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# Friction and Wear Reduction Mechanism of Polyalkylene Glycol-Based Engine Oils

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#### ABSTRACT

Polyalkylene glycols (PAG) have been explored as a possible base stock for engine oil formulation. The friction, wear, and load-carrying capacity of five different PAG chemistries were evaluated either as a base stock or as formulated oils in pure sliding and sliding-rolling conditions using various laboratory bench test rigs operating under boundary and mixed lubrication regimes. The results were compared against GF-5 SAE 5W-20 and a mineral-based oil. The wear surfaces were also characterized using various surface-sensitive techniques for analysis of tribofilms to understand the mechanism of friction reduction. The results indicated that PAG oils show lower friction/traction coefficients and improved load-carrying capability, depending on the formulation, than those of the GF-5 SAE 5W-20 and mineral-based oil. The adsorption of PAG molecules on the surface appeared to be responsible for the lower friction characteristics.

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# Introduction

Engine oils play a critical role in friction reduction. Advancements in engine oil technology over the past 20 years were influenced by changes in base oil chemistry, development of new friction modifiers and treatment level, and the total additive package consisting of various other components. Mineral oils are mostly used in today's formulations, although synthetic base stock, like polyalphaolefin (PAO), is also used in certain special formulations. The choice of base oil plays an important role in improved fuel economy. Kiovsky, et al. (1) compared three formulated SAE 5W-30 engine oils using a hydrocracked, PAO, or severely hydrogenated mineral base oil with the same additive package. The hydrocracked base oil showed a lower boundary friction coefficient than PAO and severely hydrogenated mineral oil. Igarashi, et al. (2) demonstrated 1.2% fuel economy improvement in federal test procedure road simulator tests with SAE 5W-30 engine oil formulated using severely hydrocracked base oil compared to conventional solventrefined base oil.

Polyalkylene glycol (PAG)-based engine oils are being explored as a step forward for significant fuel consumption reduction. PAGs can be classified as Group V synthetic base stocks and are currently used as fire-resistant hydraulic fluids, refrigeration lubricants, compressor lubricants, and gear lubricants. They have also been explored for lubricating two-cycle engines as early as the 1970s. PAGs offer several advantages in engine oil application, including lower boundary friction coefficient due to their polar nature, low volatility (5%) that can potentially lower oil consumption, clean burning leading to less engine deposits, and higher oxidative stability (Fitamen, et al. (3)). However, its application as a lubricant in modern engines

has not been investigated in detail. Woydt, et al. (4) showed a significant reduction in the friction coefficient of PAG-based lubricant over mineral oil-based engine oils in the temperature range 40–120°C using a laboratory bench test rig. In this test, a section of a ring was pressed against a section of a rotating (against a vertical axis) liner. More recently, Sanders, et al. (5) demonstrated a 10% friction benefit under motored (unpressurized) engine tests and about 30% friction benefit under pressurized motored engine tests over a 0W-30 formulation. Cuthbert, et al. (6) demonstrated a 1% fuel economy improvement in Environmental Protection Agency city cycles when the oil is fresh over GF-5 SAE 5W-20 formulation. Greaves and Topolovec Miklozic (7) investigated the tribofilm formation characteristics of oil-soluble PAG as an additive in PAO base oil and in PAO base oil with 1% zinc dialkyldithiophosphate (ZDDP) antiwear additive. The addition of oil-soluble PAG to PAO reduced friction and wear but no significant tribofilm was formed. When ZDDP was added, a tribofilm formed but the rate of film formation appeared slower, leading to a slight increase in wear.

PAGs are prepared by the reaction of ethylene oxide, propylene oxide, or butylene oxide with an alcohol in the presence of a catalyst. PAGs prepared from ethylene oxide and propylene oxide have limited solubility in mineral oil. However, PAGs prepared from propylene oxide and butylene oxide are soluble in mineral oil and therefore are most preferred from customer use standpoint.

The objectives of the present investigation are to evaluate the friction reduction potential, wear behavior, and load-carrying capacity of various PAG chemistries using various laboratory bench-top tests. Another objective is to elucidate the friction

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reduction mechanism of PAGs by examining the contact surfaces following bench tests using various surface-sensitive analytical techniques.

### **Experimental details**

# Laboratory bench tests

A variety of bench-top machines were utilized to elucidate the effects of various PAG chemistries and additives on the friction, wear, and load-carrying performance of formulated PAG oils over broad ranges of test conditions and compared against GF-5 SAE 5W-20 oil.

# Pin-on-disk machine

Tests were conducted using a stationary 6.35-mm-diameter ball made of AISI 52100 steel sliding against a rotating disk made of the same material as the ball. Both the ball and the disk were mirror finished. The tests were done at 10 N load corresponding to an initial contact stress of 1 GPa, sliding speed of 0.1 m/s, and sliding distance of 300 m. The tests were done at room temperature, 60°C, and 80°C. These test conditions represent boundary lubrication regime.

# High-frequency reciprocating machine

The machine was operated under two different conditions to generate friction and wear data and a Stribeck curve. To evaluate the friction and wear performance, tests were conducted using a stationary 4.3-mm-diameter, 9-mm-long pin made of AISI 52100 steel sliding (on the long axis) against a reciprocating flat made of the same material as the pin. Both the pin and the flat were mirror finished. The tests were done at 325 N load corresponding to an initial contact stress of 1 GPa, reciprocating frequency of 5 Hz, and stroke length of 6 mm. The tests were done at room temperature, 60°C, and 80°C. These test conditions represent a boundary lubrication regime. To generate the Stribeck curve, tests were conducted at 50 N normal load, 10 mm stroke length, reciprocating frequency range 0.02–33 Hz, and oil temperature 100°C.

#### Block-on-ring machine

This machine was used to determine the load-carrying capability of various PAG oil formulations as determined by the load at which scuffing takes place. Scuffing is defined by the sudden jump in friction coefficient. During this test, a stationary block of 10.15 mm (wide) and 15.93 mm (long)  $\times$  6.3 mm (high) made of SAE 01 tool steel (hardness, R<sub>C</sub> = 58–63; surface roughness, 4–8  $\mu$ m rms) is loaded against a ring of 35 mm diameter  $\times$  8.75 mm wide made of SAE 4620 steel (hardness, R<sub>C</sub> = 58–63; surface roughness, 6–12  $\mu$ m rms) rotating at 1,000 rpm while partially immersed in the oil. The load is progressively increased in steps resulting in increasing oil temperature as shown in Fig. 1. These test conditions represent a boundary lubrication regime.

# Mini-traction machine

This machine is used to evaluate friction performance under rolling/sliding conditions covering all three lubrication regimes: boundary, mixed, and hydrodynamic. The tests were conducted



Figure 1. Typical increase in oil temperature with load in block-on-ring tests.

at 30 N load (initial contact stress of 0.76 GPa), 150% slide/roll ratio, and 40 and  $100^{\circ}$ C oil temperatures. The mean sliding speed ranged from 0.002 to 2.8 m/s. A few tests were also conducted at 50 N load. Three repeats were conducted for each test conditions.

# Surface analysis

To better understand the friction reduction and wear protection capability of PAG oils, the wear tracks on disks from minitraction machine (MTM) tests and high-frequency reciprocating rig tests were examined using auger electron spectroscopy (AES), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and time-of-flight-secondary ion mass spectroscopy (ToF-SIMS).

#### Auger electron spectroscopy

The elemental compositions of the thin films that formed during the tests were measured by AES using a PHI model 680 scanning auger spectrometer. Data were collected using a 10kV, 10-nA electron beam. Areas of interest on the heterogeneous samples were selected by first collecting a secondary electron (SE) image of the wear scar. Selected-area analyses were then performed on regions that showed contrast differences in the SE images. Sputter depth profiling with a 2-kV argon ion sputter gun was employed to characterize the thin film and to examine subsurface regions. Sputter depth was calibrated using a 200-nm-thick SiO<sub>2</sub> standard film. Sputter rates of tribofilms and surface oxides likely differ from the rate of this standard so depths are best employed for relative comparisons and not accurate absolute thickness values.

#### Time-of-flight-secondary ion mass spectroscopy

ToF-SIMS was performed using a PHI model TRIFT IV spectrometer. Samples were probed using a 30-kV Au+ ion beam. Spectra were acquired without using any charge neutralization procedures. Both positive and negative ion spectra were obtained from each specimen and regions both inside and outside the wear scar were examined. The analysis region for each acquisition was 100  $\mu$ m  $\times$  100  $\mu$ m. Data acquisition times were limited to 5 min to ensure that the surface composition was not disturbed by the ion bombardment process (static SIMS conditions).

#### Table 1. Lubricants considered for investigation.

Base Oil Description	CODE	HTHS @150 C	KV 100°C	KV 40°C	VI	Ash wt%	Noack <sup>3</sup>
		сР <sup>1</sup>	cSt	cSt			wt%
Alcohol 1 initiated copolymer of ethylene oxide and propylene oxide – Capped (EO+PO)	C-EOPO-A1-B-2.7	2.7	5.6	20.3	239	<0.01	
	C-EOPO-A1-F1-2.8	2.8	5.6	22.5	233	<0.01	10.1
Alcohol 1 initiated homopolymer of propylene oxide (PO) - Capped	C-PO-A1-B-2.3	2.3	5.2	19.4	223		7.4
	C-PO-A1-B-2.6	2.6	6	23.3	223		
	C-PO-A1-F1-2.7	2.7	6.1	25.01	204	<0.01	
Alcohol 2 initiated homopolymer of propylene oxide (PO) - Capped	С-РО-А2-В-2.6	2.6	6	23.4	224		
Alcohol 1 initiated homopolymer of propylene oxide (PO) - mono functional PAG	UC-PO-A1-B-3.6	3.6	8.5	42.2	186		
	UC-PO-A1-F1-3.6	3.6	8.8	46.6	171		3.9
	UC-PO-A1-F1-2.6	2.6	6	29.1	155	<0.01	
	UC-PO-A1-F2-2.6	2.6	6.3	31.3	156		
Alcohol 2 initiated copolymer of propylene oxide and butylene oxide - mono (PO+BO) functional PAG	UC-POBO-A2-F1-2.6	2.6	6.6	35.6	144	<0.01	
Group II mineral oil	GF-5 SAE 5W-20	2.6	8.6	48	164	1.0	13
	Mineral base oil		5.6				

# X-ray photoelectron spectroscopy

Elemental composition and chemical state information were determined by XPS using a Kratos AXIS 165 Electron Spectrometer manufactured by Kratos Analytical (Manchester, England). The base pressure of the spectrometer was  $2 \times 10^{-9}$  torr. Photoelectrons were generated using a monochromatic Al-Ka (1,486.6 eV) source operated at 12 kV, 20 mA (240 W), and collected using hybrid mode magnification. The majority of the signal is collected from the top 10 nm of material. A pass energy of 20 eV was used for high-resolution spectra, and a pass energy of 80 eV was used for survey spectra. All spectra were acquired using charge neutralization with an electron flood source. Binding energies were referenced to the aliphatic C 1 s line at 284.6 eV.

#### Raman spectroscopy

Posttest characterization of the rubbing surfaces and wear debris particles was carried out with a Renishaw inVia Confocal Raman Microscope using a laser light ( $\lambda = 514$  nm).

# Lubricants

The lubricants considered for this investigation are described in Table 1 along with some of the physical property data. Various types of PAGs were evaluated to determine the impact of



Figure 2. General chemical structure of PAG.

structure on the tribological properties. The general structures of the PAGs studied are depicted in Fig. 2. The five different chemistries were created by varying the starting alcohol, R1; the oxide monomers, R2 and R3 being either -H if ethylene oxide,  $-CH_3$  if propylene oxide, or  $-C_2H_5$  if butylene oxide and R2 the same as R3 if a homopolymer or R2 different from R3 if a random copolymer and changing the end group R4. If R4 is an alkyl group, the PAG is capped or alternatively called a diether. If R4 is hydrogen, the PAG is a monofunctional PAG or simply referred to as a PAG. The five different polymers investigated are capped random copolymer of ethylene oxide and propylene oxide with alcohol 1; capped homopolymer of propylene oxide and alcohol 2; homopolymer of propylene oxide with alcohol 1; and copolymer of propylene oxide and butylene



Figure 3. Viscosity-temperature relationship for various oils tested.



Figure 4. Coefficient of friction and wear results obtained from pin-on-disk tests (load, 10 N; sliding speed, 0.1 m/s; sliding distance, 300 m).

oxide with alcohol 2. The viscosity of the polymer is determined by the molecular weight, which in turn is determined by the number of moles of oxide added to the starting alcohol (m and n in Fig. 2). It is therefore possible to create a series of chemically similar polymers with different high-temperaturehigh-shear viscosities by varying m and n. Blending chemically similar polymers with different viscosities will make fluids with viscosities between the two starting polymers. All fluids except UC-PO-A1-F2-2.6 were formulated with a proprietary additive package (Meertens, et al. (8); Thoen, et al. (9)) that was designed to be low sulphated ash, phosphorous and sulfur and low ash and to have an inherently high viscosity index. None of the fluids studied contained a viscosity index improver or an overbased detergent. In addition to the proprietary additive package, UC-PO-A1-F2-2.6 included ZDDP for improved antiwear properties and a molybdenum-based friction modifier.

The performance of various PAG oils was compared against GF-5 SAE 5W-20 oil and a group II base oil used in GF-5 SAE 5W-20 formulation. The base oil contained a viscosity index improver to match its 100°C kinematic viscosity with PAG base oil C-EOPO-A1-B-2.7. The viscosity-temperature relationship of various oils is shown in Fig. 3.

# **Results and discussion**

Figure 4 shows the combined friction and wear behaviors of PAG oils in comparison to GF-5 SAE 5W-20 oil in pin-on-disk tests at

80°C. The variation in coefficient of friction and wear volume measurements is less than 10%. Among the many PAG oils tested, UC-PO-A1-F1-3.6 gave the lowest wear volume but UC-PO-A1-F2-2.6 was the best in terms of both friction and wear performance. All five PAG base stocks (C-EOPO-A1-B-2.7, C-PO-A1-B-2.3, UC-PO-A1-B-3.6, C-PO-A1-B-2.6, and C-PO-A2-B-2.6) showed lower coefficients of friction than that of the mineral base oil. Figure 5 shows the wear scar diameters of balls tested in PAG oils UC-PO-A1-B-3.6 and UC-PO-A1-F2-2.6 (both oils have the same base oil chemistry), showing the effectiveness of an additive package in UC-PO-A1-F2-2.6 in reducing wear.

Figure 6 shows the friction and wear performance of various PAG oils at 80°C using a high-frequency reciprocating rig (HFRR). The wear protection capability of most of the formulated PAG oils was worse than that of GF-5 SAE 5W-20 oil, although some of the PAG base oils (C-EOPO-A1-B-2.7, C-PO-A1-B-2.3, and UC-PO-A1-B-3.6) were better than the mineral base oil. These PAG base oils also showed significantly lower coefficients of friction than the mineral base oil. Some of the formulated PAG oils (UC-PO-A1-F1-3.6, UC-PO-A1-F2-2.6, and C-EOPO-A1-F1-2.8) exhibited significantly lower coefficients of friction than GF-5 SAE 5W-20 oil. PAG oil UC-PO-A1-F2-2.6 showed the lowest coefficient of friction while showing wear protection capability comparable to that of GF-5 SAE 5W-20 oil. It is interesting to note that the ranking of oils in this test is different from that observed with pin-on-disk tests, possibly due to the use of different contact geometry.

Figure 7a shows the increase in temperature with successive loading and Fig. 7b summarizes the load-carrying capability of various PAG formulations, GF-5 SAE 5W-20, and the mineral base oils. The temperature of oils and the coefficient of friction increased gradually with increasing load and then at some critical load (defined as scuffing load), the coefficient of friction jumped significantly. The additive package increased the scuffing load of PAG oil C-PO-A1-B-2.3 from 500 N to about 700 N (C-PO-A1-F1-2.4). Similarly, the scuffing load of mineral base oil increased from 600 to 1,425 N when fully formulated. All but one PAG oil exhibited lower scuffing resistance than GF-5 SAE 5W-20 oil. PAG oils UC-PO-A1-F2-2.6 and UC-PO-A1-F1-2.6 have similar base oil chemistry but PAG oil UC-PO-A1-F2-2.6 contained an additional antiwear additive for improved wear protection capability. The results showed that the additional antiwear additive significantly increased the



Figure 5. Wear scar diameter of (a) PAG base oil UC-PO-A1-B-3.6 and (b) formulated PAG oil UC-PO-A1-F2-2.6 at 80°C oil temperature.



Figure 6. Friction and wear of PAG oils in comparison to GF-5 SAE 5W-20 oil using the HFRR (load, 325 N; reciprocating frequency, 5 Hz; stroke length, 6 mm).

scuffing load to 1,880 N, exceeding that of the GF-5 SAE 5W-20 oil.

Figure 8 shows the Stribeck curve behavior of various PAG oil formulations in comparison to GF-5 SAE 5W-20 oil. The GF-5 SAE 5W-20 oil showed a stable boundary friction coefficient before rapidly decreasing to a lower value when the lubrication regime became mixed. All PAG oils showed higher boundary friction coefficients than GF-5 SAE 5W-20 oil but lower friction coefficients in the mixed



Figure 8. Stribeck characteristics of PAG oil formulations in comparison to GF-5 SAE 5W-20 oil.

lubrication regime. PAG oil UC-PO-A1-F1-3.6 showed the lowest friction coefficient for the speed ranges investigated.

Figure 9 shows traction coefficients of various PAG oil formulations as a function of mean sliding speed with oil temperatures at 40 and 100°C and compared to GF-5 SAE 5W-20 oil and the mineral base oil. At 40°C, PAG oils UC-PO-A1-F2-2.6 and C-PO-A1-F1-2.7 showed higher traction coefficients than GF-5 SAE 5W-20 oil. All other PAG oils showed lower traction coefficients, including PAG oil (C-EOPO-A1-B-2.7) without any additive. However, at 100°C, all PAG oils showed significantly lower traction coefficients than GF-5 SAE 5W-20 oil.



Figure 7. Scuffing load of various formulations (ring rotation, 1,000 rpm).



Figure 9. Traction coefficient as a function of mean speed: (a)  $40^{\circ}$ C oil temperature and (b)  $100^{\circ}$ C oil temperature (load, 30 N; 150% slide-roll ratio).



Figure 10. Friction and wear performance of base PAG oil C-EOPO-A1-B-2.7 and mineral base oil.

One could possibly argue that the lower friction/traction behavior of PAG oils could be related to their elastohydrodynamic film thickness. Elastohydrodynamic film thickness was not directly measured, but pressure viscosity coefficients were measured at different temperatures for PAG oil C-PO-A1-F1-2.4 (which has the same base oil chemistry as C-PO-A1-F1-2.7 but with 2.4 mPa.s high-temperature-high-shear viscosity at 150 °C) and SAE 5W-30 oil, which are 9.1 and 10.8 GPa<sup>-1</sup>, respectively, at 100°C. Although there are no measured data for SAE 5W-20, a similar value for SAE 5W-30 can be assumed because the pressure-viscosity coefficient primarily depends on base oil chemistry, which is not very different for SAE 5W-20 and SAE 5W-30. The Dowson-Higginson equation for minimum film thickness calculation showed that PAG oil C-PO-A1-F1-2.4 will have an approximately 26% reduced minimum oil film thickness compared to SAE 5W-20. This means that the contact will experience more asperity contact or be pushed to the left side of the Stribeck curve, resulting in higher friction. However, measured data showed lower friction for PAG oils, emphasizing that PAG oil chemistry is important.

# Surface characterization

In order to better understand the friction reduction mechanism of PAG oils, the wear surfaces of flats from HFRR tests and disks from MTM tests were examined using AES, XPS, ToF-SIMS, and Raman spectroscopy. Wear surfaces generated with PAG base oil, PAG formulated oils, mineral base oil, and GF-5 SAE 5W-20 oil were examined.

#### HFRR flats—Base oils

Figure 10 shows the coefficient of friction as a function of time for PAG base oil C-EOPO-A1-B-2.7 and mineral base oil at 80°C oil temperature. Although PAG base oil C-EOPO-A1-B-2.7 showed an initial lower coefficient of friction than mineral base oil, at the end of the test both oils showed essentially the same coefficient of friction. The wear scar size on the pin was slightly smaller with PAG base oil C-EOPO-A1-B-2.7 compared to mineral base oil. Figure 11 shows the Raman spectra of the surfaces tested with the above-mentioned fluids. Several peaks can be observed in the region where iron oxides typically reside. The type of iron oxide was found to be  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. The Raman spectra of surfaces tested in C-EOPO-A1-B-2.7 were essentially similar, suggesting that regardless of base oil type, in the absence of chemical additives, the rubbing surfaces suffer tribooxidation.

#### MTM disks—base oils

MTM disks following tests at 50N load, 100°C oil temperature, and 150% slide-roll ratio were examined using AES, XPS, and ToF-SIMS to better understand the friction reduction mechanism of PAG oil. ToF-SIMS provides molecular fragment (chemistry) information of the materials that are in the top 1-



Figure 11. Raman spectroscopy of the wear surface generated with mineral base oil and C-EOPO-A1-B-2.7. Iron oxide reference is presented to show the Raman peaks corresponding to  $Fe_2O_3$ .

nm layer, whereas AES provides a measure of the elemental composition from the top 100-nm layer. The wear surface from mineral base oil shows the presence of a patchy film as shown in Fig. 12a. The auger spectrum (Fig. 12b) from one of the patchy regions show an 80-nm-thick oxide film. This suggests that metal-to-metal contact occurred, with the resulting heat generating oxide growth. The mineral oil in the absence of additives was not able to protect the metal from oxidation. In contrast, the wear surface from a PAG base oil shows the absence of any patchy film (Fig. 12c) and the auger spectrum in Fig. 12d showed a thin oxide film on the wear surface. A similar results, suggesting that the presence of a thin oxide film is naturally occurring and not formed due to sliding/rolling action at the contact.

X-ray photoelectron spectra in Fig. 13a show the presence of iron oxide on the disk surface in contact with both mineral base oil and PAG oil C-EOPO-A1-B-2.7. Figure 13b shows the chemical state of carbon, indicating the presence of aliphatic carbon with mineral base oil, whereas PAG oils showed the distinct presence of an additional peak due to ether/alcohol (corresponding to C-EOPO-A1-F1-2.7). The presence of ether/ alcohol is indicative of adsorbed PAG base oil in the wear scar because the oil backbone contains significant amounts of ether.

Figure 14 shows time-of-flight-secondary ion mass spectra obtained from wear surfaces of mineral base oil and PAG base oil UC-PO-A1-B-3.6. The spectrum of the mineral base oil (Fig. 14a) is dominated by the classic hydrocarbon fragmentation pattern as expected from a mineral oil-based lubricant.

The spectrum shows a pattern of peaks that are 14 amu apart, which is the mass of a  $CH_2$  hydrocarbon fragment, the basic building block of a hydrocarbon molecule. In contrast, the PAG base oil spectrum (Fig. 14b) is significantly different. The spectrum shows a pattern of peaks that are 58 amu apart, which is the mass of a single propylene oxide monomer. Both XPS and ToF-SIMS results indicate that a thin film of the respective base oil has formed on the rubbing surface. This spectrum is present both inside and outside of the contact area, so the formation of this film is indicative of adsorption and is not dependent on rubbing contact.

### MTM disks—formulated PAG oils

Following the tests, the disks were examined using SEM, AES, and ToF-SIMS to obtain a better understanding of the tribofilm composition. Figure 15a shows an SEM micrograph of the wear surface with GF-5 SAE 5W-20 oil. The mottled surface texture is typical of a sample tested in fully formulated oil and indicates the presence of a tribofilm that is quite uniformly distributed across the wear surface. The auger data in Fig. 15b show the depth profile of elements present in the tribofilm. The spectra show a strong presence of calcium, primarily from the detergent additive in the oil. The P and S peaks are generally representative of phosphate and sulfide in the tribofilm, but the peak intensities are quite low because these compounds decompose under the electron beam in this technique. A similar spectrum from outside the wear region shows the absence of calcium, phosphorous, and sulfur and confirms that rubbing action is



Figure 12. (a) SEM micrograph of the wear surface from mineral base oil showing patchy films, (b) auger spectrum from a patchy film in (a), (c) SEM micrograph of the wear surface from PAG oil C-EOPO-A1-B-2.7, and (d) auger spectrum from the wear surface in (c).



Figure 13. X-ray photoelectron spectroscopy of the wear surfaces generated with mineral base oil and PAG base oil C-EOPO-A1-B-2.7 showing the chemical state of (a) iron and (b) carbon.

necessary to form these films. In contrast, the SEM image (Fig. 15c) of the wear surface using PAG oil UC-PO-A1-F1-2.6 appears quite featureless except for a few scratch marks. The auger depth profile (Fig. 15d) shows a strong presence of oxygen on the top 6-nm layer. This formulation did not contain any ZDDP antiwear additive and therefore no P and S peaks are expected. However, there was a substantial amount of potassium and sodium in the top 1-nm layer, the source of which is unknown. Spectra obtained from outside the wear region looked similar except for a thinner (iron) oxide film and slightly less carbon (from PAG), suggesting that sliding/rolling action at the contact region enhanced oxide film thickness and PAG molecules are adsorbed on the steel surface. The SEM image (Fig. 15e) of the wear surface using PAG oil UC-POBO-A1-F2-2.6 shows a few scratch marks, similar to the one observed with PAG oil UC-PO-A2-F1-2.6. The auger depth profile (Fig. 15f) from the wear surface using PAG oil UC-PO-A1-F2-2.6 appears similar to that observed with PAG oil UC-POBO-A2-F1-2.6 with the exception of potassium.

This PAG oil contained ZDDP antiwear additive, although only trace amounts of phosphorous and/or sulfur could be observed. This could be due to decomposition of the tribofilm by the electron beam. Data obtained from outside the wear region looked similar.

Figures 16a and 16b show XPS data indicating the presence of phosphate and sulfate on the wear surfaces generated with GF-5 SAE 5W-20 and PAG UC-PO-A1-F2-2.6 oils. Figure 16c indicates the chemical state of carbon as aliphatic carbon with GF-5 SAE 5W-20 oil, whereas PAG oil UC-PO-A1-F2-2.6 and PAG oil UC-PO-A1-F1-2.6 show the distinct presence of ether/ alcohol. This is similar to that found with the base oils.

Figure 17 shows the negative ion spectra of wear surfaces generated with GF-5 SAE 5W-20 and UC-PO-A1-F2-2.6 oils. The spectrum of the GF-5 SAE 5W-20 oil (Fig. 17a) shows a pattern of peaks that are 28 amu apart, which is the mass of two CH<sub>2</sub> hydrocarbon fragments. In contrast, the PAG base oil spectrum (Fig. 17b) is significantly different. The spectrum shows a pattern of peaks that are 58 amu apart, which is the mass of a single propylene oxide monomer. Again, this is



Figure 14. Time-of-flight-negative ion (positive) mass spectra from wear surfaces of (a) mineral and (b) PAG oil UC-PO-A1-B-3.6 base oils.



Figure 15. SEM micrograph of the wear surface with (a) GF-5 SAE 5W-20 oil, (c) PAG oil UC-POBO-A2-F1-2.6, (e) PAG oil UC-PO-A1-F2-2.6, and corresponding auger spectra in (b), (d), and (f), respectively.

strong evidence that the base oil fluids are adsorbing onto the metal surface. In addition, Fig. 17b shows a strong presence of molybdenum oxide fragments from the friction modifier.

The findings from the surface analysis can be summarized as follows. Wear surfaces generated with base oil only contained an oxide film and either adsorbed aliphatic hydrocarbon molecules from the hydrocarbon oil or ether/ alcohol fragments from PAG molecules. When tested with formulated oils, the wear surfaces contained tribofilms containing pyrophosphates from the GF-5 oil or molybdenum oxide and pyrophosphate fragments from the friction modifier in the PAG oils in addition to PAG molecules.

It is not surprising to observe PAG molecules on the surface because of their polar nature. Past research (Hardy and Doubleday (10); Levine and Zisman (11)) has shown that oils with polar end groups such as carboxyl, ester, amine, etc., decreased the friction coefficient, and it was hypothesized that the mechanism of friction reduction was due to adsorption of polar end groups on the metal surface. More recently, Tohyama, et al. (12) provided direct evidence of the adsorption of a polar ester structure found in a polyme-thacrylate, a viscosity index improver on the wear surfaces observed using ToF-SIMS, leading to the conclusion that the adsorbed species reduced the friction coefficient. Murase and Ohmuri (13) and Kano, et al. (14) also showed similar evidence of adsorption of a glycerol monoleate friction modifier on the wear surface. In the present investigation, the presence of PAG molecules at the contact surface contributes to the observed friction reduction.

# Conclusions

The present investigation explored the friction and wear performance of several PAG oils (both base oils and formulated) with different chemistries using laboratory bench test rigs compared



Figure 16. X-ray photoelectron spectroscopy showing the chemical state of (a) phosphorous, (b) sulfur, and (c) carbon on the wear surfaces.



Figure 17. ToF-SIMS results of the wear surfaces from (a) GF-5 SAE 5W-20 and (b) PAG UC-PO-A1-F2-2.6 oil.

to GF-5 SAE 5W-20 and its mineral base oil. The following conclusions can be drawn from this investigation:

- PAG base oils showed lower friction/traction coefficients than mineral base oil at the same viscosity level.
- Formulated PAG oil UC-PO-A1-F2-2.6 showed the lowest friction coefficient, though wear was comparable to that with GF-5 SAE 5W-20 oil.
- Formulated PAG oil UC-PO-A1-F2-2.6 showed the best load-carrying capability.
- Analysis of disk wear surfaces generated with base oils under rolling/sliding conditions showed the formation of
  - thick iron oxide film and hydrocarbon fragments with mineral base oil.
  - thin iron oxide film and adsorption of PAG base molecules primarily of propylene oxide molecules with PAG base oil.
- Analysis of disk wear surfaces generated with formulated oils under rolling/sliding conditions showed the formation of
  - tribofilm consisting of pyrophosphate, sulfate (possibly calcium), and hydrocarbon fragments with GF-5 SAE 5W-20 oil.
  - tribofilm consisting of pyrophosphate, sulfate (possibly calcium), and molybdenum oxide fragments along with direct evidence of adsorbed PAG molecules with PAGformulated oils.
- The presence of polar PAG molecules on the surface is believed to be the mechanism responsible for the lower friction.

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