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# The Properties of Perfluoropolyethers Used for Space Applications

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# THE PROPERTIES OF PERFLUOROPOLYETHERS USED FOR SPACE APPLICATIONS

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## SUMMARY

The perfluoropolyether (PFPE) class of liquid lubricants has been used for space applications for over two decades. At first, these fluids performed satisfactorily as early spacecraft placed few demands on their performance. However, as other spacecraft components have become more reliable and lifetimes have been extended, PFPE lubricant deficiencies have been exposed. Therefore, the objective of this paper is to review the PFPE properties that are important for successful long term operation in space.

## INTRODUCTION

The purpose of lubrication is to separate surfaces in relative motion by a material which has a low resistance to shear, so that the surfaces do not sustain major damage. This material can be a variety of different species (e.g., adsorbed gases, reaction films, liquids, solid lubricants, etc.).

Depending on the type of film and its thickness, a number of lubrication regimes can be identified. A classical way of depicting these regimes is by use of the Stribeck curve (fig. 1). Stribeck (ref. 1) performed comprehensive experiments on journal bearings around 1900. He measured the coefficient of friction as a function of load, speed, and temperature. Some years later, Hersey (ref. 2) performed similar experiments and devised a plotting format based on a dimensionless parameter. The Stribeck curve takes the form of the coefficient of friction as a function of the viscosity ( $Z$ ), velocity ( $N$ ), and load ( $P$ ) parameter,  $ZN/P$ .

At high values of  $ZN/P$  which occur at high speeds, low loads, and at high viscosities, the surfaces are completely separated by a thick ( $>0.25 \mu\text{m}$ ) lubricant film. This is the area of hydrodynamic lubrication where friction is determined by the rheology of the lubricant. For nonconformal, concentrated contacts where loads are high enough to cause elastic deformation of the surfaces and pressure-viscosity effects on the lubricant, another regime, elastohydrodynamic lubrication (EHL) can be identified. In this regime, film thicknesses ( $h$ ) may range from (0.025 to  $1.25 \mu\text{m}$ ).

As film thickness becomes progressively thinner, surface interactions start taking place. This regime of increasing friction, in which there is a combination of asperity interactions and fluid film effects, is referred to as the mixed lubrication regime. Finally, at low values of  $ZN/P$ , one enters the realm of boundary lubrication. This regime is characterized by the following (ref. 3):

1. It is a highly complex regime involving metallurgy, surface topography, physical and chemical adsorption, corrosion, catalysis, and reaction kinetics.
2. The most important aspect of this regime is the formation of protective surface films to minimize wear and surface damage. (for space mechanisms, AISI 440C steel is the most common bearing material).
3. The formation of these films is governed by the chemistry of both the film former as well as the steel surface and other environmental factors.

4. The effectiveness of these films in minimizing wear is determined by their physical properties which include: shear strength, thickness, surface adhesion, film cohesion, melting point or decomposition temperature, and solubility.

The perfluoropolyether (PFPE) class of liquid lubricants has been in use for over 25 years for many spacecraft applications. These commercial products are made by polymerization of perfluorinated monomers. The first member of this class was made by CsF catalyzed polymerization of hexafluoropropene oxide (HFPO) yielding a series of branched polymers designated as Krytox (ref. 4). A similar polymer is produced by the UV catalyzed photo-oxidation of hexafluoropropene (Fomblin Y) (ref. 5). A linear polymer (Fomblin Z) is prepared by a similar process but utilizing tetrafluoroethylene (ref. 6). Finally, a fourth polymer (Demnum) is produced by polymerization of tetrafluoroacetone followed by direct fluorination (ref. 7). Structures for these fluids appear in table I. Table II contains property data for some members of the PFPE class of lubricants.

In addition to these commercially available PFPE fluids, a new series of structures are being prepared by direct fluorination technology (refs. 8 to 10). Some of these structures appear in table III.

Of the above PFPE fluids, only Krytox and Fomblin Z have been extensively used as liquid lubricants and greases for space applications (ref. 11). Recently, a Demnum fluid has been life tested for use as a shutter mechanism lubricant for the SOHO mission.

The objective of this paper is to review some of the properties of the PFPE class of lubricants that are important for long term operation in space. These include: boundary and EHL lubricating ability, vapor pressure characteristics, creep properties, optical properties, and resistance to radiation and atomic oxygen. This is not intended to be an extensive review of all PFPE properties, only those related to space requirements. For example, thermal and thermal-oxidative stability properties important for terrestrial applications, (refs. 12 to 17) will not be covered. In addition, many other classes of liquid lubricants are being used in space. These classes will not be discussed since adequate reviews already exist (ref. 18).

## PERFLUOROPOLYETHER PROPERTIES

As indicated in the introduction, a liquid lubricant has to possess certain physical and chemical properties to function properly in a lubricated contact. In addition to good boundary and EHL film forming capabilities, these lubricants must possess the following attributes for consideration in a space application: vacuum stability (i.e., low vapor pressure), low tendency to creep, high viscosity index (i.e., wide liquid range), resistance to radiation and atomic oxygen, and optical transparency.

### Volatility

Although labyrinth seals are extensively used in space mechanisms, lubricant loss can still be a problem for long term applications (7 to 30 years) (ref. 19). For a fixed temperature, and outlet area, lubricant loss is directly related to vapor pressure. For a similar viscosity range, the PFPE fluids (Fomblin Z and Krytox) are particularly good candidates compared to conventional lubricants (fig. 2) (ref. 11). Vapor pressure data also appear in table II.

## Creep Behavior

The tendency of a liquid lubricant to creep or migrate is inversely related to its surface tension. Therefore, the PFPE materials which have unusually low surface tensions ( $\gamma_{LV}$ , 17 to 25 dynes/cm at 20 °C) are more prone to creep than conventional fluids. However, these fluids can effectively be contained in bearing raceways by using low surface energy fluorocarbon barrier films on bearing lands (having critical surface energies of less than 11 dynes/cm) (ref. 20). However, PFPE fluids may dissolve these barrier films with prolonged contact (ref. 19).

## Viscosity-Temperature Properties

Although liquid lubricated space applications do not involve wide temperature ranges, low temperatures (i.e., -10 to -20 °C) are sometimes encountered. Therefore, low pour point fluids that retain low vapor pressure and reasonable viscosities at temperatures to 50 or 60 °C are required. The viscosity-temperature slope (ASTM) of PFPE unbranched fluids is directly related to the carbon to oxygen ratio (C/O) in the polymer repeating unit, as shown in figure 3 (ref. 21).

In addition, branching, such as the trifluoromethyl pendant group in Krytox, causes a deterioration in viscometric properties. Comparison of ASTM slopes for three commercial PFPE fluids appears in figure 4. Here the low C/O ratio fluid, Fomblin Z, has the best viscometric properties. Demnum with a C/O ratio of 3 has intermediate properties, while the branched fluid, Krytox, has the highest ASTM slope.

## Elastohydrodynamic Properties

The operation of continuously rotating, medium to high speed bearings relies on the formation of an elastohydrodynamic (EHL) film. This regime was briefly described in the introduction. A more detailed description appears in reference 22. The two physical properties of the lubricant that influence EHL film formation are: absolute viscosity ( $\mu$ ) and the pressure-viscosity coefficient ( $\alpha$ ).

Viscosity is influenced by both molecular weight and structure. Except for low molecular weight fluids,  $\alpha$  values are only related to structure (ref. 23).  $\alpha$  values can be measured directly with conventional high pressure viscometers (refs. 24 to 29) or indirectly from optical EHL experiments (refs. 23, and 30 to 32). Conventional viscometry normally uses the Barus equation (ref. 33) for correlations.

$$\mu_p = \mu_o e^{\alpha p} \quad (1)$$

where

$\mu_p$  absolute viscosity at pressure, p

$\mu_o$  absolute viscosity at atmospheric pressure, and  $\alpha =$  constant (temperature dependent but pressure independent)

This implies that a plot of  $\log \mu_p$  versus p should yield a straight line of slope  $\alpha$ . Unfortunately, this simple relationship is seldom obeyed. The pressure-viscosity properties that are important in determining EHL film thickness occur in the contact inlet. Therefore, the slope of a secant drawn between atmospheric pressure and 0.07 GPa is typically used.

Winer (ref. 24) has advocated the use of another pressure-viscosity parameter, the reciprocal asymptotic isoviscous pressure ( $\alpha^*$ ) based on work by Roelands (ref. 34).  $\alpha$  values (ref. 24) for three temperatures (38, 99, and 149 °C) are tabulated in table IV for Fomblin Z-25 and Krytox 143AB. Values for several other non-PFPE fluids are shown for comparison.

Figure 5 contains  $\alpha$  values for the branched PFPE (Krytox 143AB). Data obtained by conventional (low shear) pressure-viscosity measurements are denoted with open symbols. Indirect measurements from EHL experiments (effective  $\alpha$  values) are shown with solid symbols. There is good agreement comparing the different sources as well as different measurement techniques. Figure 6 contains similar data for the unbranched PFPE (Fomblin Z-25) as a function of temperature. Here, there is a definite grouping of the data with effective  $\alpha$  values being substantially lower than values from conventional measurements.

Two possibilities exist for this discrepancy. First, inlet heating can occur, thus leading to lower viscosities, lower film thicknesses, and resulting in lower effective  $\alpha$  values. The second possibility is a non-Newtonian shear thinning effect. Shear rates in EHL inlets can range from  $10^5$  to  $10^7$   $\text{sec}^{-1}$  (ref. 30). However, the EHL measurements do represent actual film thicknesses that can be expected in practice.

From EHL theory, the greatest film thickness should be obtained with a PFPE fluid having the largest  $\alpha$  value. However, for many applications, lubricants must perform over a wide temperature range. In this case, the EHL inlet viscosity can be the overriding factor if the temperature coefficient of viscosity is high. This can cause a cross-over in film thickness as a function of temperature as shown by Spikes et al. (ref. 23) in figure 7. However, for most space applications, bearing temperatures are typically in the range of 0 to + 40 °C. Therefore, lubricants possessing high  $\alpha$  values (i.e., Krytox) in this range would be preferred, when only considering EHL.

## BOUNDARY LUBRICATION PROPERTIES

As described in the introduction, boundary lubrication is the regime where surfaces are not completely separated which results in continuous surface asperity interactions. The most important aspect of this regime is the formation of protective surface films to minimize wear and surface damage. The formation of these films is governed by the chemistry of both the film former as well as the contacting surfaces and other environmental factors.

Nonadditive hydrocarbons, mineral oils and esters will react in a boundary contact to produce "friction polymer" (ref. 35). Except for electrical contacts, this material is beneficial but does represent loss of lubricant which requires replenishment. But these conventional lubricants are never required to act alone. Almost all are formulated with antiwear, anticorrosion, extreme pressure, or anti-oxidant additives to enhance their performance.

Contrast this with a PFPE boundary lubricant. Here we have a relatively inert, very pure fluid with no additives. If these fluids were totally inert, they should not provide any surface protection except for some fluid film effects (micro-EHL), removal of wear debris, and possibly some local cooling. Actually, in boundary contacts, PFPE fluids do react with bearing surfaces producing a series of corrosive gases which, in turn, react with existing surface oxides producing metal fluorides (refs. 36 to 38). These fluorides are effective solid lubricants which reduce friction and wear (ref. 36).

Unfortunately, these fluorides are also strong Lewis acids (electron acceptors) which readily attack and decompose PFPE molecules (refs. 38 to 40). This causes the production of more reactive species which, in turn, produce more surface fluoride, resulting in an autocatalytic reaction. Therefore, the very

reaction that allows the use of pure PFPE fluids in boundary contacts, eventually leads to their destruction and accompanying bearing failure. Of course, the progression of this mechanism is highly dependent on the local contact conditions (i.e., degree of passivation, type and thickness of surface oxide, amount of surface contaminants, temperature, load, speed, etc.).

A preliminary boundary lubrication study of three commercial PFPE fluids (ref. 41) under sliding conditions in air and vacuum has been conducted. Wear rates for these fluids appear in figure 8. The following order of lubricant lifetimes was obtained: Krytox  $\approx$  Fomblin Z  $>$  Demnum (air) and Krytox  $\approx$  Demnum  $\gg$  Fomblin Z (vacuum) (fig. 8). Although Demnum has no space heritage, both Krytox and Fomblin Z have been used extensively and successfully (GOES, TIROS, ERBE, NOAA, LANDSAT, etc.). Space experience has indicated that, in general, Krytox yields longer lifetimes than Fomblin Z for similar applications. Therefore, the vacuum four-ball results correlate with results from space experience.

A classical way of representing wear as a function of reactivity is shown in figure 9. Obviously, for any particular system, one would like to be at the minimum of the curve. Normally, this minimum is perturbed by the presence and concentration of lubricant additives. However, as previously indicated, boundary additives are not yet available for PFPE fluids. However, active research (ref. 42) is now taking place in this arena.

## OPTICAL CHARACTERISTICS

There is always the concern that liquid lubricants used in space mechanisms may contaminate sensitive optical components (mirrors, windows, etc.) and render certain measurements useless. Although great care is taken to minimize this problem, the possibility still exists. Therefore, lubricants that are optically transparent in the various sensor wavelength regions are obviously preferred. Many of these regions are in the infrared region. Since PFPE lubricants do not contain hydrogen, they are relatively transparent over most of this region (as shown in fig. 10) for a Krytox fluid. Spectral regions of interest for two Earth Observation Satellites (CERES and MODIS-N) are also shown.

## RADIATION RESISTANCE

PFPE fluids are susceptible to degradation from low energy electrons (ref. 43), high energy electrons (ref. 44) and ion beams (ref. 45). Mori and Morales (ref. 46) have reported the degradation of several PFPE fluids (Demnum S-200, Fomblin Z-25, and Krytox 16256) by x-rays. X-rays were generated by a Al K $\alpha$  source in a commercial XPS spectrometer. Thick PFPE layers were swabbed onto 440C steel substrates and exposed to x-rays for 3 hr. Degradation was measured by changes in chamber pressure as a function of time. Pressure changes for three fluids appear in figure 11. First order rate constants calculated from these slopes indicated that Fomblin Z-25 and Krytox 16256 had degradation rates approximately twice that of Demnum S-200. These data indicate that PFPE materials are very susceptible to degradation by x-ray irradiation.

## RESISTANCE TO ATOMIC OXYGEN

In low earth orbit (LEO), the principle chemical species is neutral atomic oxygen. In LEO, 4.25eV atomic oxygen will impact spacecraft surfaces. Although space mechanism liquid lubricants are not directly exposed to this particle flux, it has been shown by Gulino and Coles (ref. 47) that of several candidate radiator fluids, the PFPE class was less affected by atomic oxygen than silicone based materials.

However, Krytox 143AB and Fomblin Z-25 did show small weight losses (fig. 12) as a function of oxygen plasma exposure time.

## CONCLUSIONS

The following conclusions can be stated for the use of perfluoropolyether (PFPE) liquid lubricants for space applications.

1. The PFPE lubricant class can still provide adequate performance for less demanding space applications (i.e., pure EHL or low load, low cycle boundary contacts).

2. For more demanding applications (i.e., high load, high cycle or for contacts having high sliding components), additive technology (antiwear, EP, anticorrosion, antidegradation) will be mandatory.

3. Although active research is now taking place for the development of PFPE boundary additive formulations, they are not yet available commercially.

4. In the interim, the use of alternative bearing materials (i.e., ceramics) or steel surface treatments (i.e., ion implantation, phosphating, acid passivation) will be necessary for extension of lifetimes.

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TABLE I.—NAMES AND PRIMARY CHEMICAL  
STRUCTURES OF COMMERCIAL PFPE FLUIDS

Name	Structure
Demnum	$C_3F_7O(CF_2CF_2CF_2O)_x C_2F_5$
Krytox	$C_3F_7O[CF(CF_3)CF_2O]_x C_2F_5$
Fomblin Y	$C_3F_7O[CF(CF_3)CF_2O]_x (CF_2O)_y C_2F_5$
Fomblin Z	$CF_3O(CF_2CF_2O)_x (CF_2O)_y CF_3$

TABLE II.—PFPE PHYSICAL PROPERTIES

Lubricant	Average molecular weight	Viscosity at 20 °C, cS	Viscosity index	Pour point, °C	Vapor pressure, Torr	
					at 20 °C	at 100 °C
Fomblin Z-25	9500	255	355	-66	$2.9 \times 10^{-12}$	$1 \times 10^{-8}$
Krytox 143AB	3700	230	113	-40	$1.5 \times 10^{-6}$	$3 \times 10^{-4}$
Krytox 143AC	6250	800	134	-35	$2 \times 10^{-8}$	$8 \times 10^{-6}$
Demnum S-200	8400	500	210	-53	$1 \times 10^{-10}$	$1 \times 10^{-7}$

TABLE III.—NAMES AND PRIMARY CHEMICAL STRUCTURES  
OF CUSTOM SYNTHESIZED PFPE FLUIDS (REF. 10)

Perfluoropoly-	Structure
(methylene oxide) (PMO)	$\text{CF}_3\text{O}(\text{CF}_2\text{O})_x\text{CF}_3$
(ethylene oxide) (PEO)	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{O})_x\text{CF}_3$
(dioxolane) (DIOX)	$\text{CF}_3\text{O}(\text{CF}_2\text{CF}_2\text{OCF}_2\text{O})_x\text{CF}_3$
(trioxocane) (TRIOX)	$\text{CF}_3\text{O}[(\text{CF}_2\text{CF}_2\text{O})_2\text{CF}_2\text{O}]_x\text{CF}_3$

TABLE IV.—PRESSURE VISCOSITY COEFFICIENTS AT THREE  
TEMPERATURES (REF. 24)

$[\alpha^*, \text{Pa}^{-1} \times 10^8.]$

	38 °C	99 °C	149 °C
Ester	1.3	1.0	0.85
Synthetic Paraffin	1.8	1.5	1.1
Fomblin Z-25	1.8	1.5	<sup>a</sup> 1.3
Napthenic Mineral Oil	2.5	1.5	1.3
Traction Fluid	3.1	1.7	0.94
Krytox 143AB	4.2	3.2	3.0

<sup>a</sup>Extrapolated.

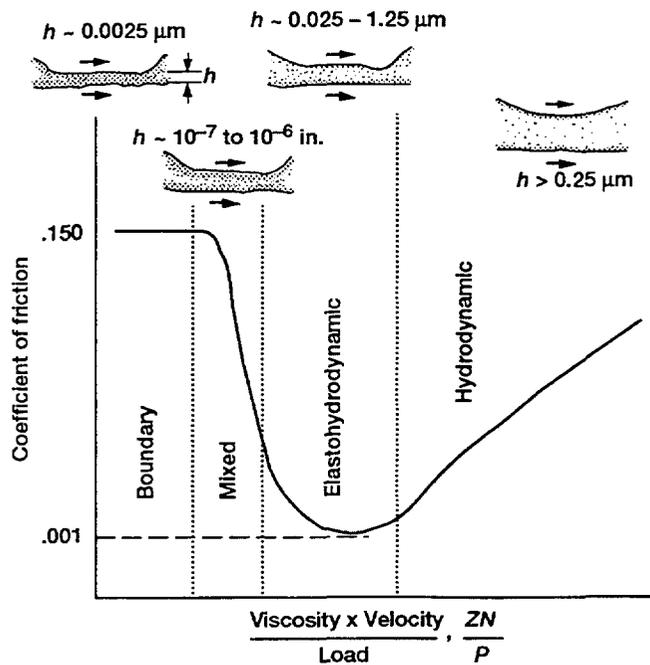


Figure 1.—Coefficient of friction as a function of viscosity-velocity-load parameter (Stribeck curve)(Ref.1).

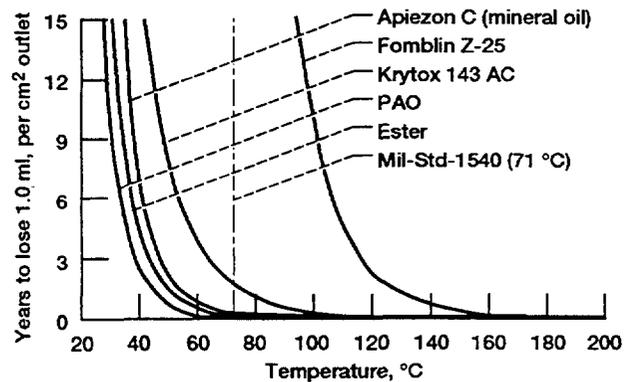


Figure 2.—Relative evaporation of aerospace lubricants (Ref 11).

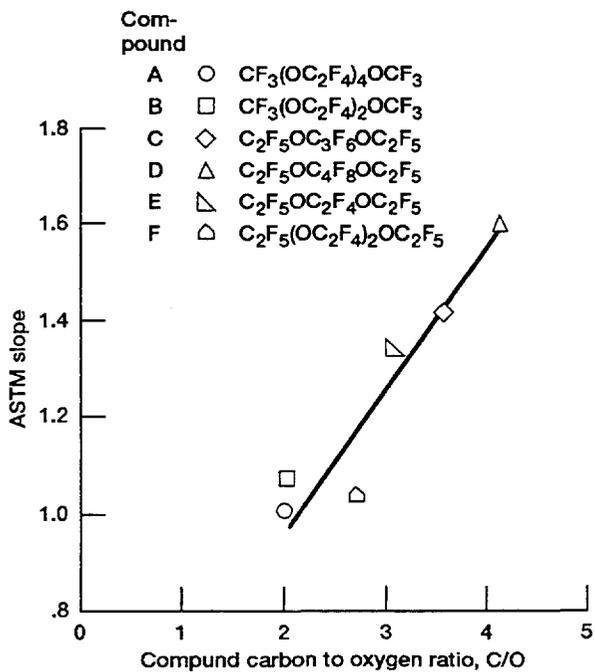


Figure 3.—Viscosity-temperature slope (ASTM) as a function of compound carbon to oxygen ratio (C/O) for a series of unbranched perfluoroalkylethers (Ref. 21).

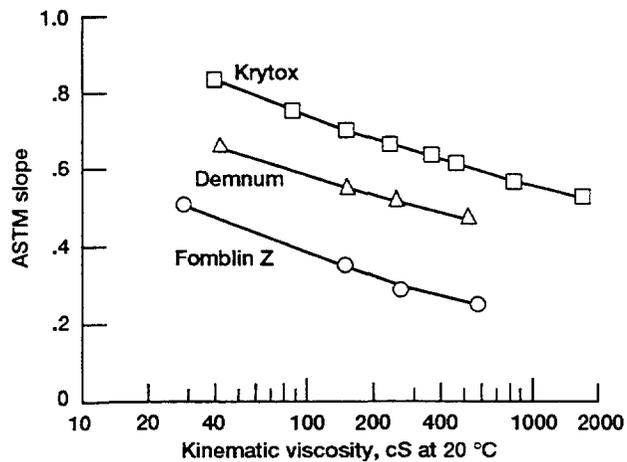


Figure 4.—Viscosity-temperature slope (ASTM) as a function of kinematic viscosity at 20 °C for Krytox, Demnum, and Fomblin Z fluids (Ref. 21).

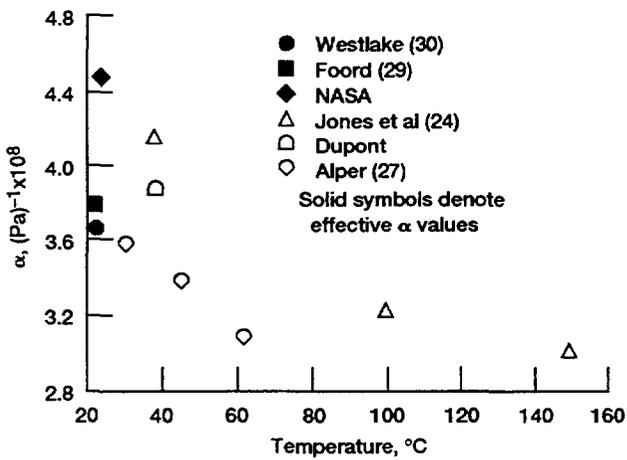


Figure 5.—Pressure-viscosity coefficients for Krytox 143 AB as a function of temperature.

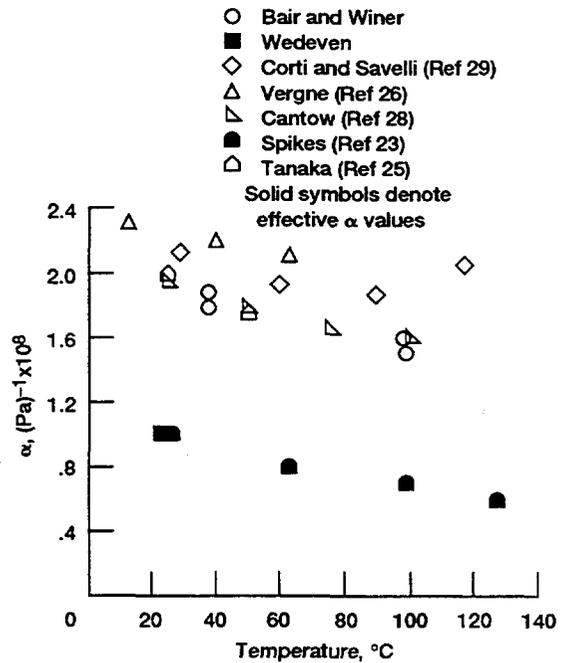


Figure 6.—Pressure-viscosity coefficients for Fomblin Z-25 as a function of temperature.

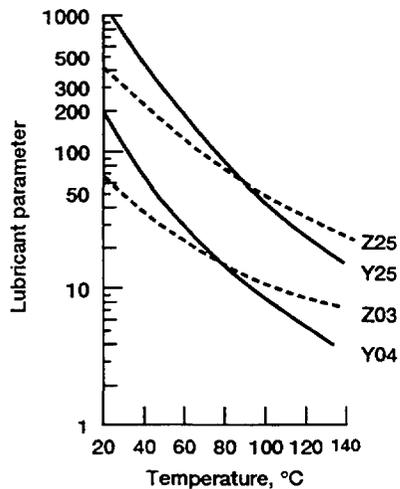


Figure 7.—Lubricant parameters for Fomblin Y and Z fluids (Ref 23).

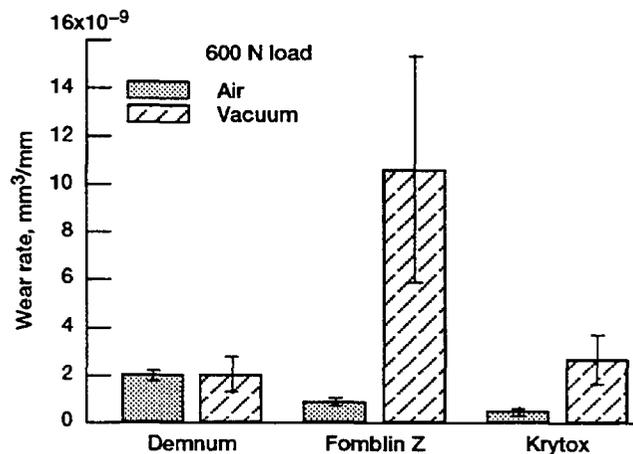


Figure 8.—Comparison of wear rates in air and vacuum for Krytox, Fomblin Z, and Demnum in a vacuum four-ball apparatus.

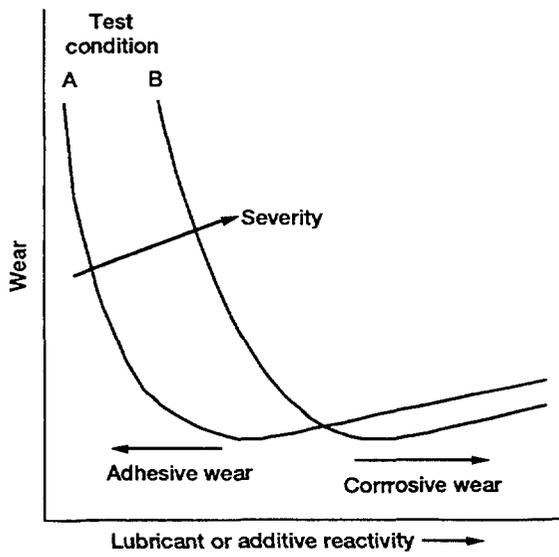


Figure 9.—Relationship between wear and lubricant reactivity.

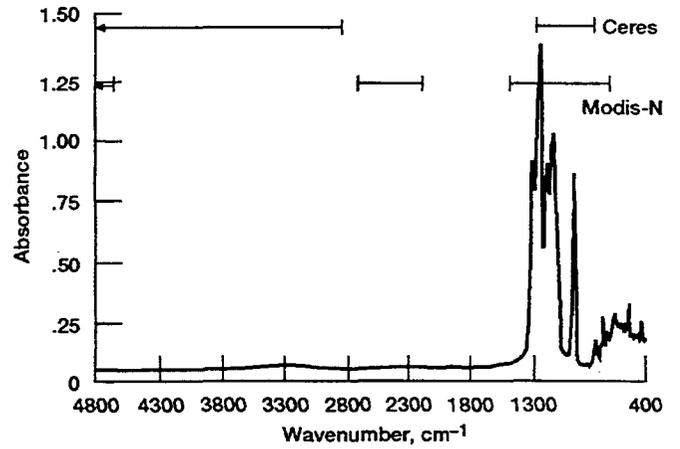


Figure 10.—Infrared spectrum of Krytox.

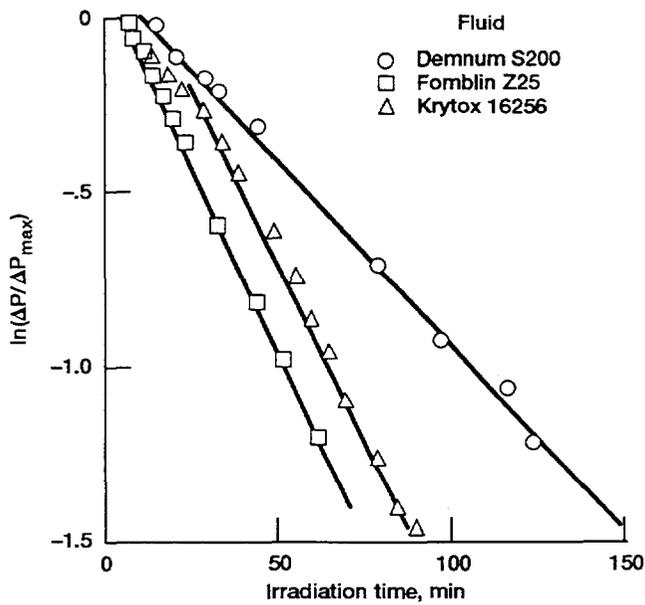


Figure 11.—Semilogarithmic relation of pressure change with irradiation time. Substrate, 440C stainless steel (Ref. 46).

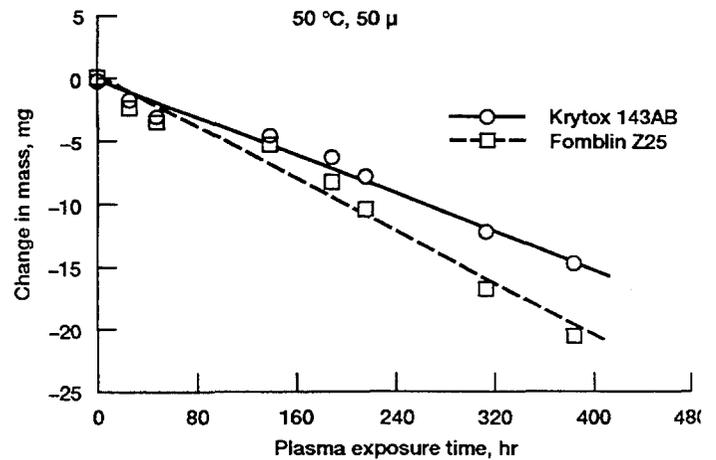


Figure 12.—Mass change as a function of oxygen plasma exposure time (Ref 47).

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