

## High Temperature Lubrication with Phosphate Esters

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**Abstract**—Recent work with phosphate esters has shown that a lubricious polymeric film can be formed from the vapor phase on interacting during and sliding. This lubrication technique has led to methods to reduce friction and wear to very low values at high temperatures up to 700°C. Preliminary work with synthetic triaryl phosphates are very promising. The vaporized lubricant forms a polymeric film on the sliding and rolling surfaces reducing the coefficient of friction below 0.05. In-situ formation of the polymeric films shows that the polymer that is formed on the surface exists in different states depending on surface temperature.

### 1. Background

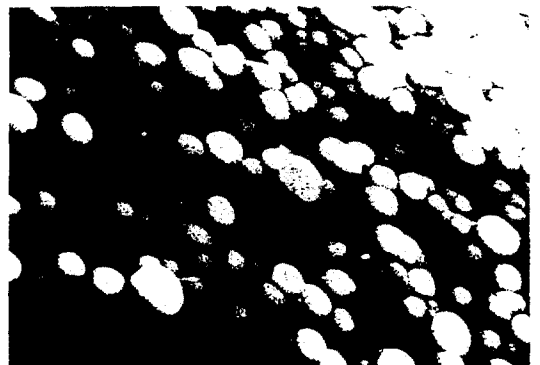
Vapor phase lubrication is a high temperature lubrication technique that can be used at elevated temperatures where conventional liquid lubrication can not be used. This technique involves the deposition of a solid or semi-solid polymeric film on the contact surfaces of rolling or sliding components [1-4].

In this technique, the lubricant is vaporized at a very low concentration at a temperature slightly higher than the boiling point in a carrier stream of heated nitrogen or air. The vaporized lubricant continuously supplied to the contact surfaces of the rolling and sliding components. The advantage of this technique is that it can be used at high temperatures from 400 to 700°C and the coefficient of friction and wear rate can be decreased dramatically. Due to the continuous supply of vapor, as the film worn away, it is continuously reformed. In principle the amount of lubricant delivered should match the amount of lubricating film worn away by wear [5-7].

Most of the work to date is done by using aryl phosphates. Aryl phosphates are used as friction reduction additives because of their ability to bond to the surface of the metal components with which they are in contact. The phosphate group serves as an attachment group by adhering to iron or iron oxide. In liquid form, in an engine as the oil serves as the hydrodynamic lubricant, the iron phosphate layer provides the boundary lubrication when the oil film is thin. As vapor phase lubricants, aryl phosphates

perform similarly. They form a thin layer of film that serve as a lubricant to reduce the friction and wear dramatically [8].

The lubricant should chemically react with the surface and form a thin polymeric layer. Studies made using cast iron, steel, monel, inconels, incolloys, M 50, T15 tool steel, silicon carbide and silicon nitride show that certain materials are active and form a tenacious polymer by reacting with the vaporized lubricant. Fig. 1 is a SEM microphotograph of the cast iron plate showing the surface morphology of the deposit formed at 600°C with 0.1% aryl phosphate in air. This tenacious deposit with a nodular structure lubricates the surfaces under dynamic conditions. The rate of formation of this polymeric layer should be same or greater than the rate of wear.



**Fig. 1.** SEM microphotograph of an iron surface deposited with 0.3% triaryl phosphate at 600°C (2000X).

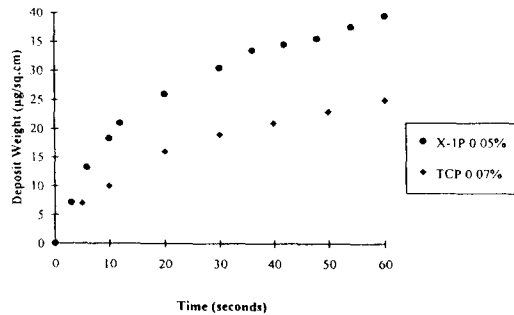


Fig. 2(a). Deposit weight vs time for TCP and X-1P.

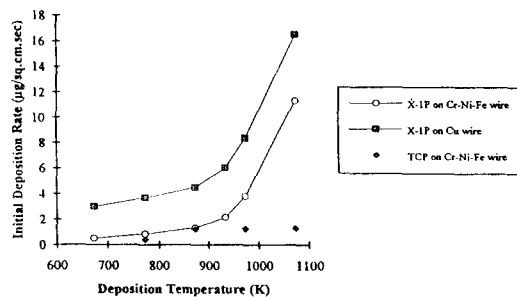


Fig. 2(b). Deposit rate vs temperature for TCP and X-1P.

This results in a dramatic reduction in the friction and wear characteristics of the surface.

Besides the catalytic nature of the substrate, the deposition temperature and the concentration of the lubricant are very important. Deposition studies were conducted with a modified TGA unit to measure the continuous deposition between 400°~800°C. Fig. 2 gives the results of the TGA deposition studies with two different lubricants and substrates [9].

FTIR studies have been made to analyze the polymer formation. Results of the studies show that the vapor initially undergoes a reaction forming an iron phosphate layer. This iron phosphate layer then catalyzes the formation of the polymer. The molecular weight of the polymer is between 6,000 to 60,000 [10]. Both static and dynamic tests have been made using vapor phase lubrication. These tests are normally performed between 300°C and 600°C at very low concentrations (less than 0.5%). In this work the mechanism of formation of the polymer has been studied by tests in which the temperature was continuously varied under dynamic sliding wear conditions.

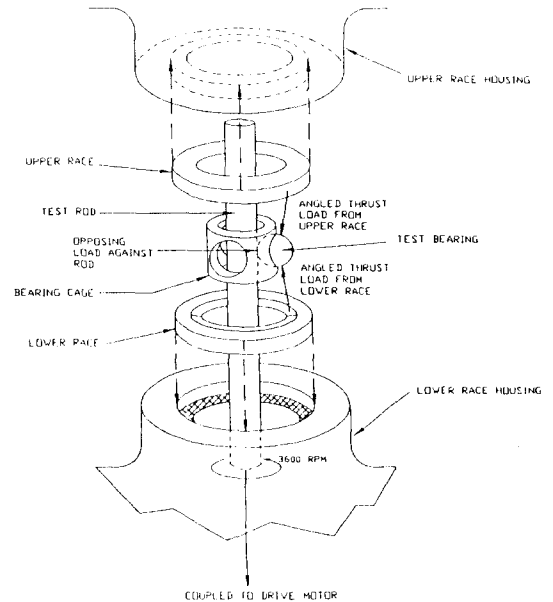


Fig. 3. Rolling contact fatigue rig schematic.

## 2. Experimental Procedures

Studies of vapor phase lubrication for rolling contact were made using a rolling contact fatigue test modified for high temperature operation (Fig. 3). Test specimens were three AISI M-50 rolling elements of 12.75 mm diameter held in position by a AISI 4340 alloy steel cage. This entire bearing assembly encompassed a 9.525 mm diameter spinning rod which was coupled into an electric drive that rotated at 3600 rpm.

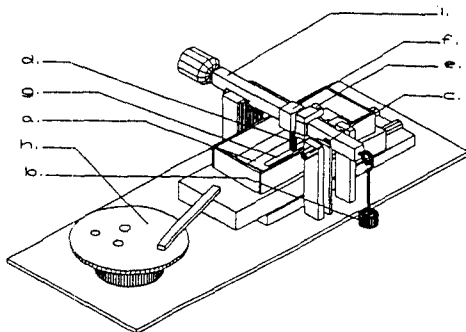
The load on the rolling element was provided by an outer housing that presses an upper and lower tapered race into the surface. Hence, there were three points of contact per rolling element; two of which were where the upper and lower race are thrust loaded into the element, and the third of which was where the element contacts the centrally located spinning rod. All of these points are places where friction and wear can occur.

The outer housing of the rig that provides loading and support was mounted on a hydrostatic air bearing that allowed for virtually friction-free rotation. The housing was then restrained with a cable connected to strain gauge. The force required to reset rotation was recorded by a data acquisition unit and converted to a friction coefficient. An accelerometer

was magnetically attached to the surface of the test rig. It was used to monitor rig vibration as well as to act as a safety switch. If the vibrations due to bearing failure became too great, an electric pulse signaled the drive motor and heating unit to shut down immediately. This allowed for the possibility of unattended tests if desired. Data was obtained via a computer data acquisition system. The data acquisition had the capability of monitoring elapsed time, friction, vibration, and temperature [9].

Studies under sliding conditions were simulated by using a universal wear tester. This equipment is designed to simulate conditions and wear under actual operating states as closely as possible. It was modified to operate in the pin on reciprocating plate mode at temperatures up to 600°C. Fig. 4 illustrates the configuration of the wear tester. The reciprocating motion of the plate results in the pin rubbing against the surface of the plate. An average linear velocity of 12.7 cm s<sup>-1</sup>(90 rpm) and a 4 cm long wear track was used. Two linear transducers were used to measure the friction force and the pin and plate wear, in terms of the wear depth. The transducers were connected to a data acquisition unit which is capable of taking up to 100 data samples per second. Wear and friction data were typically collected for one hour. This gives sufficient sliding contact to accurately characterize the wear process [7].

The vapor delivery system consisted of approximately 6 feet of 3/8" stainless steel tubing. The entire length of the tubing was wrapped with an electric heating tape which in turn was wrapped in fiberglass insulating tape to prevent extensive heat loss and vapor condensation. The temperature of the



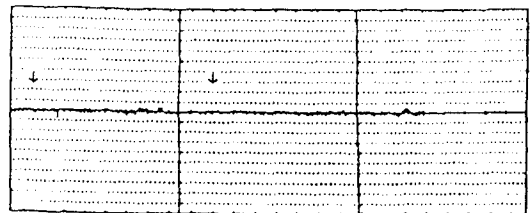
**Fig. 4.** Schematic view of the universal wear tester  
a. Plate, b. Weight, c. Friction transducer, d. Pin, e. Wear transducer, f. Force post, g. Wear track, h. Variable speed drive system, i. Lever arm.

tubing was maintained at 350°C by a temperature controller. A liquid lubricant was injected into 2000 cc/min of air at this elevated temperature, which vaporized the lubricant. During the experiments vapor lubricant was delivered continuously through a flexible tube aimed at the interface of the rolling sliding components. In these experiments, t-butyl phenyl phosphate organodiphosphate and phosphorothionate were used as lubricant.

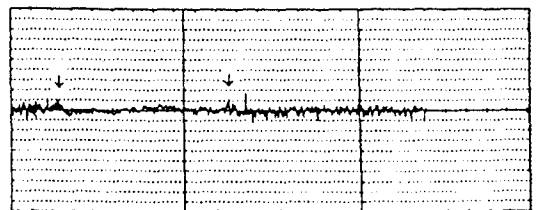
### 3. Results and Discussion

#### 3-1. Rolling tests

The first set of tests were made using an M50 rod and M50 bearings at a speed of 3600 rpm. To establish the limits of operation a run was made at room temperature using a polyol ester liquid lubricant delivered at twenty drops per minute into the contact area. After 90 minutes, the test was stopped and the surface roughness of the rod was measured using a surface profilometer. Fig. 5 shows the profilometer trace indicating there was no wear for the other limit, no lubrication was used and the surface were heated to 375°C. The test was run 30 min. Fig. 6 shows the profilometer trace of the M50 Rod after the experiment.



**Fig. 5(a).** Profilometer trace of silicon nitride rod run for 8 hours at 680°C, 3200 RPM and a pressure of 5000 Mpa. Lubricated with a vapor of 0.5% t-butyl phenyl phosphate.



**Fig. 5(b).** Profilometer trace of M50 rod run for 100 minutes at 375°C, 3200 RPM and a pressure of 5000 Mpa. Lubricated with a vapor of 0.5% t-butyl phenyl phosphate.



Fig. 6(a). Profilometer trace of M50 rod run for 30 minutes at room temperature, 3200 RPM and a pressure of 5000 Mpa. Lubricated with polyol ester.

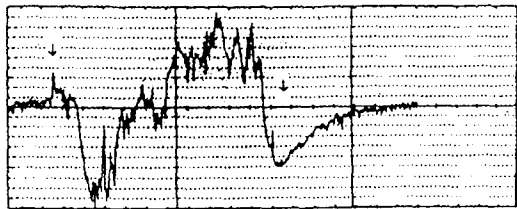


Fig. 6(b). Profilometer trace of unlubricated M50 rod run for 30 minutes at 375°C, 3200 RPM and pressure of 5000 Mpa.

The profilometer trace shows an extremely rough surface with variations of  $\pm 4.5$  microns.

To test vapor phase lubrication under these conditions the surface were heated to 400°C and a stream of 1.3% vaporized t-butyl phenyl phosphate was delivered to the bottom of the test apparatus in order to provide a pre-coat of the solid lubricant on the rod and bearings. After 20 minutes the vapor concentration was reduced to 0.5% and the wear machine was started. The test was continued for 100 minutes. When the equipment was taken apart there was no wear of the rod nor bearings. Fig. 7 shows the profilometer trace of the rod for this test. The surface roughness is very smooth comparable to a surface, lubricated with a liquid at room temperature.

An other test was made at 680°C using a silicon nitride rod and bearings in a 4340 steel cage. The test was continued for a total of eight hours. The concentration of the lubricant was 0.5%. At the end of the test, a small amount of black coating was observed on the cage. The rod and balls showed virtually no wear. Fig. 8 shows the profilometer trace for this eight hour test. The roughness was  $\pm 1.3$  microns. SEM microphotograph of the cage used during the lubricated run is shown in Fig. 9. The photograph shows a section of the cage where the deposit has broken away from the cage at a magnification of

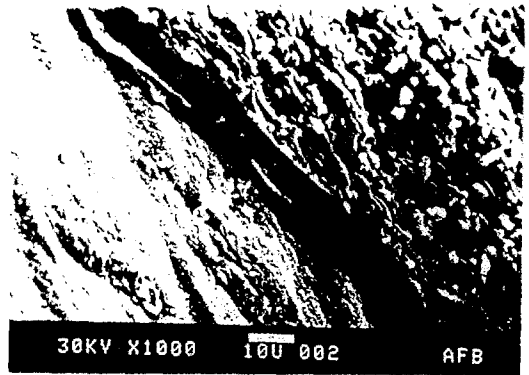


Fig. 7. SEM micropotograph of the cage from run with silicon rod and bearings lubricated with 0.5% t-butyl phenyl phosphate for 8 hours at 680°C, 1000X.

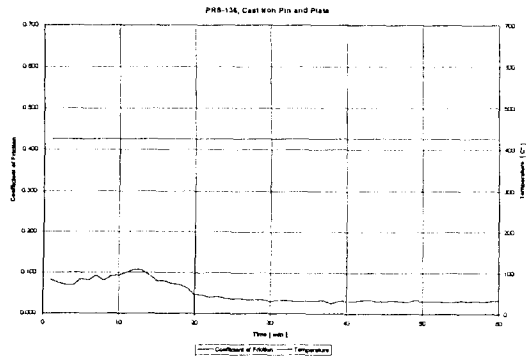


Fig. 8. Cast iron pin and plate lubricated with 0.2% diphosphate. Pressure 5.3 Mpa, temperature 475°C, sliding speed 12 cm/s.

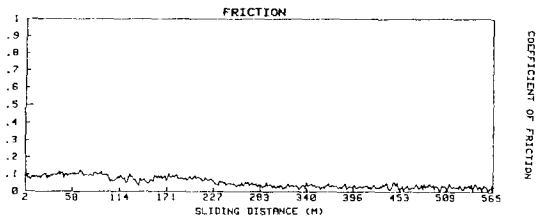


Fig. 9. Sialon pin and plate lubricated with 0.1% t-butyl phenyl phosphate. Pressure 5.3 Mpa, temperature 500°C, sliding speed 12 cm/s.

1000X. The thickness of the deposit can be seen to be uniform and approximately 10 microns thick.

### 3-2. Sliding Tests

Preliminary tests were done by using a cast iron pin and plate at 425°C with an applied pressure of 5.3 MPa and a sliding speed of 12 cm/sec. The concentration of the lubricant was 0.2% organodiphosphate in air. Fig. 10 shows the friction curve of the experiment. For the first twenty minutes of the test, the coefficient of friction was between 0.08 and 0.11. After twenty minutes the value of friction coefficient remained constant at 0.05. No wear of the metal was observed on the plate surface.

The same experiment was repeated with a ceramic plate. A Sialon plate was chemically activated by coating with a thin layer of iron oxide on the surface [12]. This iron oxide layer provided active metal sites on the plate surface to form the deposit. With an applied load of 4 kg (5.3 MPa) and a sliding speed of 12 cm/s, the Sialon pin and plate were lubricated for six hours at 500°C. The coefficient of friction between 0.08 and 0.1 for the first twenty

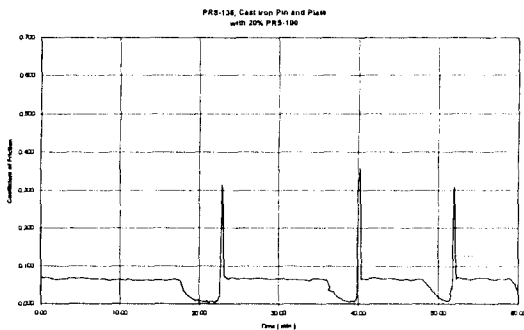


Fig. 10. Cast iron pin and plate lubricated with 0.2% diphosphate and phosphorothinate. Pressure 5.3 Mpa, temperature 575°C, sliding speed 12 cm/s.

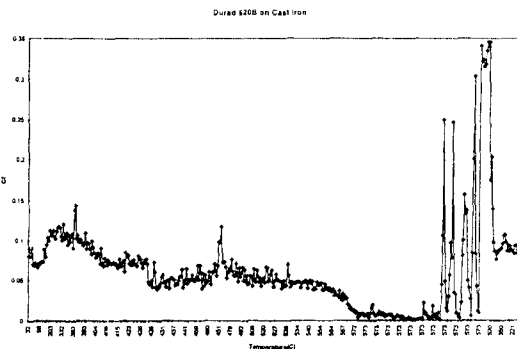


Fig. 11. Temperature test showing the solid, liquid and amorphous states of the polymeric film.

minutes of the experiment. After twenty minutes the friction value was below 0.05 (Fig. 12).

At 575°C, an experiment was made using 80% organodiphosphate and 20% phosphorothionate as a lubricant. The test was run with 5.3 Mpa pressure and 12 cm/s sliding speed. The concentration of the lubricant was 0.2% in air. The friction coefficient started around 0.07 indicating that the polymer was formed and reduced the friction coefficient. As the experiment progressed the friction value suddenly decreased and went down to 0.005 and stayed there for five minutes. After five minutes the friction value went up to 0.3 (Fig. 11) and recovered instantaneously and decreased down to 0.07 again. It was felt that the polymeric that was formed on the surface was changing states. Due to the frictional heating, the polymer melted, acted as a liquid like lubricant, and reduced the friction value. Due to the removal of the heat from the surface during melting, the polymeric film went back first to the amorphous state and then the solid state. This phenomenon was observed three times during this test.

In order to study the behavior of the polymer with changing temperatures, tests were performed by ramping the temperature between 25°C. The pressure in this test was 5.3 Mpa and the concentration of the lubricant was 0.2% t-butyl phenyl phosphate in air. The experiment started at room temperature and a drop of liquid lubricant was introduced on the plate surface (Fig. 12). As the temperature increased the polymeric coating was formed on the surface. At that temperature polymer acted as solid-like coating and reduced the friction coefficient below 0.7. At higher temperatures the

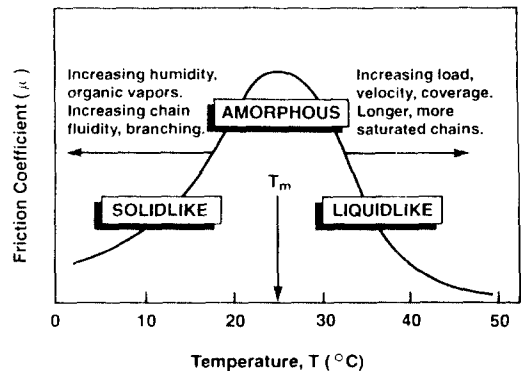
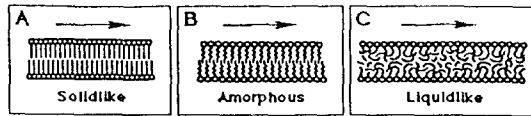


Fig. 12. Temperature test showing the solid, liquid and amorphous states of the polymeric film.



**Fig. 13. Friction coefficient with phase transitions at various temperatures.**

solid polymer melted and resulted in a liquid-like state with a coefficient of friction as low as 0.002. During melting, so much heat was removed from the system that the temperature of the interface cools down. Ultimately the temperature of the interface is cooled so much that and the lubrication of the plate begins to fail and the coefficient of friction oscillates between 0.3 and 0.002. The high friction coefficient of 0.3 is thought to be an amorphous or gel like state that a polymer can form. Finally the plate was allowed to cool down and the coefficient of friction returned to 0.07 as the solid state of the polymer was reformed.

This suggested mechanism is based on the theory of ultra-thin pressurized film rheology [13]. This field of study is currently in the forefront of atomic force microscopy, macromolecule and network polymer research. Ferry [14] states that polymers under dynamic conditions may exist in three different states depending on the temperature (Fig. 13). This type of phenomenon is commonly observed in the viscoelastic behavior of the polymers where the energy dissipation has a maximum at some temperature where the entanglement of the polymer chains are the greatest. At low temperatures the molecules are in a solid-like, frozen state and there is not much interdigitation between the two layers as they slide past each other. At high temperature the chains are in the fully liquid-like state, so, that even though the degree of interdigitation is high, the chains can also disentangle very rapidly. The boundary layer therefore behaves like a simple quasi-Newtonian liquid undergoing shear, and the friction is correspondingly low. However at an intermediate temperature, the chains are in an amorphous or glassy state, and the entanglements that occur during sliding can not be disentangle as easily, and the energy dissipation is the highest.

#### 4. Conclusions

Vapor phase lubrication can be used at high tem-

peratures (300°~700C) where liquid lubrication can not be used.

Ceramic surfaces can be activated with metal to form this polymeric film on sliding and rolling surfaces.

By using a vaporized phosphate ester, a polymeric film can be formed on sliding and rolling components. This lubricious polymeric film essentially eliminates any wear and reduces the coefficient of friction to values below 0.05.

Dynamic test results indicate that different states are observed for the formation of the polymer. In the solid state a coefficient of friction of about 0.07 was obtained while in the liquid state the coefficient of friction was as 0.002. The phase change of the states results from the addition and removal of heat from the polymer. Further experiments are being conducted in order to more clearly identify these states.

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