior of these compounds in a space environment, resulting in a large body of hard knowledge as well as considerable "space lore" concerning the suitability of the lubricants for particular applications and techniques for successful application. This paper summarizes the facts and dispels a few myths about the compounds, and provides some performance guidelines for the mechanism design engineer.

Background

Most mechanism designers have been confronted with the difficulties of effectively lubricating mechanisms for a space environment. A wet lubricant offers major advantages over a solid lubricant: the liquid will flow and replenish used lubricant, a liquid will not form unpredictable solid debris, and a liquid offers the potential for elastohydrodynamic (EHD) lubrication if speeds are great enough. However, the central problems of a deep space vacuum, long unattended operation, and severe thermal environments preclude the use of most liquids without resort to cumbersome seals or heaters.

In the early 1970's, two series of synthetic fluorinated fluids became available. One series is based on Monte Edison's Fomblin Z-25 oil and includes Bray (now Burma-Castrol) -815Z oil, along with 3L-38, 3L-38RP, 600, 601, and 602 greases. A slightly different base oil chemistry was used to formulate the Dupont Krytox 143xx series of

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fluids. These fluids are generally known as perfluoropolyalkylether (PFPE or PFAE) compounds: they are synthetic fluorocarbons.

Examples of typical oil types that have been used effectively in space are listed in Table 1, along with room temperature vapor pressure and viscosity data. Figures 1 and 2 illustrate the difficulties of a space environment in a simplified fashion. Figure 1, calculated using the Langmuir equation[1], illustrates the rapid loss of oil from a mechanism at even moderate temperatures. It is interesting to note that the natural super-refined hydrocarbon outperforms all but the synthetic fluorocarbons. Figure 2 shows the approximate pour points of the same oils, illustrating the principal disadvantage of the natural material.

It is clear that the synthetic fluorocarbons, and in particular the Bray-815Z oil, offer very clear advantages over any other available lubricant.

Drawbacks

With such an obvious advantage regarding the space environment, the synthetic fluorocarbons appeared initially to be something of a panacea for space lubrication problems. However, early testing revealed surprises regarding performance of the oils in boundary (non-EHD) lubrication situations. A few cases are listed below.

- 1980: Hughes tested several of the Bray compounds for use in a large precision oscillating gimbal application. The results were unacceptable, shown in Figure 3. At the conclusion of the test, the oil had been polymerized, resembling brown sugar.

- 1983: the European Space Tribology Lab reported[2] on a similar phenomenon, and equally unacceptable results at various speeds. The same report contains an account of severe wear, substrate damage, and lubricant polymerization using the Fomblin Z-25 oil in a relatively short-lived gear drive.

- 1984: NASA completed long-term vacuum testing[3] of a large number of lubricants in small bearings at relatively high speed as well as start/stop operation, and concluded that the PFPE lubricants performed well under these conditions.

- 1984: the authors tested bearing performance for a 10-degree scanning mirror design. Our results were extremely interesting, as shown in Figure 4. The oil was not substantially polymerized. However, grooves approximately 1.25 microns deep had been milled into the inner race along each ball path.

- 1984-1988: Aerospace Corporation published[4-6] a series of papers describing oil polymerization and the chemistry of iron fluoride formation with ball bearing steels.

- 1985: Hughes Electro-Optical Data Systems Group conducted tests[7] with PFPE oils and greases under both boundary and EHD conditions, using both steel (AISI 440C) and ceramic (Norton Noralide silicon nitride) balls and 440C races. The results confirmed those published earlier. With steel balls, the grease polymerized quickly under boundary conditions, while oil polymerized slowly and repeatably in EHD. Contaminated grease outlasted the non-contaminated sample. Most importantly, for the duration of this test, the ceramic balls prevented the now-familiar polymerization under boundary conditions.

Similar data has been reported from many sources. It has become quite apparent that the PFPE oils and greases cannot be used without a careful assessment of the real tribological conditions of an application. Applications should be reviewed in light of the conditions which are known to result in oil breakdown. With this knowledge, new applications can be evaluated quantitatively and steps taken prior to test failures.

Chemical Behavior

The unique chemistry which imparts the marvelous physical properties to the PFPEs is also responsible for their strange behavior in metal-to-metal contacts of various applications. While the PFPEs are quite similar, the Fomblin Z-25 fluid is a less branched, more linear fluid than the Dupont Krytox fluids. The two structures are shown in Figure 5. The basic repeating units of the Fomblin contain more ether linkages than the Dupont product: the ether bonds are believed to be the weak points of these molecules. As a result of these differences, the Z-25 fluids have better physical properties, but are slightly more susceptible to chemical attack.

While chemically inert to almost everything, including hot hydrofluoric acid, oxygen, and strong bases, all of the PFPEs are subject to catalytic attack by Lewis acids. Table 2 lists some of the common metals which will form fluorides that are Lewis acids. The "Achilles' heel" of these fluids is a tendency to break just a few molecules under severe mechanical stress. When used in mechanisms, this severe stress will tend to occur under boundary lubrication as shown in Figure 6. At the asperity contacts, metal flourides are formed which then go on to catalytically decompose much more of the fluid.

Contact Analysis

It is important to recognize that an exact analysis of the contact conditions in a real mechanism is problematic. In order to produce useful data, a mechanism test must instead be well characterized. To extrapolate results from one test to another, or from a wear test rig to a mechanism, the data must be grouped according to some basic rules. Using these rules, we can outline wear regimes corresponding to predictable success or failure.

1 - Determine the real speeds, loads, and life. Simple estimates of mechanism life are usually incorrect. There are several important considerations to include in a life profile.

- Many mechanisms are used within a control loop which results in a complicated tracking profile, which may include dither life about a single point.
- Payload oscillations should be calculated: these frequently contribute significantly to the worst case requirements.
- Stepping dynamics should be estimated via simulation or observation.
- Geartrain windup loads will be important for a large payload and a stiff geartrain.
- Motor rotor oscillations should be calculated for the early stages of a geartrain.

2 - Calculate lubricant stress cycles. Under the conditions found above, the actual lubricant stress cycles should be calculated. Ex-

amples are ball crossings over a given race location and the number of times an individual gear tooth moves through contact.

The catalytic reactions described in the preceding sections all require a certain number of lubricant stress cycles to develop significant products. Using stress cycles as a criterion will predict the failure of a bearing due to dither or control system noise: total degrees traveled or equivalent revolutions will not. In addition, oscillating applications can be compared directly to continuously rotating applications using the stress cycles criterion.

3 - Calculate maximum contact (Hertzian) stresses during each lubricant stress cycle. Higher loads will mean a greater amount of fresh metal exposed in the contact for catalysis, and will result in shorter lives for a given material combination. Reference 5 indicates a life dependence on contact stress, but at loads higher than would be found in a well designed mechanism. We have also found some slight correlation between loads and life: unloaded motor bearings tend to have long life expectancies.

4 - Check for EHD conditions. It has been shown[2,7] that PFPE oils will decompose under calculated EHD conditions as well as boundary, although at a much slower rate. In our experience, few space mechanisms ever get into EHD. Gear teeth are particularly unlikely to ever get out of boundary conditions.

Chemical Prevention

The key to chemically preventing the oil decomposition is to prevent the catalytic action of strong Lewis acids on the functional surfaces. The easiest way to do this is to prevent acid formation by not imparting high stress to the oil, i.e., stay in full EHD. As this is not possible, passivation of the functional surfaces is necessary. This can be accomplished by using surface materials which either don't form Lewis acids such as ceramics, or other materials which form weak acids in thin films. Curiously, normally inert gold is a moderate Lewis acid former and has been found[8] to be unacceptable when used with PFPEs in slip ring applications. The use of ceramics, in the form of hardcoatings like TiN or TiC or as a bulk like Si3N4, is an excellent way to reduce or eliminate catalytic breakdown. Conventional nitride hardcoatings, which result in inert "white layers", have also proved to be effective.

Based on the contact calculations, we suggest that life data be broken down into plots for each material system and lubrication regime. The next sections summarize some data which can be used to evaluate new designs.

Geartrain Data

Figure 7 summarizes years of data on the small geartrains typical of space mechanism design. Since we moved away from dry lubricants in the early 1980's, Hughes has successfully flown or qualified hundreds of gearhead designs using Bray 600 grease. All of these are stepper motor driven and use a martensitic steel base material, typically PH 13-8 Mo. Gear sizes run from 120 DP to 32 DP.

Several methods have been used to avoid grease degradation, depending on the severity of the application. We have selected material systems which will delay the polymerization reactions described earlier. Demonstrated performance for several material systems is shown in the figure.

It should be emphasized that none of the reported data represent a failure. However, the indicated bare steel data point is shown in Figure 8. Some evidence of tooth wear is obvious, and analysis of the grease showed steel wear particles. Even the more resistant systems begin to show evidence of wear as we move beyond a life of 1×10^8 stress cycles.

As more demanding applications come along, we intend to push the proven performance envelopes out further in all directions. With forethought about the materials system and the oil supply, the PFPE lubricants will satisfy almost any space gearing application. The environmental advantages of the PFPEs essentially demand their use.

Ball Bearing Data

Ball bearing applications will tend to be much more critical than gearing applications. Traditionally ball bearing applications have been divided into two classes: EHD conditions and boundary lubrication conditions. Our data indicates that with the synthetic fluorocarbons, one must consider oil starvation[9] as a subset of each of these conditions.

Figures 9, 11, and 12 show demonstrated life data for these classes. Taken together, the three figures show a continuous spectrum of the life which can be expected from PFPE lubricants in ball bearing applications.

EHD Data

Figure 9 shows several data points for EHD applications. Based on the information from reference 2, the erratic torque behavior found in the high-speed application could have been predicted and avoided. Instead we have more data confirming the earlier work, where it was suggested that oil breakdown gradually results in a starvation phenomenon and increased breakdown. Figure 10 shows the degraded oil following the test.

Boundary Data - Starved Conditions

Figure 11 indicates the rapid onset of bearing failure under boundary conditions if there is inadequate oil available. The result of the lubricant breakdown is a rapid increase in bearing friction torque (see Figure 3). In one of the tests shown, replacement of the 440C balls with Si_3N_4 balls eliminated the breakdown for the duration of this test.

The chemical breakdown of the oil results in a consumption of the available supply. Thus, rapid starvation of a bearing can occur with these lubricants. A bearing design used successfully with a different lubricant may seem to exhibit anomalous behavior with a synthetic fluorocarbon. Comparison of Figures 11 and 12 shows that life under starved conditions will be predictably shorter than under normal boundary conditions.

Starvation will result whenever an excess supply of oil is not available at the contact. A few situations which will cause this are:

- Grease-plating or a similar thin film deposition of oil. The original rationale for using these techniques is that only a few molecules in the contact are needed to do the lubrication. This does not allow for oil breakdown or loss.

- A non-porous ball retainer. The retainer should be designed to function as a reservoir. This will renew the oil supply in the contact and dilute the breakdown products.

- Insufficient renewal of the contacting surfaces. In 1980, our 4 degree oscillation test demonstrated this dramatically. The rocking motion did not supply fresh oil to the contact, and the foam retainer was an ineffective reservoir as a result.

Boundary Data - Flooded Conditions

Even with adequate oil available at the contact, breakdown will still occur and some chemical side effects begin to appear: great care should be exercised as we get beyond 10^6 stress cycles. Noticeable changes in bearing torque will not show up until much later, as the entire oil supply becomes affected. Figure 12 indicates the lives demonstrated for well-lubricated bearings under a variety of conditions.

On the far right of the figure are a few examples of very small (approximately 1 cm outside diameter) stepper motor bearings. They are not preloaded and are insensitive to small dimensional changes as well as torque noise. These bearings proved to be entirely satisfactory for the lives indicated, although the oil had been virtually used up, as shown in Figures 13. A reasonable upper bound for this type of application without using ceramic coatings or balls would be $5x10^8$ crossings.

The other bearings in the figure showed minor (<100%) torque increases. This will often not be significant, and the lives indicated can be realized for deployment and most positioning mechanisms. However, we find that the oil breakdown products result in a chemical wear phenomenon which could be very significant for precision gimbal applications.

Wear Rate Data

Post-test disassembly and profilometry of some of the test bearings shows that the action of the oil decomposition removes significant amounts of metal from the active race surfaces, as shown in Figure 4. The amount of material removed will most likely not be significant for bearings preloaded with a spring, or in applications which are not preload-sensitive. For rigid duplex pairs, the preload changes may result in stiffness losses which are unacceptable.

Figure 14 summarizes our available data. Note that the ordinate is the total material lost from both races. We have found that while the inner and outer races do not wear evenly, the total wear is consistent. Two types of bearing preload are represented. We have measured material lost from a bearing with a constant preload, for example that provided with a constant force spring. In the same test, we measured material lost from a rigid duplex pair of the same design.

For a bearing under constant load, we would expect that the wear rate would decrease as the surfaces become smoother and conform better, but never go to zero. We suggest that an estimate of loss rate can be obtained using an expression of the form:

$$\text{Wear} = K1*\ln[L/Lo],$$

where L is the life in stress cycles, Lo is selected as the initiation of wear at cycle 1, and K1 is a constant which depends on the application. This line is shown in the figure. The two data points indicated seem to lie roughly on the same line (K = 0.133), although they are from different bearings. The two had identical material systems and similar contact stresses and oil supply.

For the duplex pair, we would expect that the wear rate would decrease rapidly as the preload is reduced, reaching zero when the preload stickout is eliminated. This suggests an expression of the form:

$$\text{Wear} = Wo*\{1-e^{-C*\ln[L/Lo]}\},$$

where Wo is the total approach of the two races under preload, and C is chosen to match the data.

These formulas are simplified fits to a complex situation. The physics dictate that the initial wear rates would be the same regardless of loading. The form of the first equation could be altered to provide for this, but we do not feel that the data are adequate to support a more complex model.

Closure

Traditional techniques to impart enhanced boundary performance to the PFPEs by using chemical additives have also been attempted. Those efforts have been thwarted by the lack of solubility of appropriate additives in the base oils. Reports continue to circulate of new and successful compounds which will work but the published literature (and indeed the availability of such compounds) is sparse. The approach does hold merit if the chemistry can be solved.

In our experience various methods to mitigate the oil breakdown, be it deliberate contamination, surface layers, or ceramics, have extended the life of PFPE systems. The methods have widely different cost and an effectiveness that roughly parallels the increased costs. It is the responsibility of the designer to characterize a particular application and select appropriate protection from the ravages of chemistry. Instead of selecting a different lubricant, comparing the life requirements of a new application to the accumulated data may allow use of the PFPEs for their unequalled environmental properties.

References

1. Handbook of High Vacuum Engineering, Reinhold Publishing Co., H.A. Steinherz, editor.

2. Stevens, K.T., "Some Observations on the Performance of Fomblin Z-25 Oil and Braycote 3L-38RP Grease in Ball Bearings and Gear Boxes", Proc. of the 1st European Sym. on Space Mechanisms and Tribology, Oct. 1983, pp 109-117.

3. McMurtrey, E.L., "An Evaluation of Grease-type Ball Bearing Lubricants Operating in Various Environments", N85-11239 (NASA TM-86480), Oct. 1984.

4. Carre, D.J., "Perfluoropolyalkylether Oil Degradation: Inference of FeF3 Formation on Steel Surfaces under Boundary Conditions", ASLE Preprint No. 85-AM-3H-1, Feb 1985

5. Carre, D.J., "The Performance of Perfluoropolyalkylether Oils Under Boundary Lubrication Conditions", AD-A191 057, Feb 1988

6. Carre, D.J., "Perfluoropolyalkylether Lubricants under Boundary Conditions: Iron Catalysis of Lubricant Degradation", Report No. SD-TR-88-27, Mar 1988.

7. Personal conversation with L.C. Lipp and K. Christopoulos of Hughes EDSG.

8. Personal conversation with J. Glosbrenner of Litton Polyscientific.

9. Brewe, D.E. and Hamrock, B.J., "Analysis of Starvation Effects on Hydrodynamic Lubrication in Nonconforming Contacts", Trans. ASME, V01. 104, July 1982, pp 410-420.

Table 1
Typical Oils for Space Use
20 C Properties

Type Designation	Trade Name	Vapor Pressure (torr)	Viscosity (CSt)	Pressure/Viscosity Coefficient (@400 MPa)
Natural Hydrocarbon	Apiezon C	3.5×10^{-9}	283	1.2×10^{-4}
Synthetic Hydrocarbon (PAO)	Nye 176A	6.6 x 10-9	1050	1.1×10^{-4}
Synthetic Fluorocarbon	Bray-815Z Krytox 143AC	8.7×10^{-12} 1.2×10^{-9}	180 720	6.8×10^{-5}
Neopentyl-polyolester	Nye NPE UC-7 Nye NPE UC-4	5.1×10^{-9} 2.1×10^{-8}	75 44	N/A

Table 2
Representative Lewis-acid Forming Metals

Name	Relative Reactivity
Titanium	100
Aluminum	35
AISI 440C	22
Iron	12
Gold	6

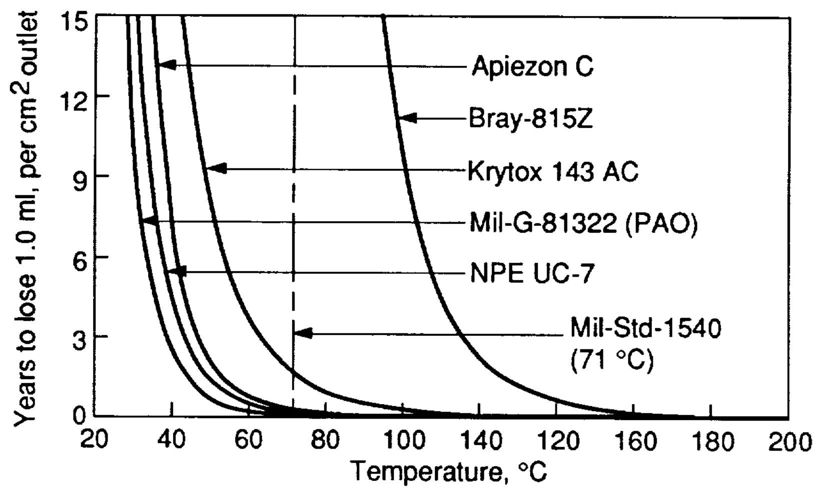


FIGURE 1. RELATIVE EVAPORATION OF REPRESENTATIVE AEROSPACE LUBRICANTS

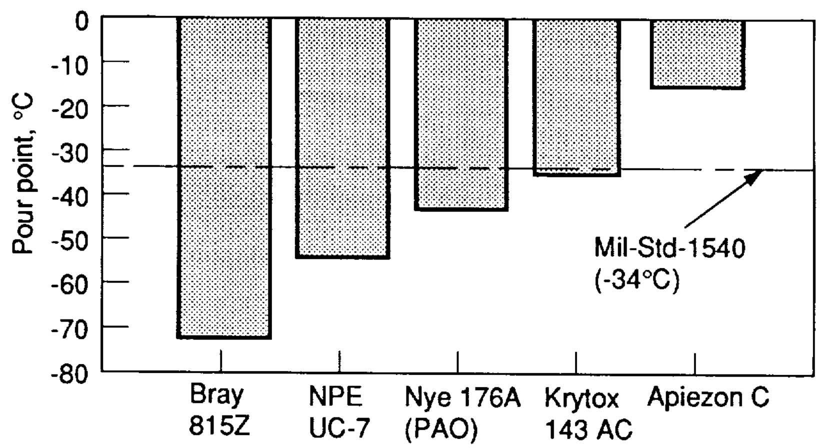


FIGURE 2. TYPICAL AEROSPACE LUBRICANT POUR POINTS

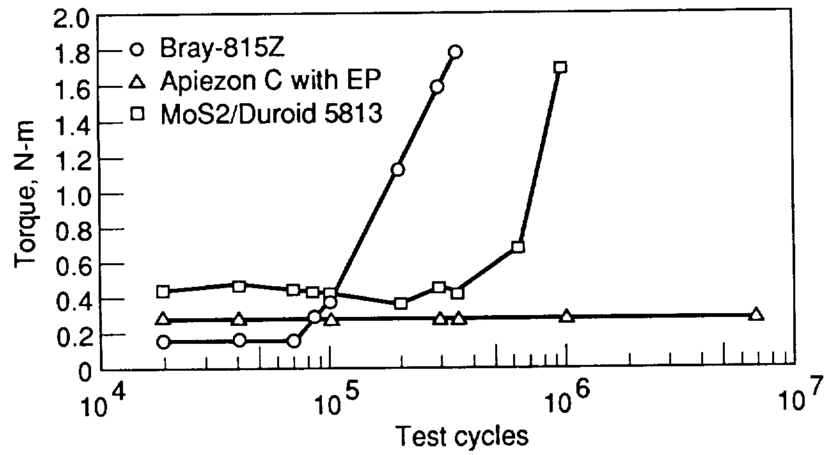


FIGURE 3. 1980 OSCILLATING GIMBAL TEST
Lubricant Comparison, 4 deg Peak-to-Peak

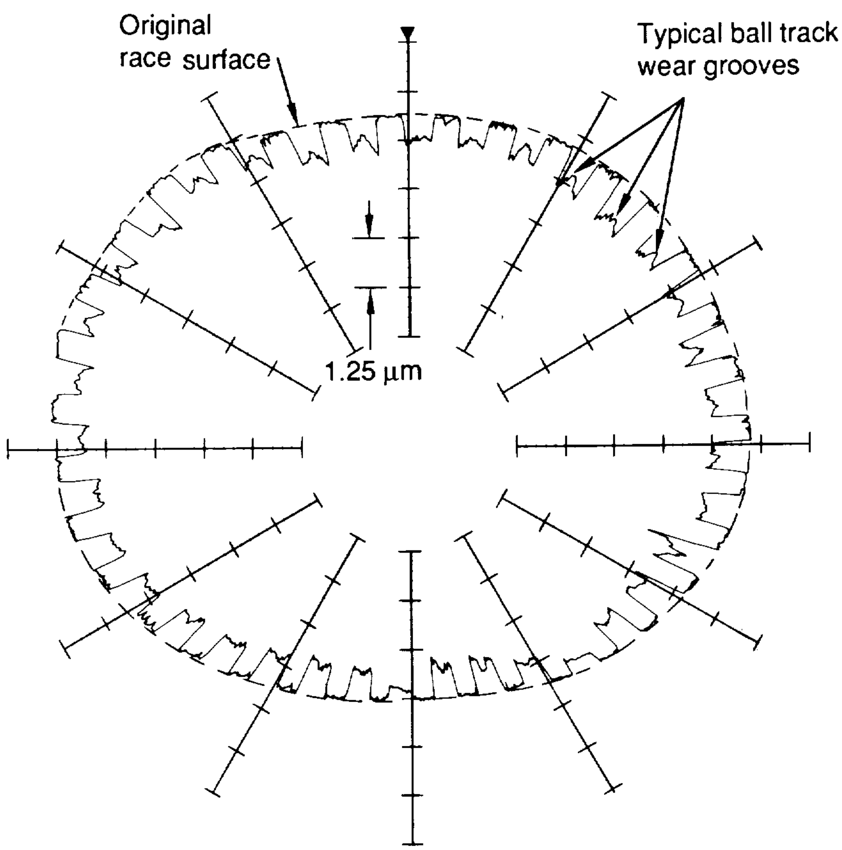


FIGURE 4. INNER RACE PROFILOMETER TRACE:
FOLLOWING 20 MILLION CROSSINGS

Bray-815Z

$$CF_3-CF_2-\left|CF_2-CF_2-O\right|_x-\left|CF_2-O\right|_y-CF_2-CF_3$$

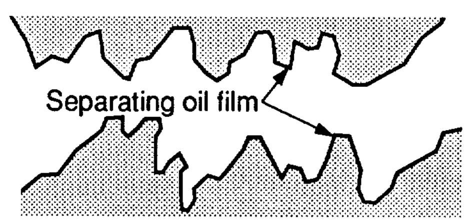
$x \simeq y \simeq 50$

Krytox 143 xx

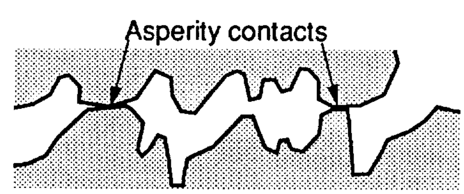
$$F-\left(\begin{array}{l}CF-CF_2-O\\ |\\ CF_3\end{array}\right)_n-CF_2-CF_3$$

$n = 10$ to 60

FIGURE 5. APPROXIMATE CHEMICAL STRUCTURE FOR TWO TYPES OF PERFLUOROALKYLPOLYETHERS (PFAE, PFPE)



a) Elastohydrodynamic Lubrication (EHD)



b) Boundary Lubrication

FIGURE 6. LUBRICATION REGIMES

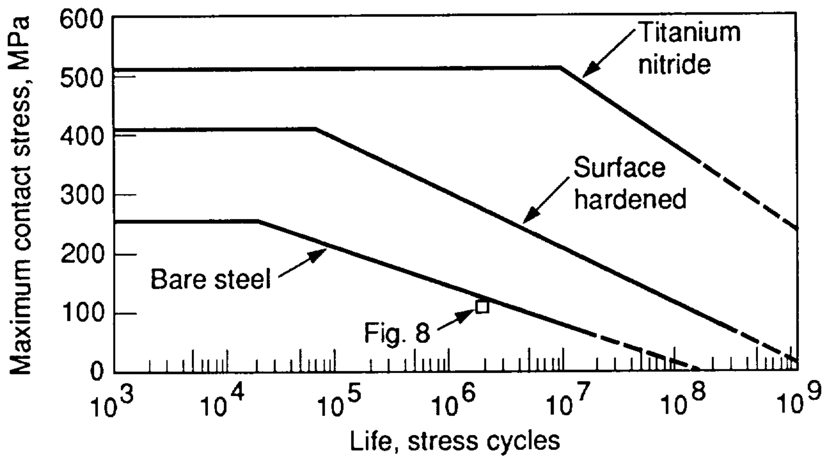


FIGURE 7. GEARTRAIN EXPERIENCE ENVELOPES
Contact Stress vs Stress Cycles
Bray-600 and Martensitic PH CRES

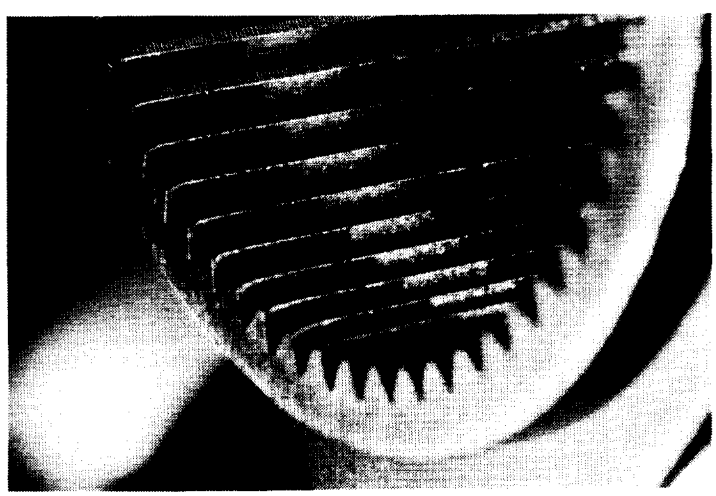


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FIGURE 8. DATA POINT FROM FIGURE 7

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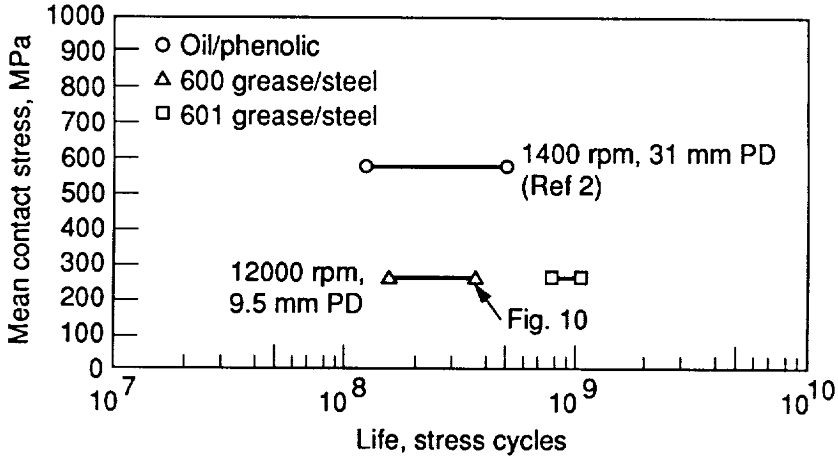

FIGURE 9. BALL BEARING DATA POINTS
Ranges of Observed Breakdown Despite EHD Prediction
Bray-815Z and Derivative Greases

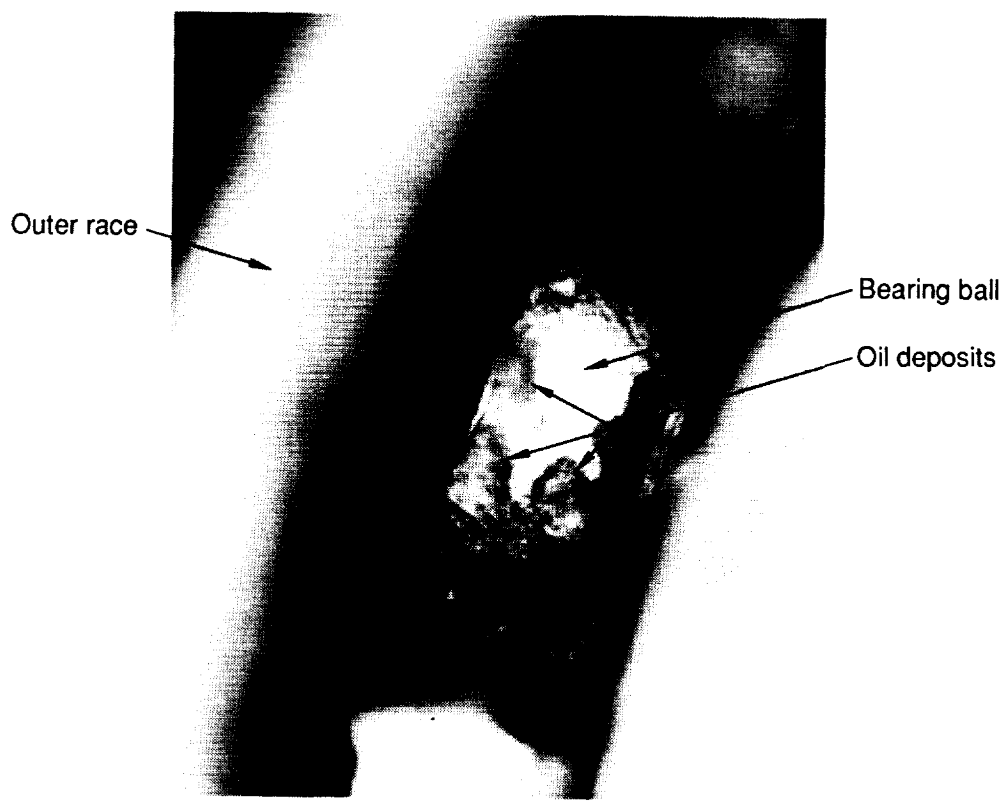

FIGURE 10. MACRO PHOTOGRAPH OF
9.5 mm BEARING FOLLOWING TEST

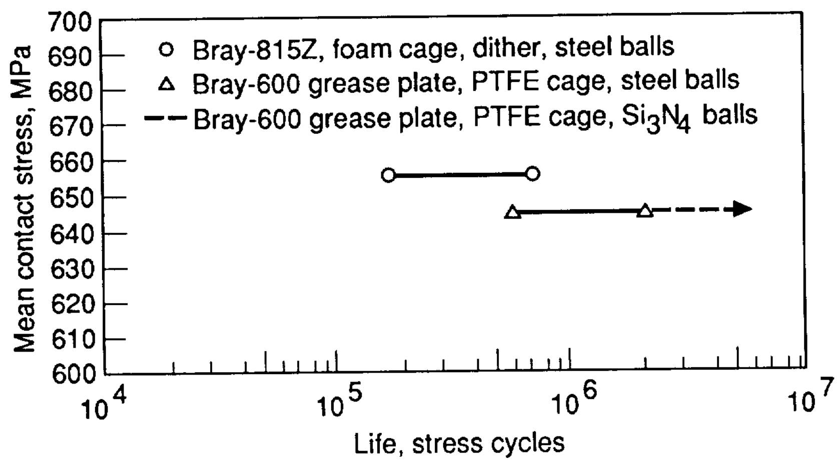

FIGURE 11. BALL BEARING DATA POINTS
Insufficient Oil Breakdown Ranges
Bray Oil and Grease, AISI 440C

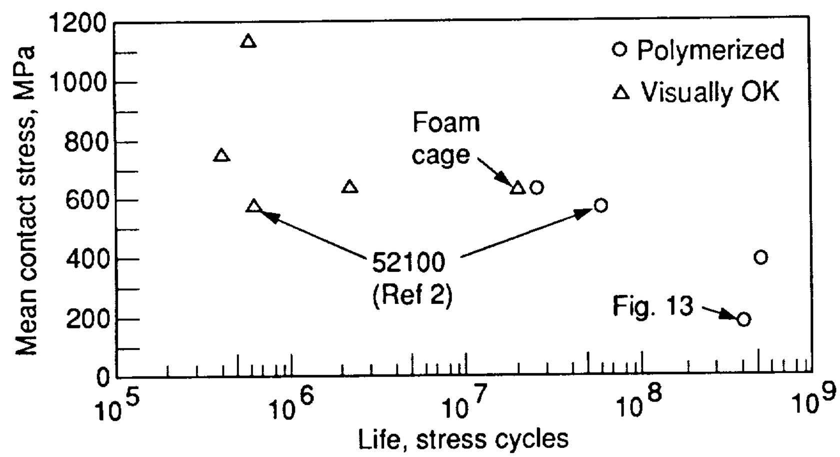

FIGURE 12. BALL BEARING DATA POINTS
Breakdown Under Boundary Lubrication
Bray-815Z, Phenolic Cage, AISI 440C

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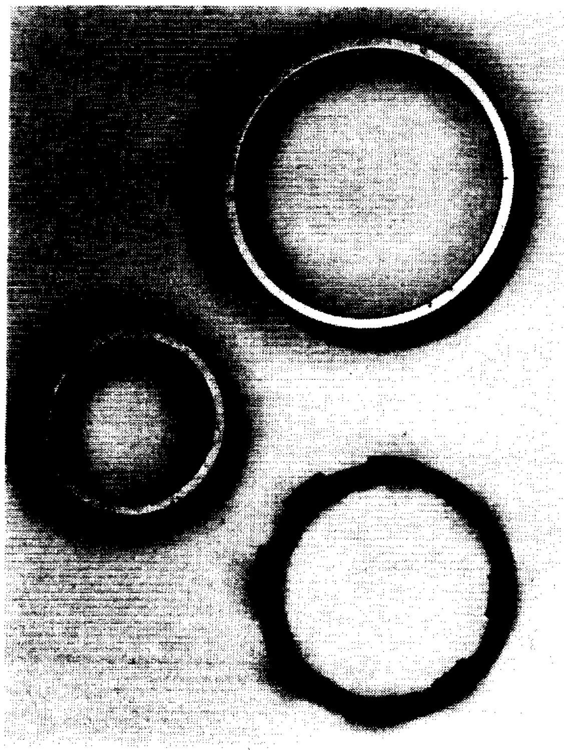

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FIGURE 13a. RACES AND RETAINER FOLLOWING TEST

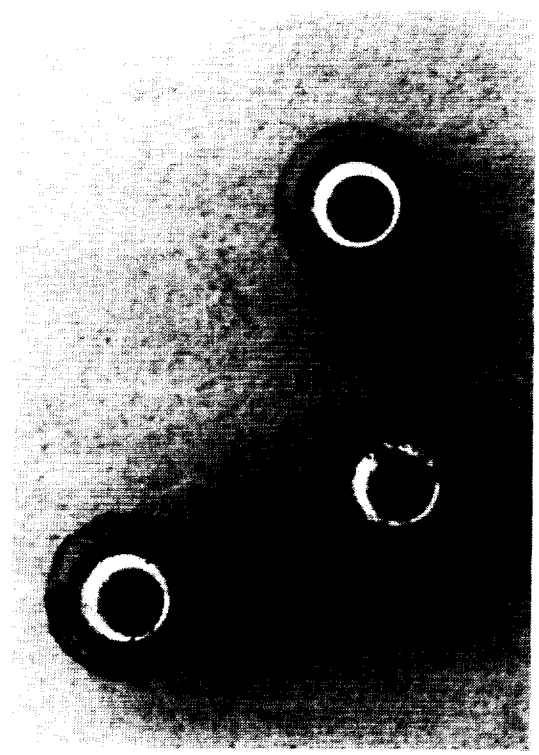

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FIGURE 13b. BALLS FOLLOWING TEST

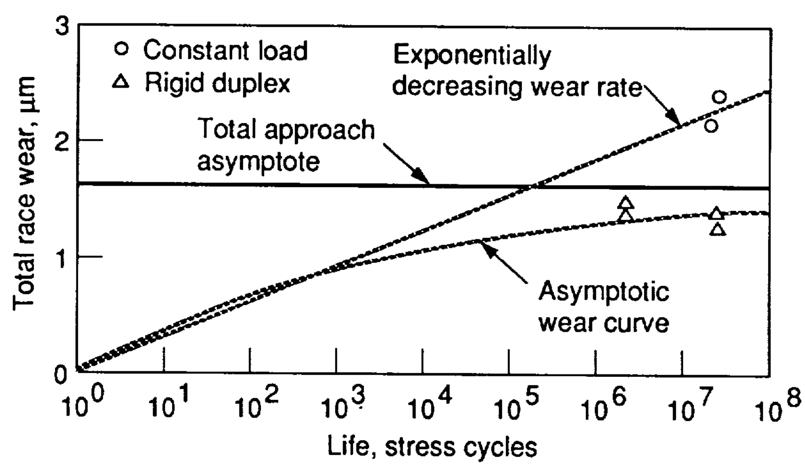

FIGURE 14. BALL BEARING DATA POINTS
Chemical Wear: Preload Loss
Bray-815Z, Foam/Phenolic, AISI 440C