Novel Polyalkylene Glycol-Based Hydraulic Fluids

Polyalkylene glycol-based fluid has been evaluated in several field trials in demanding hydraulic equipment. Lab test data and field performance of this novel hydraulic fluid are discussed, showing improvements in equipment efficiency, reliability and cleanliness.

Most hydraulic equipment in operation today uses hydrocarbon-based lubricants. However, there are some applications and industries where the use of petroleum oils is often unacceptable. These can include industries where fire safety is critical, such as steel and aluminum processing, aerospace and mining. There are also increasing requirements for fluids with better environmental properties, such as in the construction and agriculture industries, where biodegradable and renewable fluids are preferred.[1]

In environments with potential ignition sources, hydrocarbon oils present a serious fire risk, and hence fire-resistant fluids are preferred and sometimes mandated. In industries such as mining, steel processing and aluminum die-casting, hot metal, open flames and sparks are all potential ignition sources. Even small leaks of a hydraulic fluid from a ruptured hose can have catastrophic consequences if fire-resistant fluids are not used. There are many examples of industry incidents where severe equipment damage and even loss of human life has occurred.[2,4]

In the past 60 years, a significant amount of innovation has occurred to develop products that offer improved fire resistance over hydrocarbon-based products. The first products date back to the mid-1940s, when water glycol hydraulic fluids were developed by the U.S. Naval Research Laboratory.[5–6] These synthetic fluids contained water (35–40%) to provide fire resistance, ethylene glycol, a polyalkylene glycol viscosity modifier and an additive package, and today they are still widely used in some industries. Other water-based hydraulic fluids include oil-in-water emulsions and water-in-oil emulsions. These provide superior fire-resistance properties over hydrocarbon oils. One challenge with water-based hydraulic oils is they are much more difficult to maintain[7] and are limited to use in equipment operating under moderate temperatures and pressures. In addition, it is common for hydraulic pumps to be de-rated when using water-based products.

Anhydrous fire-resistant fluids were later developed that were also safer to use than mineral oils but could operate under more severe conditions than high water-containing products. For example, phosphate esters and polyol esters were extensively researched and commercialized. Phosphate esters are still used in the aviation and power generation industries[8] due to their superior fire-resistance properties compared to other common anhydrous fluids used today,[9] but they are typically much more expensive than other chemistries and their popularity is declining because of environmental and cost concerns.

Synthetic esters also offer a higher degree of fire resistance compared to mineral oils and can be used in equipment operating at high pressures and temperatures for extended periods, but they are known to show rapid hydrolysis if contaminated with trace amounts of water.[10]

Synthetic polyalkylene glycols that were initially used as viscosity builders in water glycol hydraulic fluids have, in recent years, found use as the primary base oil in formulated synthetic anhydrous hydraulic fluids.[11] Compared to synthetic esters, the new synthetic PAG hydraulic fluids offer similar fire-resistance properties but are not prone to hydrolysis, rarely form deposits in equipment, and can be used in high-temperature equipment as well as for all-season use. The steel processing industry has adopted anhydrous PAG-based fluids, and today there are more than 15 years of successful service use in demanding equipment. Furthermore, PAG chemistry is highly versatile, and it is easily possible to design polymers and formulations that are tailored to a specific application. For example, it is possible to design PAG products that offer good fire-resistance properties and are readily biodegradable. If leaks into waterways are a concern, PAGs have now been developed that are water-soluble and non-sheening but offer all the benefits described above.

A summary of some of the key benefits of using the different types of fluids for the steel processing industry is given in Table 1. In this table, the fire-resistance classification is provided as defined in ISO-12922.[12] Today, four major groups of fire-resistant fluids are recognized by the International Standards Organization. These are


Authors

Govind Khemchandani (left), senior technical specialist — PAG fluids and lubricants, The Dow Chemical Co., Freeport, Texas (gvkhemchandani@dow.com), and **Martin Greaves** (right), research leader — R & D, Dow Europe GmbH, Horgen, Switzerland (mrgreaves@dow.com)

Table 1

Comparative Properties of Fire-Resistant Hydraulic Fluids

	Mineral oils	Water glycol hydraulic fluids	Water-in-oil emulsions	Oil-in-water emulsions	Phosphate esters	Synthetic esters	Anhydrous PAG
Fire-resistance classification	none	HF-C	HF-B	HF-A	HF-DR	HF-DU	HF-DU
Fire resistance	poor	excellent	excellent	excellent	excellent	good	good
Low-temperature properties	moderate	excellent	moderate	moderate	moderate	excellent	excellent
Oxidation stability	moderate	moderate	moderate	low	excellent	good	excellent
Hydrolytic stability	excellent	excellent	excellent	excellent	poor	poor	excellent
Biodegradability	low	high	low	high	low	high	high
Fluid maintenance costs	low	high	high	high	low	low	low
Cost per liter fluid	moderate	low	moderate	low	very high	high	high

summarized in Table 1 as HFA, HFB, HFC and HFD fluids.

Fire-Resistant Properties and Testing

In the steel industry, the fire-resistance properties of fluids are often a critical requirement. Hydraulic fluids can also have different degrees of fire-resistance properties. However, fire resistance is not measured on the basis of one test alone. Today, many tests — such as Spray Flammability, Hot Manifold Ignition, Hot Channel, Wick Flame and Soaked Cube — are all used to rate fire-resistance performance from various agencies and industries. In addition, there are many authorities who test and set standards for fire-resistant fluids, including insurance companies, national governments, etc. In North America, FM Approvals, which is part of FM Global (formerly Factory Mutual), is one of the world's largest commercial and industrial property insurance organization and has developed a certification program for the examination of fire-resistant fluids. In the past, Factory Mutual used a spray ignition test to measure fluid performance under a standard called Factory Mutual Standard CN6930.[13] Recently, FM introduced a new standard (also called CN6930) based on the Spray Flammability Parameter (SFP). Fluids that pass the test are segmented into two classes — "Approved Fluids" and "Specification Tested Fluids" — based on their SFP values. Approved products provide a higher degree of fire protection. Certified fire-resistant fluids from FM Approvals are also recognized in Asia and South America, but not in Europe.

The HFA, HFB and HFC products all contain high levels of water and are typically classified as "FM Approved" products by FM Global. The HFD products have been segmented further into HFDR and HFDU fluids. Both categories are fluids based on anhydrous synthetic lubricant technologies. The HFDR fluids are phosphate esters that have excellent fire-resistant properties and are typically "FM Approved" products. A limitation of these fluids is that they are not considered environmentally friendly and are very high in cost compared to other fire-resistant fluids. The HFDU products encompass synthetic polyol esters and polyalkylene glycols. These products are usually "FM Approved" products. However, for low-viscosity products, they can be "FM Specification" tested.

Polyalkylene Glycols and Their Use in Hydraulic Fluids

There are two types of fluids where PAG-based oils can provide significant benefits in hydraulic equipment. First, there are water glycol hydraulic fluids (HF-C) in which the PAG is used as a viscosity modifier and to provide friction control. Second, PAGs can be used as the primary base oil in synthetic PAG-based hydraulic fluids (HF-DU or HEPG) to impart important properties such as friction control, fire resistance, deposit control thermo-oxidative stability and long fluid life.[14] In the past few years, extensive research has been conducted in developing new and improved lubricants to meet the future demands of servicing industries such as steel and aluminum processing. These will be discussed. Prior to describing the new fluids, a description of polyalkylene glycols and their properties shall be discussed.

Structure 1 (below) provides a generic structural definition for a PAG polymer. From this, it is evident that a PAG polymer is composed of one or more types of repeat units, the most common being ethylene oxy $[CH_2CH_2O]$ and propylene oxy $[CH_2CH(CH_3)O]$. The polymer often has a hydroxyl (OH) terminal functionality. Polymers, by definition, are characteristically long structures that contain a repeat unit structure.

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

where R = H, alkyl, aryl, etc.

When n = 1.0, the PAG polymer is typically water-insoluble. When m = 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 that can control many functional properties, and this gives PAGs more design options than any other major base oil used in the industry today. Some important properties of PAGs are as follows:

- *Viscosity:* The versatility of PAG synthesis chemistry provides options for the design of a broad range of the ISO viscosity grades. Typical standard grades range from ISO 10 to ISO 1000. The viscosity of a PAG depends mainly on the molecular weight. Very high-viscosity PAGs can be manufactured, and these are typically used as viscosity builders in water glycol hydraulic fluids or quenchants for metal processing.
- *Viscosity index*: When compared with other base fluids, PAGs show, in general, very high viscosity indexes. Values up to 400 can be reached. For mineral oils, values are typically 90–120.
- *Solubility:* It is possible to create PAG with solubility properties ranging from complete water solubility to complete oil solubility. The latter is often obtained using butylene oxide as a precursor in the polymer structure. These materials are relatively new polymers.
- *Lubricity and film-forming properties:* PAGs 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.
- *Thermo-oxidative stability*: PAGs demonstrate a very good response to antioxidants, and can therefore be formulated for high-temperature applications (i.e., up to about 250°C). Other base stocks, such as vegetable oils, some synthetic esters and mineral oils, do not offer good enough thermal stability in this temperature range.
- *Low pour points*: Pour points as low as –50°C can be obtained with PAG chemistry. This makes them suitable for low-temperature applications. Low pour points, combined with their high viscosity indexes, make PAG lubricants an excellent choice for applications requiring one product for all seasons.
- *Thermal conductivity:* In general, PAGs offer better thermal conductivity than mineral oils. This means that better cooling characteristics can be achieved with PAGs, and as a result, equipment often operates cooler than with hydrocarbon products.
- *Hydrolytic stability:* PAGs do not hydrolyze, which can be seen as a major advantage over natural esters (vegetable oils) and synthetic esters. With esters, hydrolysis leads to acid formation, which will increase the lubricant's corrosion potential and accelerate further fluid degradation. In many applications, contamination with water cannot be completely avoided. This is especially true for any operating equipment for which environmental concerns arise should there be a leak. Most of this equipment operates outside, exposed to the elements, where rain and humidity ingress into the lubricant system and the hydrolysis process starts. For polyglycols, however, this is not a problem. A further unique feature is their ability to absorb water that contaminates a lubricant through ingress into the equipment. When this occurs, the PAG can act as a polymeric sponge, which renders the water inert.
- *Elastomer/metal compatibility:* Care should be taken in the choice of elastomers with all synthetic-base fluids. A broad range of commercially available elastomers, such as NBR (acrylonitrite/butadiene rubber) and FPM (fluoro-rubber), can be used with polyglycols. The same is true for ferrous and non-ferrous metals.
- *Deposit control:* A unique benefit of PAGs is their 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 byproducts that are insoluble in their parent base oil, leading to significant residues, which can be an important disadvantage in certain applications.

For water glycol hydraulic fluids, the PAGs that are used in formulations are always water-soluble, and this can be controlled by the ratio of propylene oxy/ethylene oxy groups. Typically, water glycol hydraulic fluids contain water (35–50% w/w), a glycol, a PAG and an additive package to provide anti-wear properties, solution and vapor phase corrosion and air release benefits. The PAG architecture can be important and plays a key role in providing shear and oxidation stability, as well as rheology modification.

In the case of anhydrous PAG hydraulic fluids, relatively low molecular weight polymers are used, and the total molecular weight is dependent on the sum of m + n. Typically, but not always, molecular weights of PAG polymers used for hydraulic fluid formulation are approximately < 1,000 g/mole. An anhydrous PAG hydraulic fluid is formulated from a PAG copolymer, such as those represented in Structure 1, and additives. The additives are selected to provide desirable properties such as corrosion protection, anti-wear lubricity, antioxidant properties and others.

Field Performance of a Novel PAG Water Glycol Hydraulic Fluid (HF-C)

A new water glycol hydraulic fluid has been developed, building on 50 years of experience and field performance of such products. One key aspect of the new product is the careful design and selection of the PAG thickener. The typical properties of the new fluid are described in Table 2.

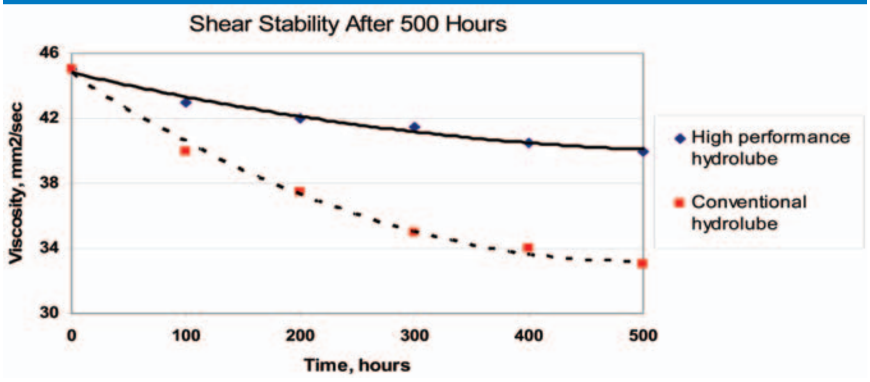
Table 2

Typical Properties of New Water Glycol Hydraulic Fluid

	Method	Typical result
Kinematic viscosity, mm^2/sec.	ASTM D445	46
Viscosity Index	ASTM D2270	195
Pour point, °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, min.	DIN 51381	13
Biodegradability, %	OECD 301F	> 80
Vickers V-104 Vane Pump Test, 100 hours at 2,000 psi and 65°C, total cam and vane weight loss in mg	ASTM D7043	8

In laboratory tests, the product 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-hour period at an outlet pressure of 2,000 psi, speed of 1,200 rpm and fluid temperature of 150°F (65°C). A conventional water glycol hydraulic fluid showed a total weight loss of rings and vanes of 25 mg and hence a wear rate of 0.25 mg/hour. The new technology showed a total weight loss of ring and vane of 8 mg, and hence a wear rate of 0.08 mg/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 1 shows the results.

Figure 1



Stability of new water glycol hydraulic fluid, based on the ASTM D7043 test.

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, including Bosch Rexroth, Eaton, Parker and Hartmann Controls. In these trials, outlet pressures were up to 4,000 psi and fluid reservoir temperatures ranged from 110 to 150°F. An example of one of the trials is described in Table 3.

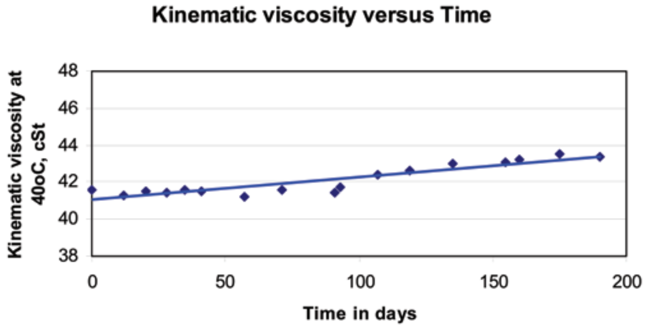
Figure 2 shows the change of viscosity of the fluid over a six-month period. Figure 3 shows the change in reserve alkalinity over the same period. Condition monitoring data displayed a number of trends. First, the

Table 3

Equipment Used in Trial

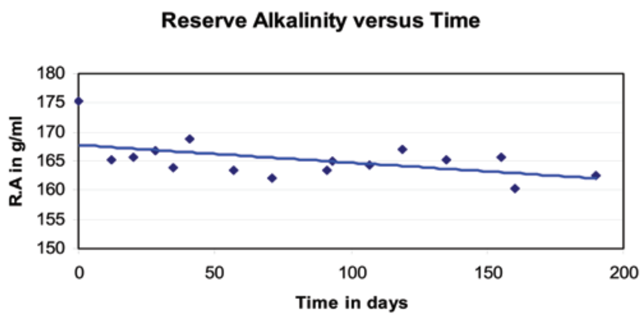
Pump type	Twin Parker piston pump
Sump size	300 gallons
Filter type and size	3 x 10 micron fiberglass filters
Inlet	Gravity fed — net positive pressure at inlet — position of reservoir above pump centerline
Outlet pressure	1,200 psi
Reservoir temperature	115–130°F (46–54°C)
Fluid leakage	Low (< 10 gallons per month)

Figure 2



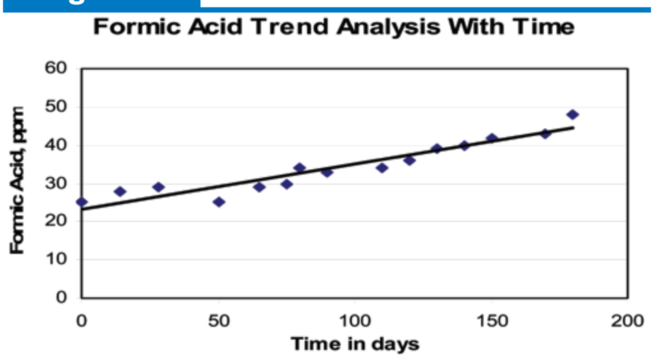
Viscosity change over the six-month test duration.

Figure 3



Change in reserve alkalinity.

Figure 4



Formic acid generation over time.

viscosity showed a gradual increase but remained essentially stable throughout the trial period. The viscosity change was < 5%. No depletion in water levels was measured, and 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. The reserve alkalinity was monitored (see Figure 2) and, although there was a minor trend toward lower values, no significant change was observed, and the fluid remained above the threshold of 130 g/ml, which is desired of water glycol hydraulic fluids.

A known degradation product of water glycol hydraulic fluids is formic acid.[15] High levels of formic acid have been identified as causing accelerated pump wear. It is believed that formic acid selectively adsorbs at the active ferrous surface, thus blocking the necessary chemisorption of the anti-wear additive. Furthermore, levels of 1,500 ppm and higher are considered to be the threshold for accelerated wear. Therefore, in this condition monitoring study, we were particularly interested in monitoring any formation of formic acid and also understanding its rate of formation. Figure 4 shows a very minor increase in formic acid levels and suggests the fluid is degrading very slowly. Formic acid levels of 46 ppm were recorded after six months from a baseline value of 13 ppm, suggesting a rate of formic acid formation of ~5 ppm/month.

This level is extremely low and would suggest the fluid could have many more successful years of service life before reaching the critical threshold value of 1,500 ppm, when the fluid would be changed.

Field Performance of a Novel PAG Anhydrous Hydraulic Fluid (HFDU) for Environmentally Sensitive Areas

A new anhydrous PAG environmentally friendly hydraulic fluid has been developed. Unlike mineral oils and esters, the product is unique in that it does not sheen on waterways if spills occur. In addition, the product outperforms many other technologies and can provide equipment reliability for all seasons. The typical properties of the new fluids are described in Table 4.

Case Study 1: Hydro Plants — As part of a shift toward more environmentally friendly operations, American Electric Power (AEP) replaced oil-based lubricants at six of its hydro plants with a new, environmentally friendly synthetic PAG-based hydraulic fluid.[16] This fluid does not contain any chemicals on the Comprehensive Environmental Response, Compensation, and Liability Act (CERLCA) list of hazardous substances. In addition, it meets the U.S. Fish and Wildlife Service requirements as "relatively harmless" or "practically non-toxic" to fish and other aquatic wildlife. The lubricant is water-soluble, fire-resistant and heavier than water.

AEP's use of this lubricant varies across the six plants:

- 4-MW Elkhart in Indiana — trash-rake equipment and wicket gate actuator tanks for all three units.
- 1-MW Mottville in Michigan — wicket gate actuator tank for one unit.
- 48-MW Racine in Ohio — ejector container of the trash raking system.
- 22.5-MW Reusens in Virginia and 19-MW Winfield in West Virginia — knuckle-boom crane.
- 5-MW Twin Branch in Indiana — trash-rake equipment.

Unlike mineral oils, which form sheens on waterways and can often be toxic, the new PAG fluid provides excellent equipment performance in both high-pressure and high-temperature systems, and also provides environmental acceptability.

Case Study 2: Tunnel Boring — Tunnel boring machines (TBMs), used to excavate underground tunnels for utility, transportation or irrigation, require a robust

Table 4

Typical Properties of Anhydrous Fire-Resistant Hydraulic Fluid

Property	Method	Results
Viscosity at 40°C, mm^2/s	ASTM D445	46
Viscosity Index	ASTM D2270	200
Pour point, °C	ASTM D97	–48
Flash point/fire point, °C	ASTM D92	295/315
Flash point, °C	ASTM D92	296
Copper corrosion, 24 hours at 100°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
Four ball EP test	ASTM D2783	
Load Wear Index		33.1
Last non-seizure load, 80 kg (scar, mm)		0.40
Weld load, kg		160
Vickers Vane V-104C, total weight loss of ring and vanes, mg	ASTM D7043	3

hydraulic fluid capable of withstanding operating pressures in excess of 4,500 psi and temperatures of > 90°C while providing favorable environmental characteristics. A new PAG-based ISO 46 synthetic hydraulic fluid (Table 4) was successfully used for a TBM that burrowed nearly two miles under Lake Michigan. The potential for fluid leaks and environmental impact is ever present in large-scale tunneling operations. Huge hydraulic cylinders exert millions of pounds of pressure against the tunnel walls to grip and propel the tunnel boring machine forward. Hydraulics also stabilize and support the massive machine and are used to drive the cutting head through subterranean rock and soil. Thrust, torque and other forces generated during tunnel boring are enormous and are accompanied by high fluid flowrates within the hydraulic systems. Under these conditions, even a small leak in a hydraulic line or a seal failure can quickly discharge large amounts of fluid into the tunnel, and leaks may go undetected until machine performance is affected. If a spill does occur, on-site cleanup is extremely difficult. The spilled fluid becomes mixed with the slurry of pulverized rock and soil produced by the boring operation, and is then carried with the waste stream to settling basins on the surface, where it can complicate secondary wastewater treatment as well. Using a new PAG-based ISO 46 synthetic hydraulic fluid with a favorable environmental profile and low toxicity helped to minimize the impact of leaks or spills, and also simplified water treatment requirements. This new fluid, which readily dissolves in water, reduced the need for centrifuge, flocculant or other wastewater treatment operations. In addition to a favorable environmental profile, it also provided the necessary load-carrying, heat and wear performance critical to tunnel boring operations for the $105 million tunnel project for a Wisconsin power station.

References

1. Martin Greaves and Jim Knoell, "A Comparison of the Performance of Environmentally Friendly Anhydrous Fire-Resistant Hydraulic Fluids," *J. ASTM Int.,* Vol. 6, No. 10, 2009.

2. "Wrestling With Fire Safety," *Lubes'N'Greases,* October 2007, Vol. 13 (10), pp. 42–47.

3. T. Noblit, "Biodegradable hydraulic fluids prove beneficial — Fire resistance a plus," *Machinery Lubrication*, March 2005.

4. "Fire Hazards of Hydraulic Fluids," *The Journal of Controlled Mechanical Power*, 2005, Third Quarter Edition.

5. F.H. Roberts and H.R. Fife, U.S. Patent 2,425,755 (1947).

6. G.E. Totten and R.J. Bishop, "Historical Overview of the Development of Water-Glycol Hydraulic Fluids," *SAE Technical Paper Series*, Paper No. 952076, 1995.

7. R.J. Bishop and G.E. Totten, "Maintenance and Analysis of Water Glycol Hydraulic Fluids," *Machinery Lubrication*, January 2003.

8. M.P. Marino, "Phosphate Esters" in *Synthetic Lubricants and High Performance Functional Fluids*, R.L. Shubkin, ed., Marcel Dekker, New York, 1992.

9. J. Anglin, "Fire resistant hydraulic fluids for aluminum processing," *STLE National Conference*, Cleveland, May 2008.

10. S. Boyde, "Hydrolytic Stability of Synthetic Ester Lubricants," *J. Syn. Lub.,* 2006, 16, 4, 297.

11. K.P. Kovanda and P.R. Miller, "Field Experience With a New Generation of Polyether Polyol Hydraulic Fluid," *Iron & Steel Engineer*, 1998, Vol. 75, No. 12, pp. 30–34.

12. "Lubricants, Industrial oils and related products (class L) — Family H (Hydraulic systems) — Specifications for categories HFAE, HFAS, HFB, HFC, HFDR and HFDU," IS0-12922.

13. *Factory Mutual System Approval Guide*, 1973-96, Factory Mutual Research Corp., Norwood, Mass.

14. G.E. Totten and R. Bishop, "Anhydrous Polyalkylene Glycol Hydraulic Fluids," SAE 2000-01-2557, September 2000.

15. G.E. Totten, "Emulsions," *Handbook of Hydraulic Fluid Technology*, pp. 917–979.

16. *Hydro Review*, May 2009. ✦

This paper was presented at AISTech 2010 — The Iron & Steel Technology Conference and Exposition, Pittsburgh, Pa., and published in the Conference Proceedings.