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ABSTRACT

Six additives were synthesized and evaluated as boundary lubrication enhancers for perfluoropolyethers. These additives included a phosphonate, a thiophosphonate, a β -diketone, a benzothiazole, an amide and a sulfite. These additives were evaluated in a vacuum four-ball apparatus, at a one weight percent concentration in a perfluoropolyether based on hexafluoropropene oxide. Tests were performed in vacuum ($<5.0 \times 10^{-6}$ Torr), at room temperature (~ 23 °C), at an initial Hertzian stress of 3.5 GPa (200N load), and a sliding velocity of 28.8 mm/sec (100 rpm). Infrared (IR) and Raman spectroscopies were used to analyze the 440C specimens after testing. Wear rates for each formulation were determined from the slope of wear volume as a function of sliding distance. All additives yielded reductions in mean wear rates of at least 55 percent, with the exception of the benzothiazole which had no effect. Two of the additives, an amide and a sulfite, reduced the mean wear rate by at least 80 percent. IR and Raman analysis indicated the severity of wear can be correlated to the amount of surface fluorinated polymeric acid species ($R_f\text{COOH}$) and amorphous carbon, in and around the wear scar.

Keywords: Perfluoropolyethers, boundary lubrication, additives

INTRODUCTION

Perfluoropolyethers (PFPE) are widely employed as lubricants for space applications because of their excellent thermal (1) and chemical stability (2) and are particularly effective in the elastohydrodynamic regime (3). However, when used as a boundary lubricant, PFPE performance is more variable and less predictable (4), (5). The most significant problem encountered when using PFPE's in the boundary lubrication regime is the unavailability of soluble additives. This results from the fact that the vast additive technology developed for hydrocarbon and ester based lubricants cannot be applied to PFPE's because of their inherent insolubility. Soluble phosphorus based additives (phosphines and phosphotriazines) have been developed for anti-corrosion and anti-degradation (6), (7) but these have little or no boundary lubrication activity (8), (9).

Masuko et al. (10) studied a series of PFPE derivatives (acids, alcohols, and phosphate esters) in a linear PFPE basestock produced by the polymerization of tetrafluorooxetane followed by direct fluorination (D fluid)(11). A vacuum four-ball apparatus was used. These additives yielded some antiwear activity, with the PFPE terminated acid being the most effective. Sharma et al. (12) reported anti-wear activity for an additive (structure not disclosed) in a linear PFPE based on tetrafluoroethylene (Z fluid)(13). Later, this additive was identified as a PFPE alcohol (8). Reference (8) also reported antiwear behavior for a PFPE ketone. Antiwear activity has also been reported (14) for two other PFPE derivatives: a polar amine salt and a phosphorus containing end group. Nakayama et al. (15) reported wear behavior in vacuum and various atmospheres for two PFPE additives: a carboxylic acid and an aminophenylsulfone. The carboxylic acid additive reduced wear in vacuum, while the sulfone accelerated wear under the same conditions.

Recently, NASA has developed a four-ball apparatus and a test protocol for the evaluation of liquid lubricants and greases for space applications (16). This device can operate as a vacuum tribometer or with a series of different atmospheres. A series of mono and diaryl esters were evaluated as antiwear additives in a Z fluid using a dry air atmosphere (17). Under these conditions, two monoesters yielded wear reductions of 60 and 35%. One diester had no effect, while two other diesters were actually prowear.

Therefore, the objective of this work was to evaluate a series of newly synthesized soluble additives for their antiwear activity in a poly (hexafluoropropene oxide) basestock (K fluid). Types of additives included a phosphonate, a thiophosphonate, a β -diketone, a benzothiazole, an amide and a sulfite. Additives were evaluated at a one weight percent concentration by measuring steady state wear rates and coefficients of friction using the four ball apparatus. Test conditions included: vacuum ($< 5.0 \times 10^{-6}$ Torr), 200 N load, a speed of 100 rpm, room temperature (~ 23 °C), 440C stainless steel bearing balls and a total test duration of approximately four hours.

EXPERIMENTAL

Lubricant Basestock

A branched PFPE basestock, poly (hexafluoropropene oxide) fluid, was chosen for the evaluations. This is a commercially available fluid made by CsF catalyzed polymerization of hexafluoropropene oxide yielding a series of branched polymers (K fluids). These lubricants have been used extensively in various space applications, such as filter wheels and scanning mechanisms (5), (18). Physical properties for the fluid used in this study appear in Table 1.

Lubricant Additives

Six different additives with various functional groups were synthesized for this study. These included: a phosphonate, a thiophosphonate, a β -diketone, a benzothiazole, an amide and a sulfite. All had long PFPE groups for solubilization, and high molecular weights to maintain low vapor pressures. Structures for these additives appear in Table 2. Each additive was evaluated at a one weight percent concentration in the poly (hexafluoropropene oxide) basestock.

Tribometer

A four-ball tribometer (Figure 1), operating in the boundary lubrication mode, was used to measure steady state wear rates and friction coefficients for each lubricant formulation and the additive-free basestock. Specimen configuration (Figure 2) is the same as the conventional four-ball apparatus, except for the use of 9.5 mm (3/8 in.) diameter precision bearing balls (grade 10). A complete description of this device appears in reference (16).

Procedure Prior to Testing

Prior to testing, the balls and lubricant cup were ultrasonically cleaned in hexane, acetone and finally methanol for ten minutes each. The lubricant cup was then ultrasonically cleaned for ten minutes in two consecutive trifluorotrichloroethane baths. The balls were then blown dry with nitrogen, followed by UV/ozone treatment (19) for 15 minutes. Within 5 minutes of UV/ozone treatment, three of the balls were placed into the lubricant cup and covered with the test lubricant, and the remaining ball was placed into the nitrogen-backfilled tribometer and used as the rotating ball. After the balls were secured in the lubricant cup, it was evacuated in a bell jar for one hour at 0.01 Torr to remove dissolved gases. The cup was then placed into position inside the tribometer and the chamber evacuated.

Test Procedure

After reaching the desired base pressure ($< 5.0 \times 10^{-6}$ Torr), the stage was pneumatically loaded against the rotating ball and rotation initiated. The load was $200 \text{ N} \pm 5\%$, giving an initial Hertzian stress of 3.5 GPa . The sliding speed was 28.8 mm/sec (ball rotating speed of 100 rpm).

Friction torque was recorded continuously by using a Hall-effect position sensor. The Hall-effect position sensor provides an indirect measurement of torque by measuring the relative angular displacement of the lubricant cup which is attached to a flex pivot.

Wear was determined by measuring wear scar diameters on the three stationary balls using an optical microscope. The average wear scar diameter was used to calculate a wear volume. A sample stage on the microscope was so designed that the wear scars could be measured without disassembling the balls from the cup. The experiment was then continued using the same set of balls. Typically, the four hour test was interrupted three times (on each hour) for wear scar measurements. After the test was completed, final wear scar measurements were taken. A wear rate (mm^3/mm) was calculated from the slope of the straight line obtained by plotting wear volume as a function of sliding distance. An example of data for the PFPE base fluid using the aforementioned conditions is shown in Figure 3. Each of the four data points represents the average of the three balls for one wear scar measurement. The wear rate for this particular test was calculated to be $0.690 \times 10^{-9} \text{ mm}^3/\text{mm}$.

A total of eight tests were performed using the additive-free base fluid. Each additive formulation was run either three or four times (limited by the amount of available additive). After each set of tests for either the base fluid or the additive formulation was completed, the lubricant cup was ultrasonically cleaned for ten minutes in two consecutive trifluorotrichloroethane baths.

Lubricant Degradation Characterization

The balls of one test, both for the base fluid and each additive formulation, were analyzed using a FT infrared microscope (μ -FTIR) and a Raman microscope (μ -Raman). The FTIR analysis was performed in the reflectance mode using a 32X infrared objective and a $100 \mu\text{m}$ diameter spot size. The spectral resolution and acquisition time were 8 cm^{-1} , and 400 seconds, respectively. A gold coated glass slide was used to acquire a background spectrum.

Raman analysis was performed using a 15mW Ar laser (514.5 nm wavelength), with an analyzing spot diameter of $2 \mu\text{m}$, and a 50X objective. The acquisition time was 50 seconds and the spectral range was 150 to 3200 cm^{-1} . The instrument was aligned to both the type-2A diamond line at 1331.2 cm^{-1} , and Si (111) at 520.8 cm^{-1} . Care was

taken when exposing the organic films to the laser beam since damage can occur that results in similar degradation to that produced by a tribological process.

Efforts were made to only compare spectra taken from areas of the scar with similar characteristics. Analysis of each ball was performed at several locations, both on and off the wear scar. The balls of each test were analyzed under two different conditions with the FTIR and Raman, the first, with the bulk lubricant on the ball, and, the second, after being rinsed with a fluorinated solvent (X-100) that removed the excess lubricant. Generally, many features not noticeable before rinsing, were apparent around the scar after rinsing.

RESULTS

Wear

The wear results are tabulated in the first three columns of Table 3. The numbers appearing within parentheses in the standard deviation column are the number of tests performed using that formulation. The wear data of table 3 is shown graphically in Figure 4. The bar graphs represent the mean wear rates of the specified formulations, whereas the error bars signify one standard deviation.

The tabulated results in table 3 indicate that the additive formulations yielded reductions in the mean wear rates of at least 55 percent compared to the base stock's value, with the exception of the benzothiazole which had no effect. The benzothiazole's mean wear rate improvement of 5 percent is well within the standard deviation, as seen in figure 4. The β -diketone additive reduced the mean wear rate 70 percent. The amide and the sulfite were the most active, reducing the mean wear rate by 85 percent and 80 percent, respectively.

Friction

The friction results are tabulated in the last column of Table 3. The mean friction coefficient appears outside the parentheses, whereas the ranges are contained within the parentheses. These values were taken from the compilation of all the tests. These data are shown graphically in Figure 5. The bar graphs represent the mean friction coefficient, whereas the error bars signify the minimum and maximum friction coefficient for each formulation. Each of the mean friction coefficients are ≈ 0.13 , and have ranges that overlap one another. Therefore, it is concluded that the various additives did not have an effect on the wear couple's friction coefficient.

DISCUSSION

Under boundary lubrication conditions, PFPE base fluids normally operate in the corrosive wear regime. In this lubrication regime, PFPE's decompose producing a series

of corrosive products, which, in turn, react with existing surface oxides, producing metal fluorides (4), (20). These fluorides provide lubrication protection to the contacting surfaces, reducing friction and wear (20). Unfortunately, these fluorides also attack and further decompose the lubricant, producing more reactive products. Surface fluorides are constantly removed from the contact region, resulting in high wear of the substrate (i.e. corrosive wear). Therefore, a PFPE lubricated couple, operating in the boundary regime, relies upon the wear process for its tribological protection.

In contrast, conventional unformulated hydrocarbon and ester based lubricants are relatively unreactive with the wear couple's surface and operate in the adhesive wear regime in boundary contacts. Typically, these fluids' commercial versions are fortified with reactive extreme pressure and/or anti-wear additives to encourage the formation of surface films. The resulting surface films reduce wear and friction and increase load capacity. Thus, these fluids' protection does not necessarily depend upon the decomposition of the basestock, but rather, a formation of protective surface films whose existence and effectiveness depends upon the type and concentration of additives.

Since conventional hydrocarbons and PFPE's undergo fundamentally different wear mechanisms in boundary lubricated contacts, additives that perform well in one may not necessarily perform well in the other. Additives used in hydrocarbon based lubricants are not soluble in fluorinated lubricants. Methods to render them soluble sometimes results in loss of additive function. Since PFPE's are already operating in a corrosive wear mode, an effective additive must reduce this wear rate to an acceptable level. This can be accomplished by incorporating an additive which poisons enough catalytic sites to reduce reaction rates. An additive may also be effective reacting with the substrate to form secondary compounds. The formation of these compounds would have a two fold effect; 1) these compounds may provide additional wear protection, and 2) because they react with the substrate, they occupy the metal-sites, which indirectly reduces the formation of the PFPE-degrading metal fluorides.

β -Diketone Additive

β -diketone compounds are not normally used as additives for conventional hydrocarbon oils because they are considered surface site blockers, and not protective film providers. β -diketones are well known complexing agents for polyvalent metals in their enolate form (21). It was thought that, as a PFPE additive, β -diketone might effectively block catalytic sites which would reduce reaction rates. In this study, the β -diketone formulation proved effective in enhancing the performance of the base stock.

Phosphorous Additives

Phosphorous based additives are the most common anti-wear additives formulated for conventional lubricants. It is thought that these additives adsorb onto the surface,

degrade under the contact stresses to form species which react with the substrate to form organo/inorgano phosphorous compounds (22). Thus, a functioning phosphorous additive in a PFPE would, 1) block catalytic sites, and 2) reduce the concentration of the PFPE-degrading metal-fluorides indirectly by providing competition (via the formed surface species) for the lubricant molecules for the remaining active sites. In addition, the formed surface species and organo/inorgano phosphorous compounds could provide additional wear protection. Both the phosphonate and the thiophosphonate compounds were effective in enhancing the performance of the base stock.

Sulfur Additives

Sulfur, along with chlorine, based additives are the most common extreme pressure additives formulated for hydrocarbon oils. These additives function the same way as anti-wear additives, but are generally less reactive, requiring higher temperatures or loads to form protective films. Both the amide and sulfite formulations improved the wear performance of the base fluid, whereas, the benzothiazole was ineffective.

IR and Raman Observations

The additives were not detectable by IR or Raman in the additive formulations because of their low concentrations. However, other distinguishable features were apparent. Figure 6 shows a typical wear scar before and after solvent rinsing. After the excess lubricant was removed by rinsing, features previously hidden were observed. Of interest is the brownish material around, and on the wear scar, which began to accumulate after initiation of testing. The relative amount of this brownish material correlated to the severity of wear. This brownish material has been observed before, and has been described as a "friction polymer" (23). This friction polymer is not soluble in fluorinated solvents, is strongly attached to the metal surface, and has several unique chemical features, absent from the unused PFPE. IR and Raman analysis of this friction polymer has indicated that it contains both polymeric fluorinated acid species ($R_f\text{COOH}$), and amorphous carbon (23). The formation of this friction polymer is seen as a measure of PFPE degradation.

Figure 7 compares the IR spectra of the friction polymer region before and after solvent rinsing (b and a, respectively) for the benzothiazole-formulated test, to that of unused PFPE on a 440C surface (c). Both the unused PFPE spectra, and the spectra prior to solvent rinsing contain the characteristic C-F vibrations of this particular PFPE at 990 cm^{-1} , and in the region between 1127 and 1310 cm^{-1} . These peaks have nearly disappeared from the spectra of the rinsed surface, indicating that the majority of the PFPE has been removed. The absence of the C-F peaks in this spectra has amplified the signals of other notable peaks. In particular, the peaks at 1436 , 1669 cm^{-1} , and the broad band between 3000 - 3600 cm^{-1} . The broad band (3000 - 3600 cm^{-1}) has been assigned to hydrogen bonded hydroxyl groups, whereas, the other two bands have been assigned to carboxylic acid species (23). These peaks also appear in the spectra of the "before-

rinsed” surface, but are not as distinguishable due to the low concentration of these species, and the shadowing-effect by the signal from the base lubricant.

The relative intensities of the above mentioned peaks were found to directly correlate with the amount of wear. Figure 8 shows the typical IR spectra of the friction polymer region after solvent rinsing for each formulated test, and the additive-free test. The amount of polymer present is directly related to the relative intensities of its peaks. The legend indicates the specific wear rates for each test represented, as well as the mean wear rate for that additive’s set of tests (from Table 3). For example, the spectra for the β -diketone additive was taken from a ball from a test that had a wear rate of $2.14 \times 10^{-10} \text{ mm}^3/\text{mm}$. Whereas, the mean wear rate for all the β -diketone tests was $1.88 \times 10^{-10} \text{ mm}^3/\text{mm}$. The additives can be ranked according to the relative strengths of these peaks (relative amount of polymer present) as follows: benzothiazole > base fluid > thiophosphonate > β -diketone > sulfite > phosphonate > amide. Therefore, it can generally be said that the higher the wear rate, the more polymer is present.

Typical Raman spectra of the region from 1000 to 1900 cm^{-1} for each formulated test (except amide), and the base fluid test are shown in Figure 9. These spectra were taken from within the scar after solvent rinsing, where the polymeric material was not as dense to prevent signal saturation. Similar to the IR spectral peaks of 1436 , 1669 cm^{-1} , and $3000\text{-}3600 \text{ cm}^{-1}$, the Raman spectral peaks 1364 and 1604 cm^{-1} represent products of tribo-induced, chemically degraded poly (hexafluoropropene oxide) PFPE (23). The Raman peak at 1364 cm^{-1} can be assigned to the so called “D” band, and serves as a direct measure of the order, or disorder, of this tribologically created structure. The broad band at 1604 cm^{-1} is the “G” peak found in highly oriented pyrolytic graphite at 1576 cm^{-1} . This peak has been previously assigned to scattering by graphitic optic zone center phonons (24). This band shifts, and broadens, primarily as a result of the change from C sp^3 to C sp^2 bonding (24). The occurrence of these two Raman peaks strongly suggests C=C sp^2 type bonding, and therefore, the presence of a cross-linked-induced C-C network. Cross linking has long been thought of as being the critical, and final, step in the degradation process of perfluorinated materials (25).

The “G” and “D” peaks are absent in the spectra of unused PFPE on 440C steel, and are absent in the β -diketone, phosphonate, and thiophosphonate spectra. These peaks are more profound in the additive runs containing benzothiazole, sulfite, and the additive-free run. Theoretically, the relative heights of these peaks should correspond to the amount of wear, as did the subject spectral peaks of the IR data. In fact, given a larger analyzing area, it is suspected that a better correlation between the relative absorbances of the 1364 and 1604 cm^{-1} Raman peaks and wear could be attained. It is thought that the small spot size used to obtain these data (diameter of $2 \mu\text{m}$) prevented sufficient averaging over the analyzed area. This, coupled with the inherent nonuniform nature of the wear scar produced wide variations in spectral absorbances of these peaks when analyzing areas in proximity to one another on the same wear scar. This was not a significant problem with the IR analysis, as it utilized the larger analyzing diameter of

100 μm . This allowed for averaging over a larger area, and a better representation of the features that are present.

SUMMARY OF RESULTS

- 1) Five different additives with various functional groups: a phosphonate, a thiophosphonate, a β -diketone, an amide and a sulfite, all exhibited antiwear activity in a poly (hexafluoropropene oxide) basestock at one weight percent concentration.
- 2) The amide and the sulfite additive at one weight percent were the most effective, reducing the mean wear rate, from that of the additive-free base stock, by 85 percent and 80 percent, respectively.
- 3) One additive with a benzothiazole functional group showed no antiwear activity at one weight percent concentration.
- 4) The wear couples mean friction coefficient was not affected by any of the six additive formulations tested.

CONCLUSIONS

- 1) Soluble additives can be developed that reduce wear in vacuum for poly (hexafluoropropene oxide) PFPE fluids.
- 2) The severity of wear can be correlated to the amount of fluorinated polymeric acid species (R_fCOOH), and the amount of amorphous carbon in and around the wear scar.

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Table 1. Properties of the PFPE Basestock

Average molecular weight	6250 amu
Vapor pressure at 38 °C at 260 °C	8 x 10 ⁻⁸ Torr 2 x 10 ⁻³ Torr
Kinematic viscosity at 20 °C at 99 °C	800 centistokes 26 centistokes
Density at 24 °C at 204 °C	1.90 g/ml 1.59 g/ml
Surface tension at 25 °C	19 dynes/cm

Table 2. Additive Structures

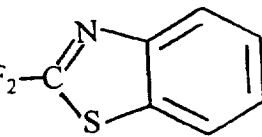
Name	Structure
Phosphonate	O=P (OCH ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ CF ₂ CF ₃) ₃
Thiophosphonate	S=P (OCH ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ CF ₂ CF ₃) ₃
β-Diketone	CF ₃ CF ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ COCH ₂ COCH ₃
Benzothiazole	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ - 
Amide	CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ OCF ₂ CF ₂ CONHCH ₂ CH ₂ SH
Sulfite	(CF ₃ CF(CF ₃)CF ₂ CF ₂ CF ₂ CF(CF ₃)CF ₂ CH ₂ O) ₂ S=O

Table 3. Wear Rate and Friction Summary

Name	Mean Wear Rate ($\times 10^{-10}$ mm ³ /mm)	Wear Rate Standard Deviation (No. of Tests) ($\times 10^{-10}$ mm ³ /mm)	Mean Wear Rate Improvement	Mean & (Range) of Friction Coefficient
Base Stock	6.34	3.01 (8)	-	0.13 (0.10-0.21)
Phosphonate	2.16	1.41 (3)	65%	0.14 (0.10-0.19)
Thiophosphonate	2.92	1.59 (3)	55%	0.13 (0.11-0.14)
β -Diketone	1.88	0.23 (4)	70%	0.12 (0.10-0.14)
Benzothiazole	6.09	3.81 (3)	5%	0.13 (0.11-0.14)
Amide	1.01	0.42 (4)	85%	0.12 (0.09-0.13)
Sulfite	1.20	0.15 (3)	80%	0.13 (0.12-0.13)

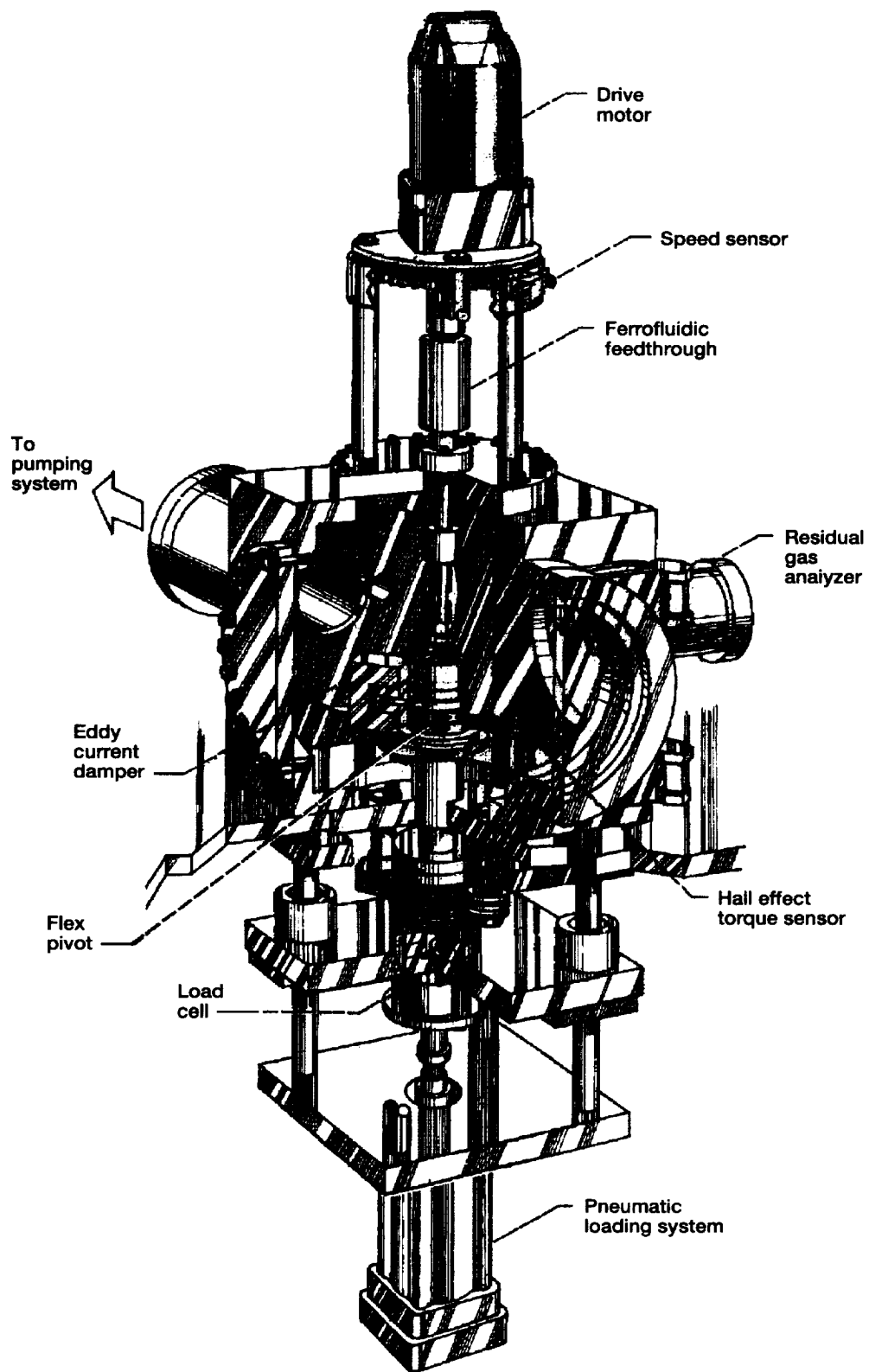


Figure 1.—Vacuum four-ball tribometer.

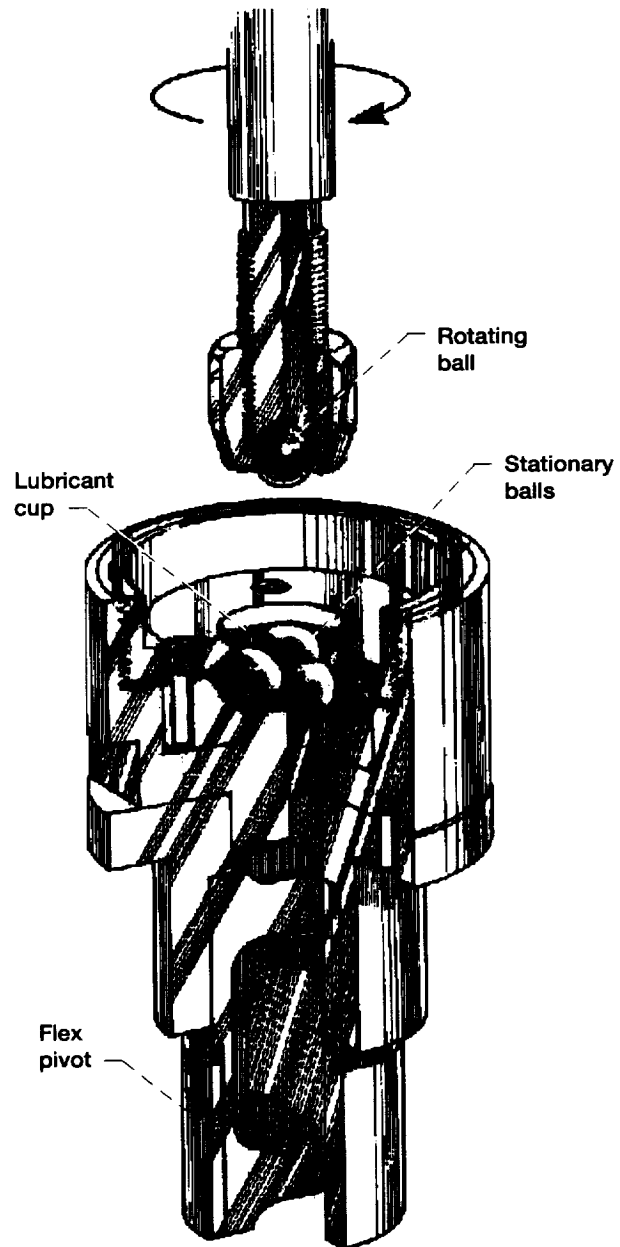


Figure 2.—Test specimen configuration.

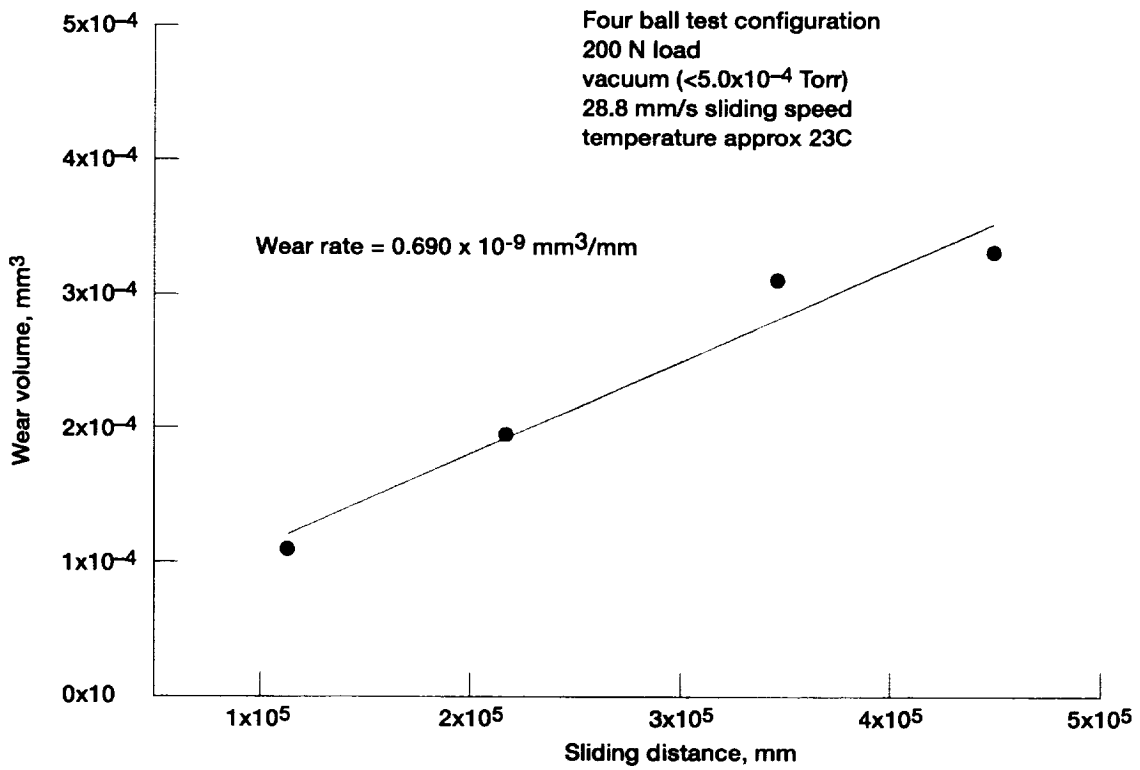


Figure 3.—Wear volume as a function of sliding distance for the unformulated lubricant.

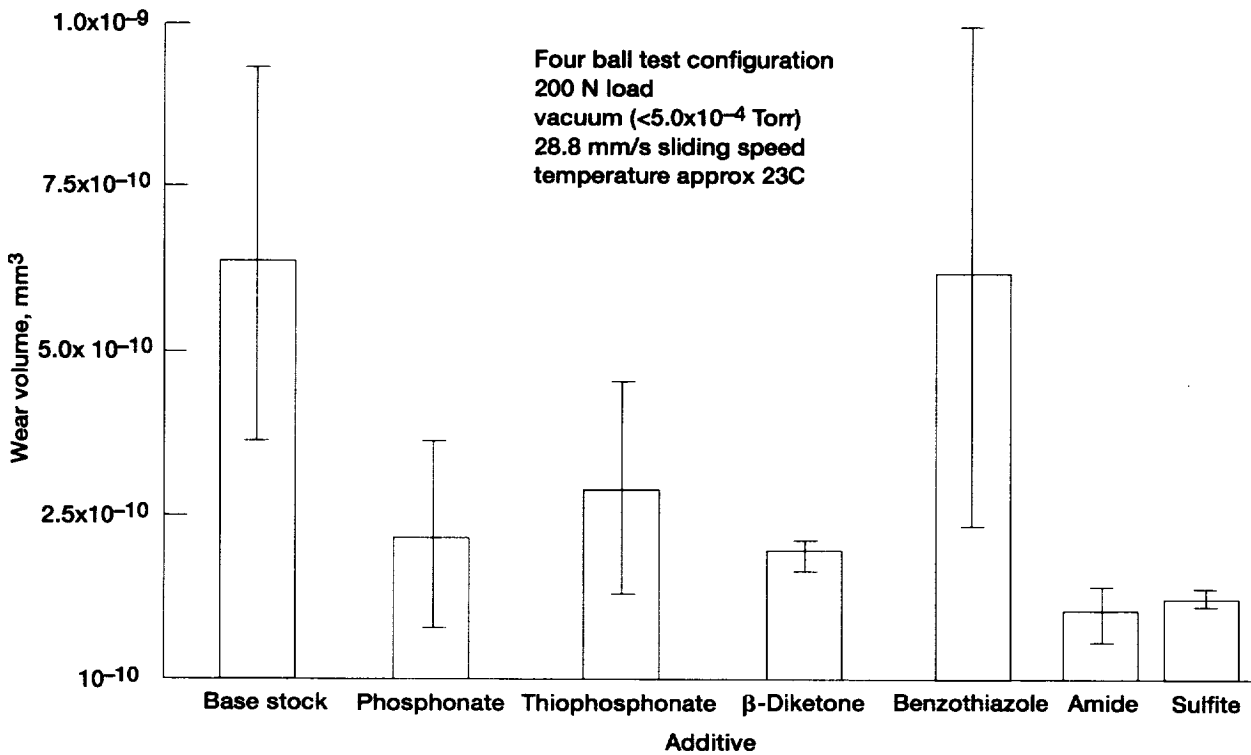


Figure 4.—Mean wear rates of the formulated and unformulated tests. Error bars represent one standard deviation.

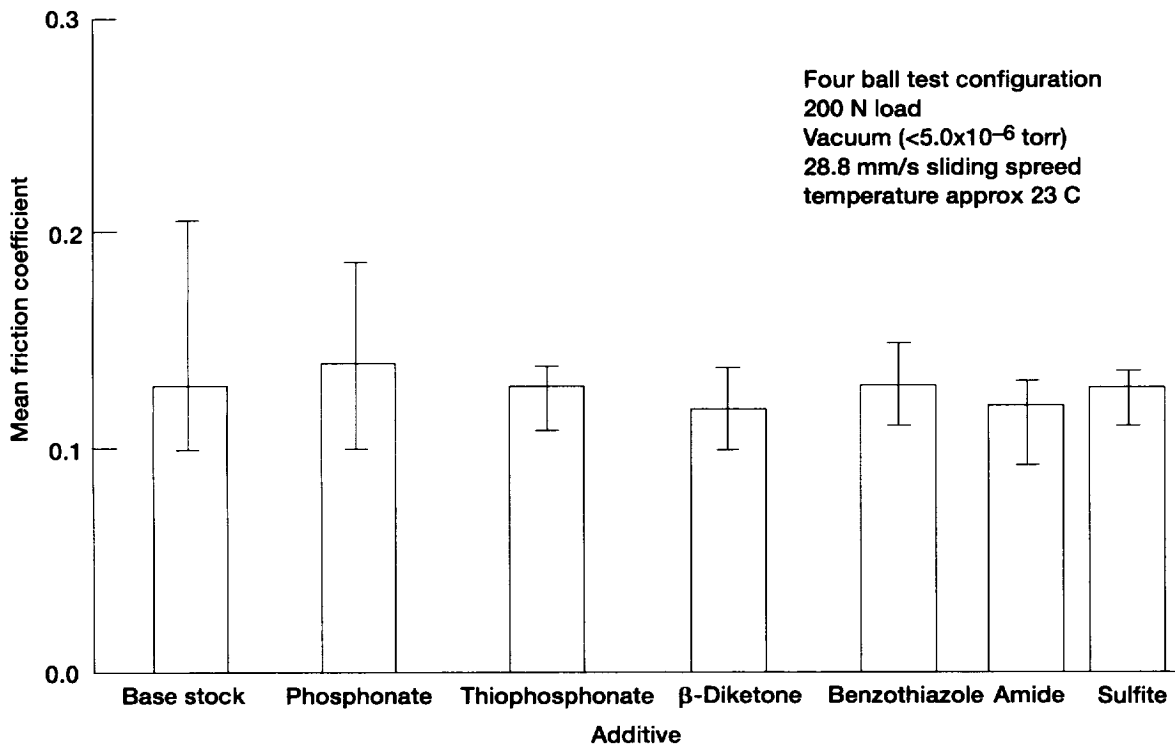


Figure 5.—Mean friction coefficients of the formulated and unformulated tests. Error bars represent minimum and maximum.

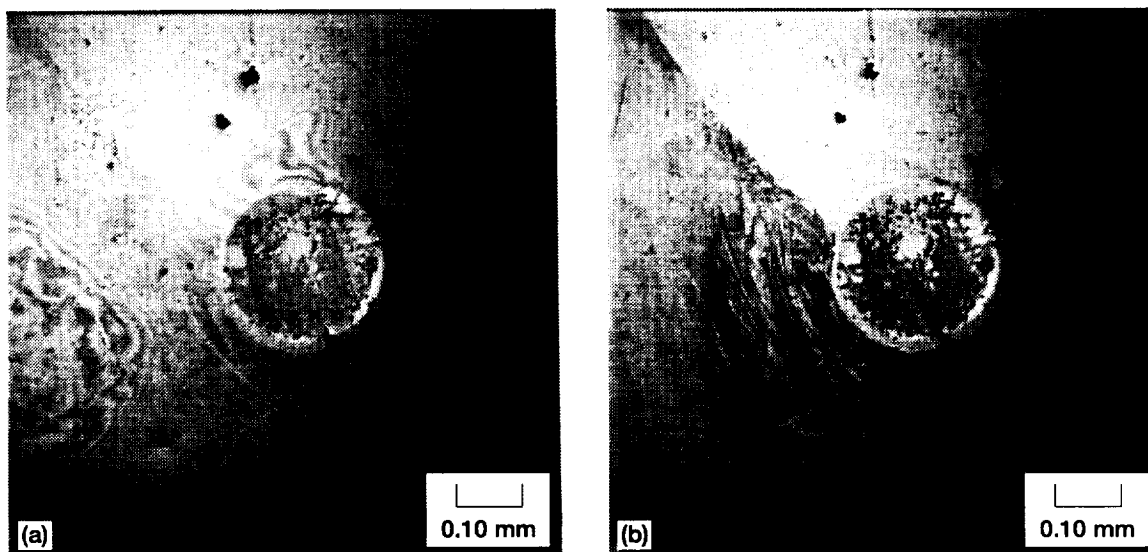


Figure 6.—Typical wear scar before (a) and after (b) solvent rinsing.

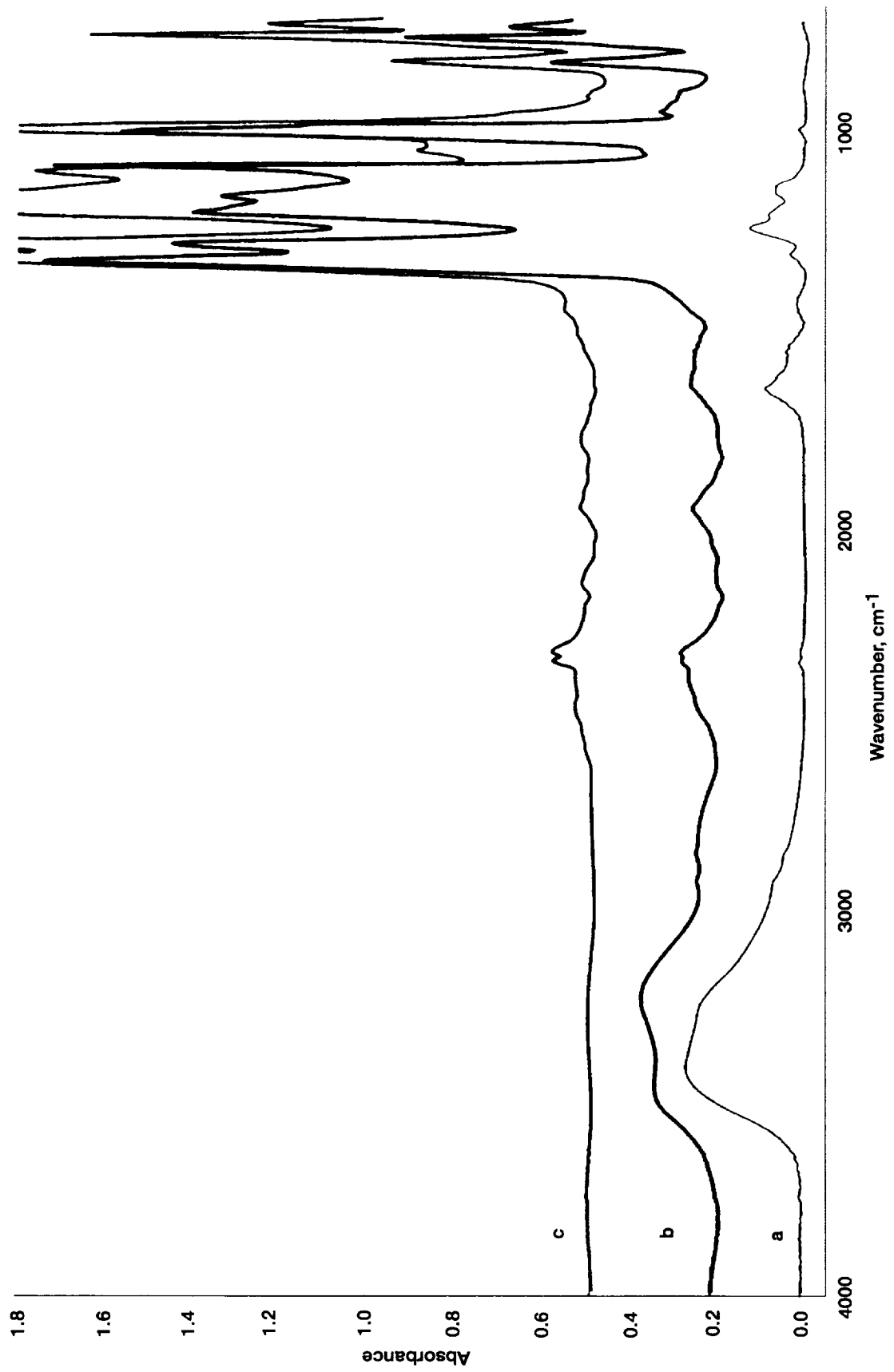


Figure 7.—FTIR spectra of regions off the scar after (a), and before (b) solvent rinsing, and unused PFPE on 440C steel (c).

Name	Wear rate for the test of this spectra (x 10 ⁻¹⁰ mm ³ /mm)	Mean wear rate (x 10 ⁻¹⁰ mm ³ /mm)
Base stock	10.32	6.34
Benzothiazole	2.47	6.09
β-Diketone	2.14	1.88
Thiophosphonate	1.44	2.92
Sulfite	1.05	1.20
Amide	0.81	1.01
Phosphonate	0.68	2.16

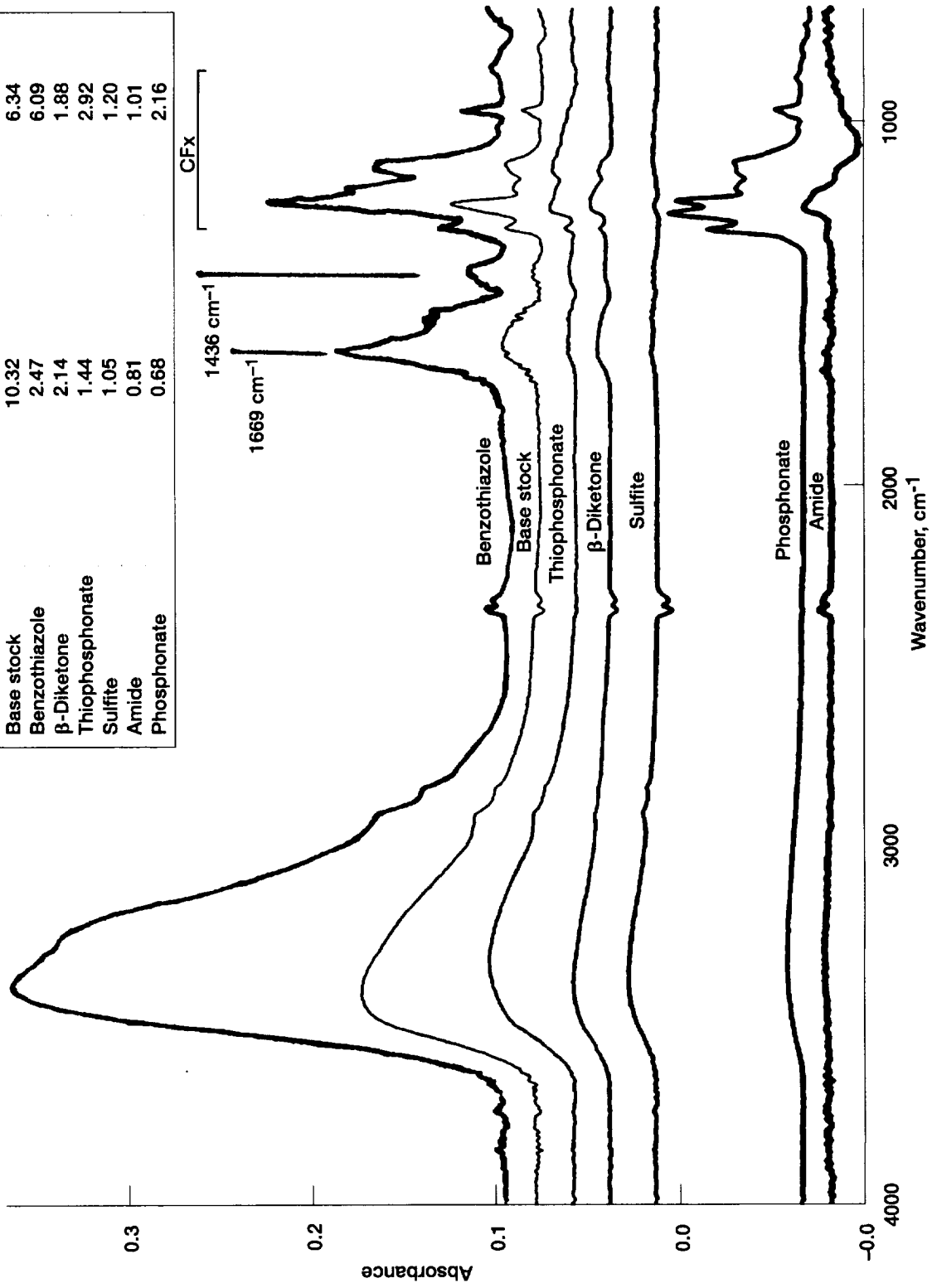


Figure 8.—FTIR spectra of regions off the scar after solvent rinsing for the formulated, and unformulated tests.

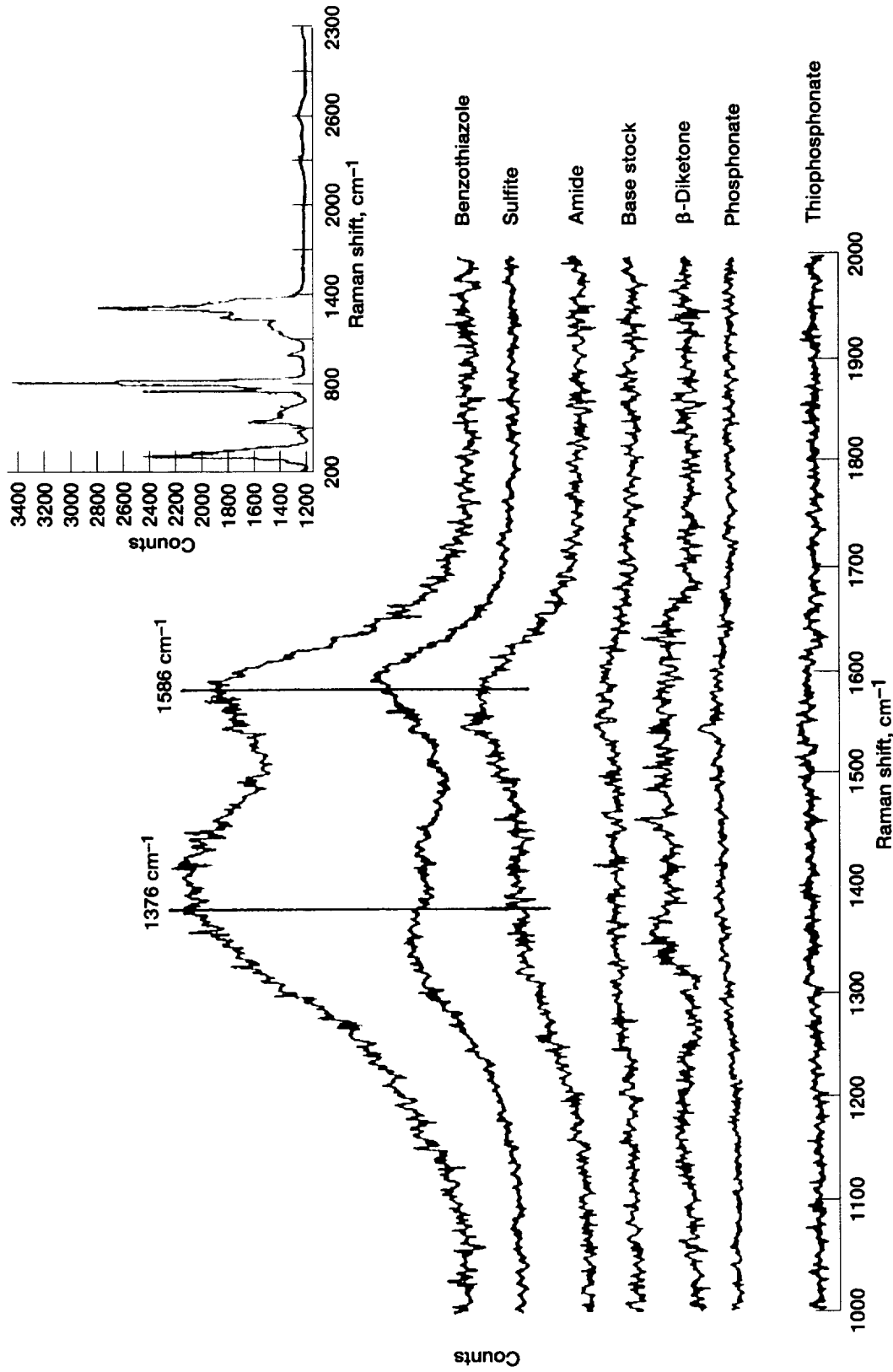


Figure 9.—Raman spectra of regions on the scar after solvent rinsing for the formulated (except amide), and unformulated tests. The insert is the Raman spectrum of a thin (2000 Å) lubricant film before the test.

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13. ABSTRACT (Maximum 200 words) Six additives were synthesized and evaluated as boundary lubrication enhancers for perfluoropolyethers. These additives included a phosphonate, a thiophosphonate, a β -diketone, a benzothiazole, an amide and a sulfite. These additives were evaluated in a vacuum four-ball apparatus, at a one weight percent concentration in a perfluoropolyether based on hexafluoropropene oxide. Tests were performed in vacuum ($<5.0 \times 10^{-6}$ Torr), at room temperature (~ 23 °C), at an initial Hertzian stress of 3.5 GPa (200N Load), and a sliding velocity of 28.8 mm/sec (100 rpm). Infrared (IR) and Raman spectroscopies were used to analyze the 440C specimens after testing. Wear rates for each formulation were determined from the slope of wear volume as a function of sliding distance. All additives yielded reductions in mean wear rates of at least 55 percent, with the exception of the benzothiazole which had no effect. Two of the additives, an amide and a sulfite, reduced the mean wear rate by at least 80 percent. IR and Raman analysis indicated the severity of wear can be correlated to the amount of surface fluorinated polymeric acid species ($R_f\text{COOH}$) and amorphous carbon, in and around the wear scar.			
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