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TRIBOLOGICAL PERFORMANCE OF PAG FLUIDS AND LUBRICANTS[1]

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Abstract
Emerging demanding tribo systems and new fluid introductions has put a pressure on lubricant formulators to study tribological characteristics of fluids for proper applications in these systems. The focus of this paper is to evaluate polar, non varnishing polyalkylene glycols chemistry and their tribological characteristics useful for high temperature, high pressure turbo machinery applications. Friction and wear characteristics of PAG's are determined and compared with hydrocarbon oils for efficient operation of heavy duty gas turbines and steel plants machinery. The most common PAGs are water soluble and water insoluble types. However, recently new oil tolerant and oil soluble PAG's have been introduced to fill the gap in PAG chemistry. The approach of this paper is to subject PAG's and PAG based synthetic lubricants to MTM rig, Four ball wear, SRV and vane pump test to explore their low coefficient of friction and wear rates. On the basis of these tribological characteristics, PAG lubricants were recommended in three different tribo systems wherein hydrocarbon based lubricants have not met performance specifications. These systems involved heavy duty gas turbine, steel plant machinery and environmentally sensitive tunnel boring operations. Theses trials clearly demonstrate and confirm advantage of using PAG based lubricants in meeting tribological demands of these systems.
Key words: Non-varnishing; Poly alkylene glycol; Traction coefficient; Tunnel boring.

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1 INTRODUCTION

PAG's are unique in that they represent a class of lubricants that not only pass the stringent environmental tests; they also provide the end-user with unmatched long-term performance. For over 50 years PAG's have been solving problems that hydrocarbon lubricants cannot.

PAG's can be chemically designed to meet an extensive range of performance needs. No other base oil chemistry has such versatility. Generally speaking, a PAG (also known as a polyglycol, a polyol, and a polyether) is prepared by reacting an initiator with one or more alkylene oxides under alkaline conditions and elevated temperatures. Within this reaction, there are four variables: the initiator, the oxides, and the way the oxides are reacted on to the initiator (i.e. random or block additions), and the molecule weight. This gives PAG chemistry its versatility, which makes it possible to create tailor-made products that meet desired requirements.(1)

The *initiator* gives the PAG its 'chemical functionality', and influences the physical properties of the resulting product, for example imparting hydrophobicity to the polymer. Most initiators are alcohols such as butanol, mono-propylene glycol or glycerine. Oxides are then grafted on to their labile hydrogens to produce linear or branched structures depending on the functionality of the initiator. The choice of *oxides* will influence the hydrophilic/hydrophobic character of the resulting PAG. The most commonly use oxides include ethylene oxide, propylene oxide and butylene oxide. A high content of ethylene oxide will normally result in fully water-soluble products, while a high content of butylenes oxide will provide oil solubility. By combining the oxides, the solubility behavior of the products can be adjusted.

Molecular weight of the PAG will affect the viscosity of the product. With PAG chemistry, almost the complete ISO VG viscosity range can be covered.
Structure 1 below represents PAG in general:

$$RO\text{-}[CH_2CH_2O]_m\text{-}[CH_2CH(CH_3)O]_n\text{-}H \text{ ……….. Structure 1}$$

Where R= H, alkyl, aryl etc

When n is 1.0 the PAG polymer is typically water insoluble. When m is 0, then the PAG polymer is freely water-soluble. Varying levels of water solubility can be obtained by controlling the ratio of m/n. PAGs can be engineered to be low or high molecular weight and therefore can be tailored to have a low or high viscosity. Low temperature properties can be controlled by careful selection of the "R" group. Thus if R is branched lower pour points are often achieved for the same m/n ratio. Other properties such as heats of combustion, fire resistance, friction control and biodegradability can all be controlled in a similar fashion. It is this chemical versatility which can control many functional properties and this gives PAGs more design options than any other major base oil used in the industry today.(2)

1.1 Important Properties of Polyglycols

Viscosity With PAG chemistry, a broad range of the ISO VG viscosity classes can be covered. Typical standard grades range from ISO 10 to ISO 1000. As indicated

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above, the viscosity of a polyglycol depends mainly on the molecular weight: the viscosity will in general, increase with increasing molecular weight.

Viscosity Index When compared with other base fluids, PAG's show, in general, very high viscosity indexes. VI values up to 400 can be reached.

Solubility As mentioned above, it is possible to create polyglycols with solubility properties ranging from complete water solubility to complete oil solubility.

Lubricity Polyglycols show excellent lubrication properties, due to the high affinity of the oxygen atoms in the polymer with the metal surface. This feature also provides mild extreme pressure properties. Typical lubrication performance data for commercially available PAG fluids can be found in Figure 7.

Thermal stability Polyglycols demonstrate a very good response to anti-oxidants, and can therefore be formulated for high-temperature applications (that is up to about 250°C). Other base stocks, such as vegetable oils, some synthetic esters, mineral oils and PAO's, do not offer good enough thermal stability in this temperature range.

Low residue Polyglycols show superior deposit control characteristics over all other base oil classes. Oxidation of polyglycols results in a partial breakdown of the product into volatile components and polar compounds soluble in the base fluid, resulting in low formation of residue. In the case of most other base stocks, oxidation normally leads to polymerization, which produces high molecular weight polar by-products which are insoluble in their parent base oil leading to significant residues, which can be an important disadvantage in certain applications. Figure 1 provides an explanation of the oxidation process for polyglycols and mineral oils.

Thermal conductivity In general, PAG's offer better thermal conductivity than mineral oils. This means that better cooling characteristics can be achieved with PAG's, and as a result, a smaller heat exchanger can be used.

Hydrolytic stability Polyglycols do not hydrolyze, which can be seen as a major advantage over natural esters (vegetable oils) and synthetic esters. A further unique feature is their ability to absorb water that contaminates the lubricant through ingress. When this occurs in the equipment the PAG can act as a polymeric sponge which renders the water inert.[3,4]

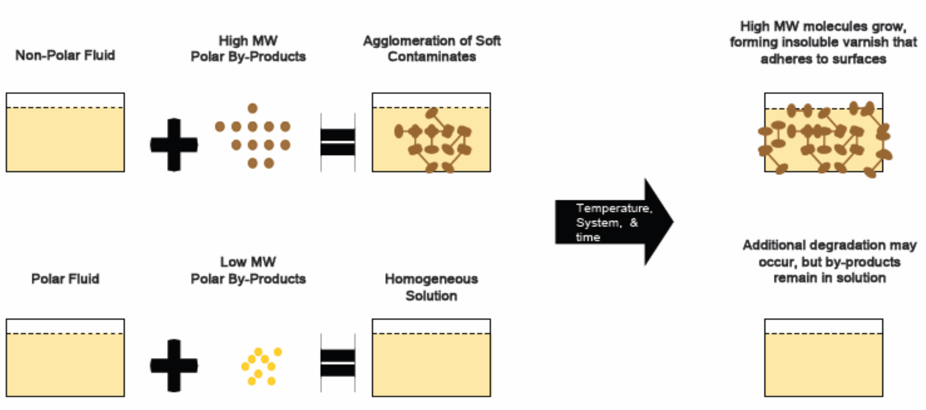

Figure 1. Oxidation Process Comparison PAG vs. Hydrocarbons

With this background of basic PAG chemistry these molecules were subjected to various tribological tests. Their excellent tribo properties were again checked in fully formulated anti-wear hydraulic oils, fire resistance water glycols and non varnishing

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turbo fluids used in steel, power and compressor industries. Next session describes the test methodology used in this paper.

2 MATERIALS AND METHODS

2.1 Tribology Measurements

Several bench tests can be thought of to investigate the frictional properties of base fluids and formulated products. One of the recently developed methods is a MINI TRACTION MACHINE (MTM) from PCS Instruments. This machine measures Traction curves which provide useful information on the friction (traction) performance of fluids under different temperatures, pressures and operating slide/roll ratios. The MTM rig is capable of measuring either constant or varying slide/roll ratios if required. Standard specimens are a 19.05-mm-diameter ball as upper specimen and a 50 mm diameter disk as lower specimen. Both are manufactured from AISI 52100 bearing steel. The standard disk is smooth, which allows measurement of mixed film and full film friction. Alternatively, rough disks are available for measurements in the boundary lubrication regime. The type of specimen contact is shown in Figure 2.

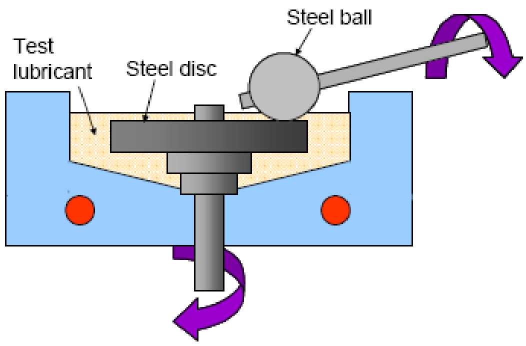

Figure 2. Mixed rolling-sliding contact
Courtesy: Hugh Spikes; Imperial College London, SAE Powertrain 2005

2.2 Four Ball Wear Test

The Four Ball Wear Test determines the wear protection properties of a lubricant. Three metal balls are clamped together and covered with the test lubricant, while a rotating fourth ball is pressed against them in sliding contact. This contact typically produces a wear scar, which is measured and recorded. Its self-aligning nature and ready availability of inexpensive high quality test specimens make it ideally suited to being an accurate and repeatable screening test. The most widely used wear test method for this apparatus is ASTM D 4172 for lubricants.[5] Four Ball configurations is shown in Figure 3.

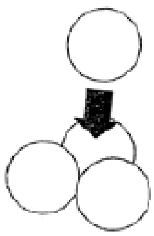

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Figure 3. Four Ball Principle

2.3 Measurement of Dynamic Friction Coefficients by SRV

Dynamic friction coefficients were measured using an SRV friction testing apparatus. Principal of the SRV experiment: A steel ball oscillates on a steel plate on which three drops of the product are deposited and a load is applied on the ball perpendicularly to the plate. The resistant force against the oscillated movement of the ball is then measured during a definite time. The friction coefficient is then calculated and is defined as the resistance force over the applied force. In the experiment, several parameters can be set:

The frequency of the oscillation (Hz)

- The load applied on the ball (N)
- The distance of oscillation (mm)
- The temperature of the plate (°C)
- The test duration (minute)

In the experiments reported here a load of 200N was applied, with a frequency of 50 Hz, stroke length of 1mm and test duration of 60 minutes. In these experiments the temperature of the plate is the only parameter varied which is 30°C.

2.4 Eaton (Vickers) Vane Hydraulic Pump Testing - ASTM D-7043 (modified)

Internal wear performance testing was conducted in our lab using hydraulic pump stand number 2. Each hydraulic pump experiment was conducted at 65°C for 100 hours using a speed of 1200rpm and a reservoir capacity of 1 gallon. The weight loss of the vanes and the ring (cam) are recorded and reported as total weight loss. In addition the condition of the fluid before and after each experiment was recorded using analytical techniques.

3 RESULTS AND DISCUSSIONS

Figure 4 shows that PAG polymerization technology produces a broad molecular weight distribution suitable for various industrial equipment applications. Typical viscometric and friction data for these fluids are described in Table 1. From this table it is obvious that base neat PAGs have higher VI, low pour and excellent EP and wear characteristics as shown by FZG, four ball and SRV tests.

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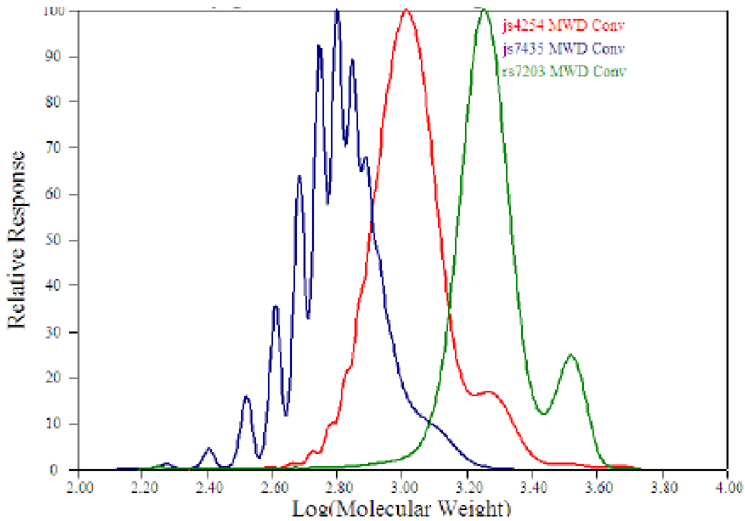

Figure 4. GPC - Molecular Weight Distribution

Table 1. Viscometric & Friction data

ASTM/DIN Test	Test	PB60	PB185	PB 680
D 445	Viscosity 40 °C, cst	58	186	669
	Viscosity 100 °C, cst	9.3	25	76
D 2270	Viscosity Index	143	165	194
D 92	Flash Point COC, °C	232	238	243
D 97	Pour Point, °C	-42	-33	-30
D 2266	4- Ball Wear, Scar, mm	0.54	0.54	0.55
51834	SRV, 200N,50HZ, 30 °C	0.13	0.13	0.14
51354	FZG, Damage Load Stage	-	10	12

Figures 5 and 6 show MTM traction curves of different PAG molecules compared to hydrocarbon oils and shows how traction coefficient of polyalpha olefins is improved by PAG molecule. Figure V clearly demonstrates that EO/PO based PAGs give 75% less friction compared to mineral oil under chosen test parameters. Besides Figure 6 also indicates that PAG can stabilize the systems overall friction properties even at a low dosage of 10% in PAO blend.

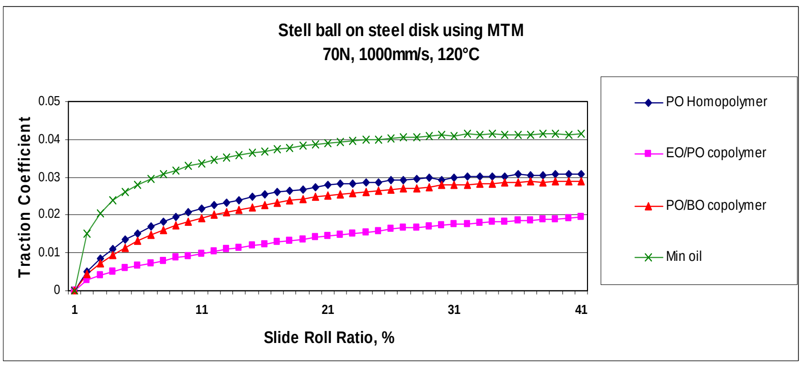

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Figure 5. Traction Curves of pure PAGs vs. HC oil

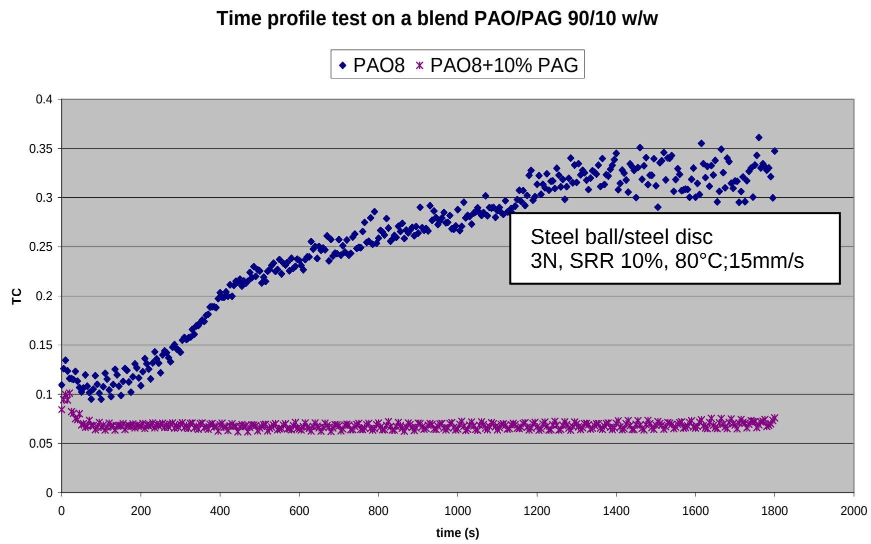

Figure 6. Upgrading HC oils friction performance with PAGs

3.1 Field Performance of Formulated PAG Lubricants

Three Fluids: HFC, HFDU and turbo bearing oil were formulated and evaluated against commercial fluids. Reserve alkalinity method [6] is used. Tables 2, 3 and 4 show viscometric and tribological test data of these fluids:

Table 2. Typical Properties of New Water Glycol Hydraulic Fluid

Property	Method	Typical Result
Kinematic viscosity, mm^2/sec	ASTM D445	46
Viscosity Index	ASTM D2270	195
Pour point, ^{o}C	ASTM D97	-50
Reserve alkalinity, g/ml	Dow Method	175
Specific gravity, g/ml	ASTM D1298	1.09
Foam sequence I, II and III	ASTM D892	10/0, 10/0, 10/0
Air release, minutes	DIN 51381	13
Biodegradability, %	OECD 301F	>80
Vickers V-104 Vane Pump Test, 100 hours at 2000psi and $65^{o}C$, total cam and vane weight loss in mg	ASTM D7043	8

Table 3. Typical properties of anhydrous fire resistant hydraulic fluid

Property	Method	Results
Viscosity at $40^{o}C$, mm^2/s	ASTM D445	46
Viscosity Index	ASTM D2270	200
Pour Point, ^{o}C	ASTM D97	-48
Flash Point/Fire Point, ^{o}C	ASTM D92	295/315
Flash Point, ^{o}C	ASTM D92	296
Copper Corrosion,24 hours at $100^{o}C$	ISO-2160	1A
Ferrous Corrosion	ASTM 665A	Pass
FZG Gear Test, stages passed	ASTM D5182	12
Four ball, anti-wear, mm	ASTM D4172	0.80

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Four Ball EP test Load Wear Index Last non-seizure Load, 80kg (scar, mm) Weld load, kg	ASTM D2783	 33.1 0.40 160
Vickers Vane V-104C, total weight loss of ring and vanes, mg	ASTM D7043	3

Table 4. Comparative Properties of Bearing Oils

Typical Physical Properties*	PAG-based Synthetic Turbine Fluid	Typical Petroleum-based Turbine Oil
Viscosity Grade	25	32
Kinematic Viscosity @ 40°C cSt (104°F cP) (ASTM D445)	26.23 (25.84)	32.44 (27.90)
Kinematic Viscosity @ 100°C cSt (212°F cP) (ASTM D445)	5.19 (5.11)	5.56 (4.78)
Viscosity Index (ASTM D2270)	132	109
Specific Gravity (relative density) (ASTM D941)	0.985	.86
Pour Point, °C (°F) (ASTM D97)	-48 (-55)	-30 (-22)
Flash Point, °C (°F), Closed Cup (ASTM D92)	242 (468)	215 (420)
Specific Heat @ 40°C (104°F), joules / g°K (ASTM E1269)	2.017	2.064
Thermal Conductivity @ 40°C (104°F), watts / m°K (PLTL-73)	0.145	0.1

HFC Fluid based on new PAG technology showed many performance improvements versus conventional water glycol hydraulic fluids. One of these was related to shear stability in a vane pump test. The industry standard method for measuring wear performance of water glycol hydraulic fluids is ASTM D7043 (“Standard Test Method for Indicating Wear Characteristics of Petroleum and Non-Petroleum Hydraulic Fluids in a Constant Volume Vane Pump”). The test measures the weight loss of a ring and vanes over a 100 period at an outlet pressure of 2000psi, speed of 1200rpm and fluid temperature of 150F (65°C). A conventional water glycol hydraulic fluid showed a total weight loss of rings and vanes of 25mg and hence a wear rate of 0.25mg/hour. The new technology showed a total weight loss of ring and vane of 8mg and hence a wear rate of 0.08mg/hour. The test was modified to evaluate the condition of the fluid, particularly its shear stability after 500 hours of operation under the same test conditions. Figure 7 shows the results.

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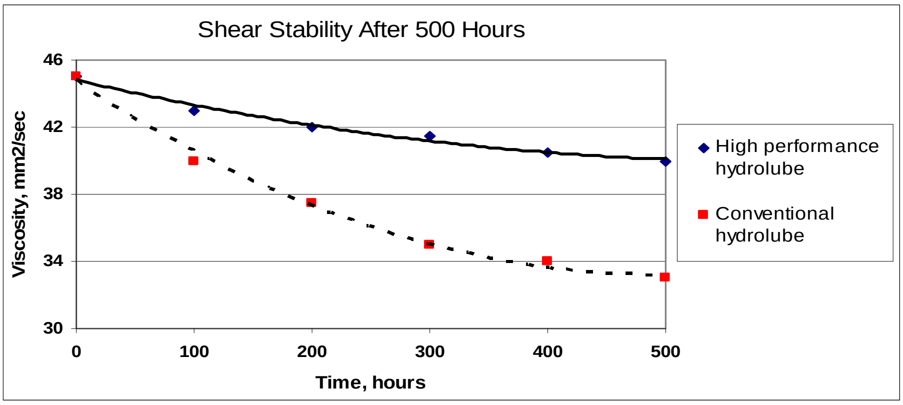

Figure 7. Shear Stability Profile of New Hydraulic fluid – ASTM D 7043

Simplistically the new technology showed much greater stability compared to the conventional water glycol hydraulic fluid over the test duration. The shear loss (viscosity change) after 500 hours for the new technology was much superior. One can observe that after 100 hours, the conventional product showed the same viscosity loss as the new product did after 500 hours. The primary reason for this difference is related to the choice of PAG viscosity builder in the formulation. In the new technology a much more stable product is generated.

The new technology has been evaluated in several equipment trials in vane and piston pumps from many original equipment manufacturers (OEM) including, Rexroth, Eaton, Parker and Hartmann. In these trials outlet pressures were up to 4000 psi and fluid reservoir temperatures ranged from 110-150F. An example of one of the trials is described below.

Equipment used in Trial:

Pump Type	Twin Parker Piston Pump
Sump Size	300 gallons
Filter type and size	3 x 10 micron fibre glass filters

Gravity fed-net positive pressure at inlet-position of reservoir above pump centre line

Outlet pressure	1200psi
Reservoir temperature	115-130F (46-54°C)
Fluid Leakage	Low (<10 gallons per month)

Figure 8 shows the change of viscosity of the fluid over a six month period. Condition monitoring data displayed a number of trends.

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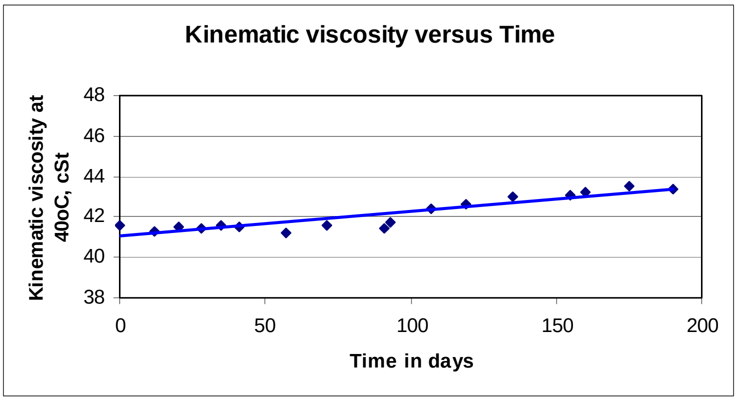

Figure 8. Viscosity Tracking Six Months Period

Firstly, the viscosity showed a gradual increase but remained essentially stable throughout the trial period. The viscosity change was <5%. The pH of the fluid remained unchanged. The total acid number also remained stable and thus demonstrated no loss of anti-wear additive during the test period.

HFDU Novel PAG Anhydrous Fluid:

It is apparent from Table III that novel anhydrous fluid has excellent tribo properties namely four ball passing 12 FZg stages and extremely low wear rate characteristics as shown by Vickers test at 0.03 mg/hour which is shown to sustain high pressure environment in tunnel boring operations. Three trials so far have been done successfully. Tunnel boring machines (TBMs) are used to excavate underground tunnels for utility, transportation, or irrigation require a robust hydraulic fluid capable of withstanding operating pressures in excess of 4500psi and temperatures of >90°C while providing favorable environmental characteristics. A new PAG based synthetic hydraulic fluid was successfully used on a TBM in Wisconsin, USA. Figure IX is a picture of a tunnel boring machine similar to the ones used on these projects.[2,7] Typical operating parameters are as follows:

- Reservoir size: 1,000 – 1,500 gallons (3,785 – 5,678 liters)
- Loop temperature: 165°F (74°C)
- Pump type: Axial piston, variable displacement
- Pump speed: 1,800 RPM
- Pump flow: 10 – 50 GPM (37.85 – 189.25 LPM)
- Pump pressure: 3,500 – 4,500 psi (241 – 310 bar)

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Figure 9. TBM Machine

These high stress applications indicate the superior tribo capability of this fluid.

NON VARNISHING BEARING FLUID

This fluid after three years of operation in heavy duty gas turbine has not formed any varnish because of the polar and non varnish forming properties of PAG fluids. MTM machine data are shown in Figure 10 and four ball wear test is displayed in Table 5. During three years of operations(8) at heavy duty gas turbine this fluid has not formed any varnish and is being used without any servo valve failure.

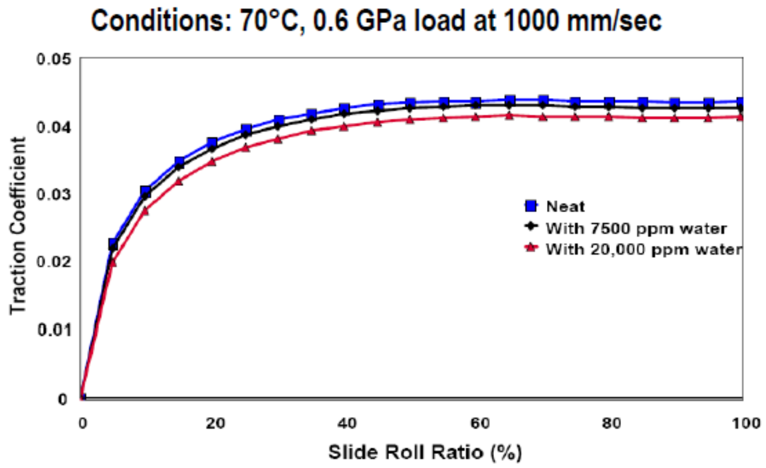

Figure 10. Traction Curves PAG based Bearing Fluid

Table 5. Four Ball Wear of Bearing Fluid in the presence of water

Fluid	Scar Diameter, mm
PAG-based Fluid neat	0.65
PAG-based Fluid + 7500 ppm water	0.67
PAG-based Fluid + 20,000 ppm water	0.66
PAG-based Fluid + 2900 ppm water after 1411 operating hours in GE 7FA Turbine	0.66

4 CONCLUSIONS

Poly alkylene glycols can be designed per the need of tribo system conditions. Poly alkylene glycols base properties like low friction, low wear and no deposit forming properties remain in tact in fully formulated hydraulic fluids and bearing fluids.

Three case studies of turbo machinery provide superior performance of tribological characteristics of these fluids compared to hydrocarbon oils. Viscosity stability, high viscosity index and high thermal conductivity along with biodegradability can be designed by varying proportions of monomers and alcohol initiators.

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