Polyphenyl Ethers: Lubrication In Extreme Environments

by

John F. Herber, Sr., PhD

and

Manuel E. Joaquim

Santovac Fluids, Inc.

St. Charles, Missouri USA

Polyphenyl Ethers: Lubrication In Extreme Environments

by John F. Herber, Sr., Ph.D and Manuel E. Joaquim

Polyphenyl ethers are a class of lubricants having unusual properties, most significantly high thermal and radiation resistance, chemical stability, a high refractive index, and positional stability. They are most useful as robust lubricants in a variety of extreme environments.

In 1906, during the exciting early days of synthetic organic chemistry, a German researcher named F. Ullman set out to make diphenyl ether. By substituting an oxygen atom between two benzene rings, he reasoned that he would produce a substance that would remain liquid at lower temperatures.

Ullman was successful in creating the first polyphenyl ether - a class of compounds having from 2 to 10 benzene rings with ether linkages between them. Initially the compound that Ullman made had no immediate application. It was simply a chemical oddity.

What Ullman could not have known was that he had created the first compounds with characteristics that would be badly needed during the second half of the 20th century, and the beginning of the 21st century, the time when engineers would begin designing and building complex machinery, aircraft, automobiles, space vehicles and communication equipment whose lubrication needs constituted what could only be described as “extreme environments.”

A 5-ring polyphenyl ether is shown in Figure 1. Each polyphenyl ether has numerous isomers. The positions of the four oxygen atoms on the benzene rings are a very critical feature: they permit molecular rotation of the various parts of the molecule. This flexibility in turn means that a polyphenyl ether can remain liquid at fairly low temperatures - an important characteristic for many lubricants. The pour point of a 5-ring polyphenyl ether, for example, is 4° C. (40° F.). A sequence of 5 benzene rings without the oxygen atoms would be extremely rigid, would pack tightly, and would consequently become solid at higher temperatures.

Although a polyphenyl ether molecule is flexible, it is extremely stable chemically. Benzene rings tend to have a high resonance energy - a measure of the energy that must be overcome. The bonds holding the molecule together by their resonance energy cause the polyphenyl ethers to boil only at high temperatures (476° C., or 889° F., at atmospheric pressure). The temperature at which the molecule decomposes also tends to be very high.

The thermal stability of polyphenyl ethers led to their first major use as a lubricant. In the 1960s, the SR-71 spy plane was under development by the Air Force. No lubricant based on petroleum distillates could be used for the turbine engines, because the plane was designed to fly too high (>60,000 feet) and, as a result, the temperature of the bearing surfaces was too high (316° C., or 601° F.). A 5-ring polyphenyl ether was found to be stable at these temperatures.

It was not only the 316° C. temperature that made the SR-71 turbine engine an extreme environment. The lubricant must not evaporate at the low atmospheric pressures of high altitude, and in this atmosphere the lubricant could oxidize to unstable molecules. Polyphenyl ethers have an extremely low vapor pressure, and hardly evaporate at all under standard temperature and pressure. At 260° C. (500° F.), the vapor pressure of a 5-ring polyphenyl ether is only 0.0102 mm Hg. At 343° C. (650° F.) - a temperature well above the SR-71's requirements - vapor pressure increases, but is still only 11.8 mm Hg.

The oxidative stability of polyphenyl ethers is high because the resonance stability of the π electron cloud of the benzene rings. This reduces the possibility that oxygen can attack the molecule. Mixing a very small quantity of an oxygen-grabbing additive to the polyphenyl ether made the lubricant even more stable at the high temperatures found in the SR-71. The effect of the additive is dramatic: in a standard oxidation-corrosion test at 650° C., the additive lowers the 100° F. viscosity increase from 1809% to 22%. The result was a lubricant that permitted continuous operation at temperatures beyond those that could be tolerated by petroleum/ester-based lubricants.

When applied to a surface, molecules of a polyphenyl ether are more attracted to each other than they are to the surface. Like water, but unlike hydrocarbon fluid lubricants, they have a very high surface tension. At 25° C. (77° C.) the surface tension of a 5-ring polyphenyl ether is 49.9 dynes/cm; that of water is 60.8 dynes/cm. In both cases, surface tension measures the force needed to spread the liquid over a distance of one centimeter. On many surfaces, water will arrange itself in discrete droplets. A polyphenyl ether does the same thing. A “coating” of polyphenyl ether on a lubricated surface is not a coating at all, but a field of microscopic droplets. Each droplet vibrates constantly from forces similar to Brownian movement. The droplets are densely arranged, and the whole field of vibrating droplets tends to stay where it has been applied. This is true even at high temperatures such as those found in the SR-71; the surface tension is somewhat reduced by temperature, but the fluid still forms a stationary field of microscopic droplets.

The general stability of polyphenyl ether molecules extends also to another area - nuclear radiation. Herr Ullman could never have anticipated that lubrication would be needed for switch contacts and other moving parts in nuclear reactors, but this has become an application where these extreme-environment molecules are badly needed. The main impact of gamma and neutron radiation on aliphatic hydrocarbons or esters is similar - the molecules decompose into by-products, sludge is formed, and vapors are given off. A 5-ring polyphenyl ether is resistant to gamma and associated neutron radiation at doses up to 10^{10} ergs per gram of carbon, and up to temperatures of 316° C. (600° F.). (An erg is the energy of one neutron or one alpha particle). Since a 5-ring polyphenyl ether is about 81% carbon, a gram of the lubricant can absorb about 1.23×10^{10} ergs before decomposing. This very high level of resistance is why the lubricants are widely used not only in land-based nuclear power plants but also in nuclear-powered submarines.

Nor could Ullman have foreseen back in 1906 that polyphenyl ethers would be widely used in earth-orbiting satellites. Satellites pose two problems for lubricants: temperature extremes and the lack of atmospheric pressure. The very low vapor pressure of polyphenyl ethers keeps them from evaporating at any significant rate even in the low vacuum of earth orbit, where the boiling point is low. Temperature extremes, though, were not so easily dealt with. Satellites spend part of their time in direct sunlight, and are heated to high temperatures, and part of their time in darkness, where temperatures plummet. Think of the surface of the moon, where temperatures between day and night can range from -184° C. to +214° C (-299° F. to 417° F.). Most polyphenyl ethers become a glass at around 4° C. (40° F.). A separate class, where sulfur atoms replace some oxygen atoms, remains liquid down to –29° C. (-20° F.). This class, called polyphenyl thioethers, greatly extends the range of earth-bound applications, but does not even begin to approach the cold of space.

Satellite engineers studying the problem realized that satellites spend much more time in sunlight, where the high temperatures are well within the operational range of polyphenyl ethers, than in darkness. The solution was to add small heaters to keep lubricated surfaces above the glass transition temperature of polyphenyl ethers in darkness. This was a more feasible approach than using aliphatic hydrocarbon lubricants, which would lubricate at lower temperatures but which would need to be cooled to prevent decomposition at higher temperatures. The use of polyphenyl ethers also solved a peculiar design problem: in the tight geometry of a satellite, lubricated surfaces are often very close to surfaces such as heat dissipators or solar cells whose surfaces must be kept clean. The ability of polyphenyl ethers to stay in one place removed this danger.

Constant microscopic vibration (also referred to as “fretting” or “fretting corrosion”) is one of the extreme conditions in which polyphenyl ethers are most useful. Such vibration occurs most critically in the pin-in-socket electronic connectors in cell phones, computers, instruments and numerous other electronic products. Vibration may come from audio speakers, vehicle movement, temperature variation, or some other source. Relative movement between the pin and the contact point within the connector may be only a few microns, but the repetitive nature of the vibration causes fretting. Even gold-plated pins soon have their more reactive interior metals exposed, and corrosion from air-borne water vapor and contaminants begins. Great attention is usually given to the design and packaging of integrated circuits and other components, but the more exposed connector is often the “weakest link” in the electronic system.

When a connector pin is coated with a polyphenyl ether, damage from fretting stops. The longevity of the pin and socket becomes so great that in fretting experiments it is hard to measure. Because of its low vapor pressure, the polyphenyl ether will evaporate from the pin only after some 40 to 50 years. Even some inexpensive cell phones and other equipment, designed using non-noble metals (i.e., tin/lead), now have coated pins to prevent connector failures.

Summary

Their chemical structure gives polyphenyl ethers unusual thermal, radiation, chemical, and positional stability. In many areas of advanced technology, one or more of these properties is needed to provide lubrication and long-term protection in an extreme environment.

###

Figure captions for Polyphenyl Ethers: Lubrication In Extreme Environments:

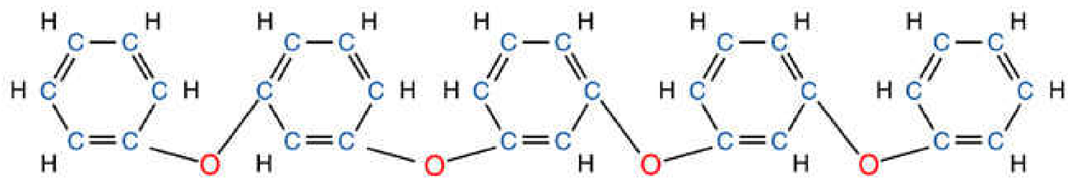

Figure 1 Polyphenyl ethers have from 2 to 10 benzene rings. The resonance energy in the benzene rings provides chemical and thermal stability to above 316° C. (600° F.). The molecule is flexible because the critical oxygen atoms are points of rotation. The high surface tension of a polyphenyl ether fluid is so high that it coats surfaces as a stationary field of microscopic droplets, rather than as a continuous film. [Courtesy Santovac Fluids.]

Figure 2 The high engine temperatures in the SR-71 Blackbird required a lubricant having extraordinary thermal stability. A polyphenyl ether was selected. [Photo courtesy NASA].

Polyphenyl Ether	Appearance	Pour Point °F.	Thermal Stability, ° F. (isoteniscope)	Viscosity (cSt) at 100° F.	Viscosity (cSt) at 210° F.
Six-ring 6P5E	Clear Liquid	50	836	2000	25
Five-ring 5P4E	Clear Liquid	40	847	360	13
Four-ring 4P3E	Clear Liquid	10	825	70	6
Three- and four-ring oxy-thio	Hazy liquid	-20	693	25	4
Three-ring 3P2E	Solid	-	800	12	3
Two-ring 2P1E	Solid	-	>600	2.4	1.6

Figure 2 Physical Properties of Polyphenyl Ethers.

Shell Four-Ball Wear Test

Load	Scar Diameter
10 kg	0.80 mm
30 kg	0.89 mm
50 kg	1.13 mm

5-Ring Polyphenyl Ether, 400° F. (204° C.)
600 rpm, 1 hour duration

Figure 3 Results of the Shell Four-Ball Wear Test Using Polyphenyl Ether Lubricants.

Temperature	Rating In Pounds Per Inch
at 167° F. (75° C.)	2450 ± 300 ppi
at 400° F. (204° C.)	1000 ± 150 ppi

Results of Ryder Gear Scuff Test Using Polyphenyl Ether Lubricants

Figure 4 Results of Ryder Gear Scuff Test Using Polyphenyl Ether Lubricants.

	Base Fluid 600° F.	Base Fluid Plus Inhibitor 600° F.	Base Fluid 650° F.	Base Fluid Plus Inhibitor 650° F.
% Change in Viscosity @ 100° C.	32%	17%	1809%	22%

Fluid stability as measured by viscosity reduction at temperatures of 600° F. and 650° F., with and without an inhibitor

Figure 5 Fluid Stability Test.

Contact information:

Santovac Fluids, Inc.
8 Governor Drive
St. Charles MO USA 63301-7311
Phone: 636 723-0240
Fax: 636 723-4210
Web: www.santovac.com
E-mail: mjoaquim@santovac.com

###