Des-Case Technical Bulletin
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Maintenance of Fire-Resistant Phosphate Ester Fluids

The United States is the highest producer of industrial lubricants in the world. These products are typically categorized as either mineral-based or synthetic fluids. *Mineral oil* is the category derived from crude and represents about 95% of the industrial market. There are many brands and types of mineral based fluids on the market, but what really differentiates one from another is the chemical additive package included during the blending process.

The second category of lubricants is referred to as *synthetic*. Synthetic fluids are formulated in a laboratory and manufactured from raw materials such as methane, carbon monoxide, carbon dioxide, and isopropyl. Synthetic oils outperform mineral fluids, but due to cost, they are less popular and only represent about 5% of the market. They are formulated for specific applications and broken into sub categories based on formulation type. Examples include: *polyalkylene glycol (PAG), polyol ester (POE), and phosphate ester*, all of which are designed for particular uses. Polyalkylene glycol fluids are turbine oils used in a wide range of industries as both gear and hydraulic lubricants. Polyol ester fluids are particularly effective for refrigeration compression because they are compatible with Freon® (DuPont).

The high operating temperatures associated with some equipment and processes require the use of special fire-resistant products. Like other synthetics, phosphate esters are top performers in the field, but what really sets them apart is their fire-resistant qualities. Two types of phosphate ester include *triaryl and trialkyl*. Triaryl phosphate ester is a great boundary lubricant, which means it performs well on load-carrying and rolling surfaces typically associated with bearings. Most lubricants lose viscosity during service due to water contamination, depletion of additives, or polymer shearing. Triaryl phosphate has excellent thermal stability and is formulated without the need for viscosity modifying polymers. It retains its viscosity indefinitely and provides the user with long service life. These features make it ideal for high-temperature industrial applications. Trialkyl phosphate ester is also a high performance product specifically used in aviation hydraulics.

Most synthetic fluids are considered fire resistant, by the manufacturer, simply based on their flashpoint, which is typically higher than that of mineral oil. Synthetics composed of POE and polyol ether (a.k.a. PAG) may be more difficult to ignite than mineral oil; however, like mineral oil, they will sustain combustion, even after the ignition source is removed. This is not true of phosphate esters. Instead, when the ignition source is removed they are unable to sustain a flame and are therefore considered *self-extinguishing*.

All synthetic lubricants do not respond the same way when exposed to an open flame. That is why fire resistance requirements must be clearly defined for each application. When choosing a fire resistant fluid it is important to review the manufacturer’s data in order to align product performance properties with application requirements and materials compatibility. Traditionally there are three terms that have been used in reference to the fire resistance of fluids:

1) **Flashpoint** is the most common term and represents the temperature at which a fluid will emit sufficient vapor, at atmospheric pressure, to ignite when exposed to a flame. Some volatile fluids with low flashpoints include gasoline – 43°C (-45°F) and propane -104°C (-156°F). A highly refined mineral-based hydraulic fluid may have a flashpoint of 177°C (350°F), whereas a synthetic may be more than 300°C (575°F).
2) **Fire Point** is the temperature at which a fluid will emit sufficient vapor to sustain burning even after the source of ignition is removed. With regard to industrial oils, the fire point is typically 8-10% higher than the flashpoint. The flashpoint of a fluid is lower than the fire point, which is why Material Safety Data Sheets (MSDS) usually only reference the flashpoint. It is the safer of the two.

3) **Autoignition** is the temperature at which a fluid will spontaneously ignite simply based on temperature without exposure to a flame or ignition source. It is acceptable to use fluids above their flash or fire points, but not above their autoignition point.

According to manufacturers, these terms are not meaningful when referencing phosphate ester fluids. Rather than flashpoint, a phosphate ester MSDS may list a very high “ignition point” of perhaps 593°C (1100°F) with a note that says “unable to sustain a flame.” According to one manufacturer, the accepted definition of a truly fire resistant fluid is as follows: “A fire resistant fluid is a fluid that does not undergo self-sustaining combustion and that remains difficult to ignite during service.”

**Applications**
Like other oils, phosphate esters normally see operating temperatures of less than 54°C (130°F). Triaryl phosphate ester, for example, is not recommended for use above 71°C (160°F). However, some equipment can generate high levels of radiant heat, which poses fire hazards. Though the lubricity of mineral oil and many synthetics may be adequate for these applications, they would not be appropriate as a spill could cause a fire, the results of which could be catastrophic. What really sets phosphate ester apart from other fluids is its inability to sustain combustion once the ignition source is removed. Some high-temperature applications appropriate for phosphate ester include:

- Superheated steam
- Furnace hydraulics
- Steam turbine electro-hydraulic control systems
- Gas turbines
- Steel and aluminum foundries
- Tilting systems (cast iron melting furnaces)
- Die casting machine hydraulics
- Reciprocating air compressors
- Aviation hydraulic

**Contamination**
Contamination and deterioration are normal consequences of hydraulic fluid use. Systematic fluid analysis is an important part of any fluid management program as it alerts operators as to when and to what degree corrective action must be taken. Oil contaminants, such as particulate and water, are always a problem for equipment. Mineral oil solubilizes water until saturation. Once saturation occurs, excess water remains present in an *emulsified* or *free* state, where it is visible to the naked eye and causes the most direct mechanical damage to equipment. Solubilized water is also destructive because it breaks down oil additives and promotes oxidation. Mineral oil can hold as much as 200-600 ppm dissolved water. For phosphate ester a high percentage of dissolved water contamination can be removed with the use of water removal elements or vacuum dehydration.

Phosphate esters require more attention than mineral oil because they are about five times as expensive, react differently to water contamination, and maintain particles in suspension longer. As noted, water is always a problem, but when it comes to phosphate ester the operator’s focus must broaden. New phosphate ester fluid may contain 200-400 ppm of dissolved water. It is hygroscopic so it absorbs water readily from the atmosphere and can easily reach 4000 ppm during operation. Water absorption also increases at elevated temperatures and increased acidity levels. Unlike mineral oil which
degrades through oxidative (oxygen) decomposition, phosphate ester degrades hydrolytically. This means the first step in oil degradation occurs through a chemical process called hydrolysis. In hydrolysis water molecules are added to the oil and the additional hydrogen ions elevate the level of acidity. Though water is a required component for hydrolysis it is not the primary driver of the hydrolytic reaction. As the fluid is used in the field and its temperature is elevated, the presence of dissolved water encourages some hydrolysis to occur. This results in the formation of phosphoric acid derivatives (acid phosphates). Acid phosphates break down and shorten the life of the oil. They also combine with impurities to form metal salts that, upon saturation, fall out to form destructive gel like precipitates, which cause stickage and are destructive to equipment surfaces. They also attack soft metals such as brass and aluminum.

As acid phosphates accumulate, they increase the oils ability to solubilize water. The increased dissolved water in turn accelerates the formation of acid phosphates and the cycle continues. As a result fluid acidity increases exponentially.

Oil acidity is measured in terms of Total Acid Number (TAN). TAN refers to how many milligrams of potassium hydroxide (KoH) are required to neutralize one gram of oil.

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TAN = \frac{\text{mg KoH}}{\text{gram of oil}}
\]

**Fluid Maintenance**

It is nearly impossible to remove all dissolved water from oil; therefore, with regard to the condition of phosphate ester fluid, TAN is actually of greater concern than the water itself. As acid phosphate levels increase TAN also increases and provides the most important indicator of the fluid’s remaining useful life. For example, a new phosphate ester fluid may have a TAN of 0.01-0.02 and is reasonably maintained in the field between 0.05 and 0.10. A TAN of greater than 0.15 should be considered abnormal. Under these conditions hydrolysis occurs readily. A TAN of 0.20 is usually considered the condemning value or point at which the fluid must be replaced.

At 110°F, newer phosphate ester well maintained at a TAN of less than 0.10 may take up as much as 4000-4500 ppm of water in solution. Other factors such as temperature and acidity will impact how much water can actually be absorbed. As temperature and acidity increase, the solubility of water in the fluid also increases. As noted, higher TAN levels accelerate degradation caused by hydrolysis.

It is imperative to consult the oil supplier to verify best practices and TAN targets in any given application. However, good general rules for maintaining phosphate ester include removing particulate, keeping fluid as dry as possible, and maintaining the TAN at 0.10 or lower. Overall benefits include improved operational safety and increased fluid and equipment life.

Reducing water and particulate can be accomplished through the use of dessicant breathers, good transfer practices, filtration, and dewatering. Phosphate ester is actually heavier than water. An effective way to remove free water is to wet vacuum from the top of the reservoir. For ongoing maintenance water can be removed with water-absorbing filter media or vacuum dehydration, which is typically recommended for larger fluid fill systems. A properly functioning vacuum dehydration unit
can reduce water levels to below 100 ppm. For phosphate ester, a good goal is 500 ppm or less with a maximum recommended water content of 1500 ppm.

Wherever lubricants are used, Des-Case offers superior products to combat particulate and water contamination. To maintain phosphate ester, offline filtration systems must include special media able to control acid phosphate levels (TAN). Phosphate ester lubrication systems should be equipped with TAN maintenance equipment at the time of the original installation.

Technology for reducing TAN has evolved over the past few decades. There was a day when Fuller’s Earth was the media of choice. Today, however, many claim it is not effective for synthetic oils. After Fuller’s Earth, activated alumina became popular. After that, recommendations began to shift to BASF Selexsorb®, then to Selexsorg® GT. At the time of this writing, cutting-edge technology includes: Selexsorb® GT and specially formulated Dry Ion Exchange Resin, both of which are very effective.

The media mentioned above are available through Des-Case for custom 6x18”, 6x36”, and 4000 size canisters. Special larger canisters are also available. Elements must be sized correctly in order to meet acid maintenance goals. Following are some general guidelines for TAN control:

**Rule of Thumb for TAN Maintenance**

- To achieve a 50% TAN reduction, use .45 kg (1 lbs) Selexsorb® GT for each gallon of fluid in the reservoir.
- To achieve a 75% TAN reduction use, .64 kg (1.4 lbs) Selexsorb® GT for each gallon.
- Flow rate should not exceed 1.89 lpm (½ gpm) for every 5.9 kg (13 lbs) of media (per 6x18” element).
- Nominal micron rating: 4um
- Replacement pressure: 20 PSI

**Canister and Element Specifications**

<table>
<thead>
<tr>
<th>Canister Size</th>
<th>Selexsorb® GT Per Element</th>
<th>Elements Required Per Canister</th>
<th>Selexsorb® GT Per Canister</th>
<th>Max Recommended Flow Rate</th>
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<td>6X18”</td>
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<td>1.89 lpm (½ gpm)</td>
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<td>20.9 kg (46 lbs)</td>
<td>13.5 lpm (3.5 gpm)</td>
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</tbody>
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**Material Compatibility**

Special precautions must be taken when constructing filtration equipment for maintaining phosphate esters as they are not compatible with some common materials of construction. The table below shows recommendations under normal conditions.
Sample Equipment Recommendation
Taking all of the above into consideration, the following represents a sample Des-Case equipment recommendation.

Field Conditions
Application: Lubrication (Triaryl Phosphate Ester)
Reservoir Size: 473 liters (125 gallons)
Viscosity: ISO 220
Operating Temperature: 52°C (120°F)
TAN: 0.12
Water Content = .8% or 3.79 liters (1 gallon)
Ingression Rate = 1.89 liters (.5 gallons)/week
Electrical Supply: single phase, 230 vac, 60hz

Fluid Handling Equipment Recommendation
Custom T-Stand Filtration System
Includes: 1 gpm pump, 1hp electric motor, single phase, 230 VAC, 60 Hz, 1800 rpm. 6x36” water removal filter (holds ~9.5 ltrs or 2.5 gallons), high viscosity sample port, Y-Strainer.

Additional Equipment
Acid Reduction Skid
Includes: Three 4000 size canisters, each contain four Selexsorb® GT filter elements. Total Selexsorb® GT per canister is 20.9 kg (46 lbs). Followed by 6x18” 6um particulate filter.

Special Materials Include:
Nickel plated filter canisters, Selexsorb® GT filter media, no aluminum or brass wetted components, viton seals and o-rings.

Conclusion
Phosphate ester fluids are specifically formulated to emit low vapor pressure during operation. This characteristic makes them self-extinguishing and ideal for applications that may pose a fire hazard. They have unique properties that demand special attention with regard to contamination control. Along with particulate filtration and water removal, TAN must be taken into consideration when recommending Des-Case filtration equipment.