Stability of Phosphate Ester Aviation Hydraulic Fluids

Introduction

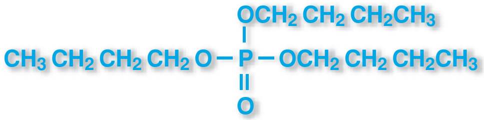
The fluid of an aircraft hydraulic system may require replacement because it has been contaminated by solids and/or other fluids such as water, engine oil, strut fluid, or cleaning solvent. It may also require replacement because it has degraded to a level that could be harmful to hydraulic system materials and components. Degradation is the consequence of the limited stability of the fluid.

We will describe the chemical mechanisms that cause degradation of the phosphate ester base oils, which are the major constituents of all fire-resistant commercial aircraft hydraulic fluids. We will also review the consequences of severe fluid degradation and provide comparisons of the stability of commercial fluids.

General Description of Phosphate Esters Used in Aviation Hydraulic Fluids

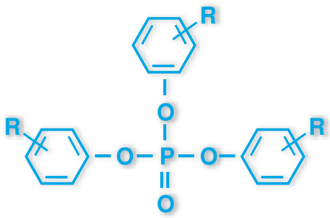
Aviation hydraulic fluids use a mixture of alkyl and aryl phosphate ester base oils. An ester is a reaction product of an acid and an alcohol or a phenol. In this case, the acid portion of the molecule comes from phosphoric acid, and imparts the fire resistant properties to the ester. The alcohol/ phenol portion of the phosphate ester imparts the desirable flow properties.

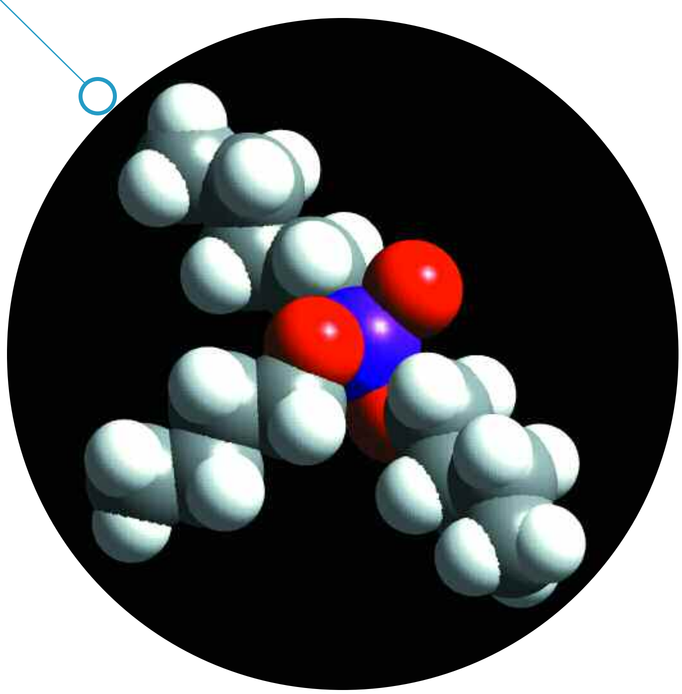
- Alkyl phosphate esters are made from alcohols. A good example is tributyl phosphate, where you have three butyl alcohols (4 carbons) around the phosphate group.



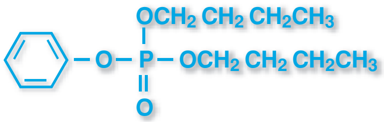
$$CH_3CH_2CH_2CH_2O-\overset{\overset{OCH_2CH_2CH_2CH_3}{|}}{\underset{\underset{O}{\|}}{P}}-OCH_2CH_2CH_2CH_3$$

- Aryl phosphate esters are constituted from phenol or alkyl phenols. In the example shown, the R group can be hydrogen, isopropyl, tert-butyl, etc.





- An example of a mixed alkyl/aryl phosphate is dibutyl phenyl phosphate.



Each type of constituent described above would have a different level of resistance to chemical reactions that result in fluid degradation.

Phosphate Ester Degradation Mechanisms

Three mechanisms contribute to the degradation of phosphate esters. Each path can become significant at different environmental conditions to which the phosphate ester is exposed in an aircraft hydraulic system. All three paths produce acid phosphates (phosphoric acid derivatives) as the main harmful degradation product.

Decomposition Pathways for Phosphate Ester Fluids

Pyrolysis or thermal degradation of phosphate esters only becomes significant at very high temperatures (above 300°F or 150°C), which is not normally encountered in aviation hydraulic systems. This degradation path becomes significant in cases of equipment malfunction or in some special situations such as brake system cylinders where the fluid is not sufficiently insulated from high temperatures reached by carbon brakes. During pyrolysis, alkyl groups of the phosphate esters break up from the molecule to form unsaturated hydrocarbons (such as butene) and leave behind a phosphoric acid derivative. Aromatic (phenol and substituted phenols) groups are more resistant to pyrolysis than alkyl groups.

Phosphate esters are quite resistant to oxidation, and aircraft hydraulic systems are closed systems with limited availability of oxygen from air. Therefore, oxidation is not a significant degradation path in this application.

The most significant fluid degradation path in aviation hydraulic systems is hydrolysis (reaction with water), because this reaction occurs even at moderate temperatures. Of course hydrolysis will occur at a faster rate at higher temperatures. Phosphate esters are very hygroscopic (they absorb water from the atmosphere very rapidly), thus the hydraulic fluid normally contains several thousand parts per million of water available to decompose the ester. Aryl and alkyl/aryl phosphates are more prone to hydrolytic degradation than alkyl phosphates.

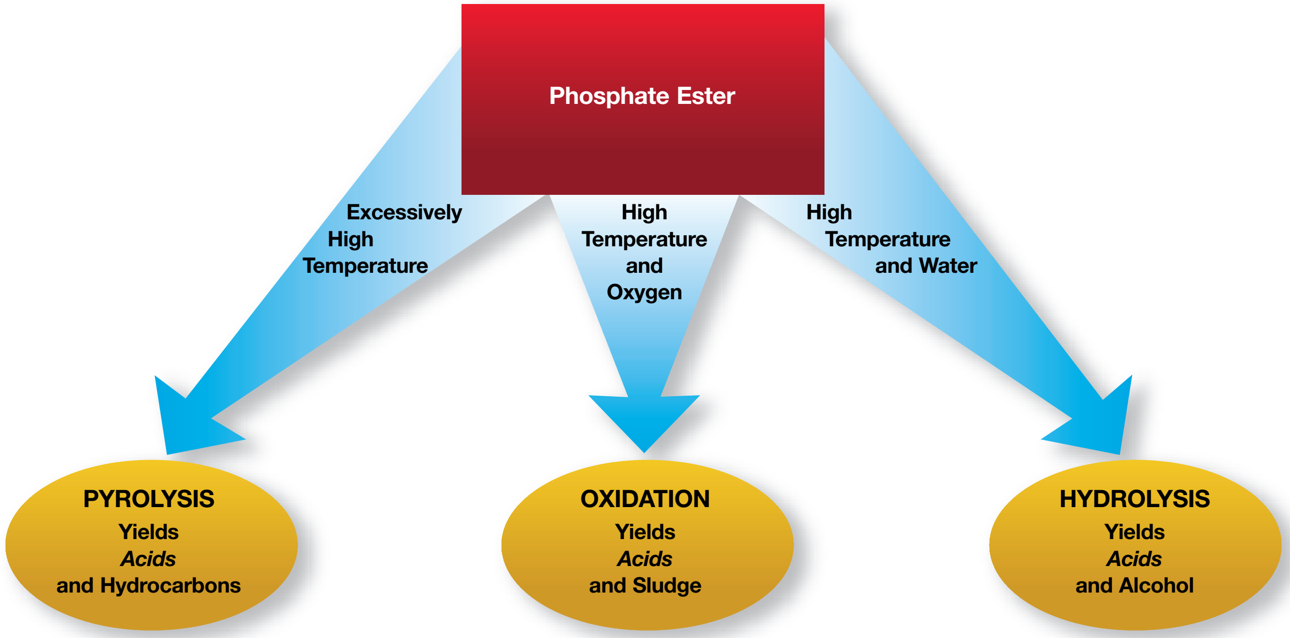
All three degradation mechanisms progress at increasing rates, as temperature increases. Oxidation and hydrolysis are also catalyzed by metals such as iron and copper. The harmful byproduct in all cases is a phosphoric acid derivative, a “strong” acid that can damage hydraulic system components, attack and degrade elastomers, and etch metal parts and tubing.

Acid Control

In the early days of introduction to the market, the utilization of phosphate ester aviation hydraulic fluids involved very high maintenance. Because acid formation by hydrolysis is prevalent with phosphate esters due to the presence of normally high levels of water, acidified fluids had to be replaced frequently. In the late 1960s acid control additives called epoxides were developed to address the problem. These additives react even at normal ambient temperature with the phosphoric acid derivatives formed by the degradation of the phosphate esters, and convert them to harmless, neutral species.

Today, an aircraft system’s aviation hydraulic system remains free of strong acids until the acid control additives are essentially depleted. However, because the amount of allowed acid control additive in an aviation hydraulic fluid is limited by seal swell and flammability considerations, all commercial Type IV and Type V hydraulic fluids contain similar amounts of acid control additive.

Decomposition Pathways for Phosphate Ester Fluids



Since all commercial aviation hydraulic fluids are comprised of phosphate esters and they all contain essentially the same amount of additive, are they all equally stable? The answer is no, because of differences in the resistance of the base oil constituents to hydrolysis. Furthermore, supplementary additives can be used to slow down the rate of hydrolysis.

Resistance to Hydrolysis

Resistance of the fluid to hydrolysis is important. If the fluid make-up rate is not enough to balance the extent of water absorption, strong acids may ultimately be formed in a hydraulic system.

Acid number (which used to be called neutralization number) is a measure of acidic species present in the fluid. It is obtained by titration. The units are mg KOH (potassium hydroxide) equivalent per gram of fluid tested. This is a small unit of measure. To put it in perspective, 0.5% water, which is not uncommon to encounter in aircraft hydraulic systems, would upon complete hydrolysis produce an equivalent acid number of 15.6 mg KOH, as illustrated by the following equation:

$$\frac{5 \text{ mg } H_2O}{\text{g fluid}} \text{ X } \frac{56.1 \text{ (Molecular wt of KOH)}}{18 \text{ (Molecular wt of } H_2O)} = \frac{15.6 \text{ mg KOH}}{\text{g fluid}}$$

In absence of acid control additives, very high levels of strong acid would be reached (in fact, used to be reached with Type I fluids in the 1950s). Fluid with high strong acidity, if present in an aircraft system, would react with iron and aluminum to damage parts, and form deposits and gels.

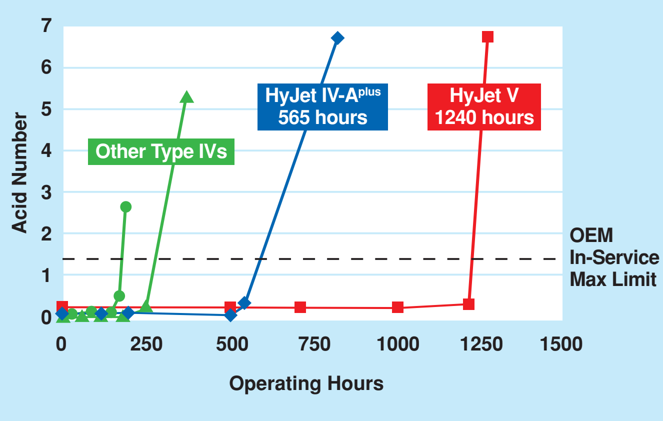
Fresh hydraulic fluid typically has the additive capacity to neutralize the hydrolysis products of about 0.4% water (acid number equivalent of about 13). Thus, there exists quite a bit of acid control capacity. However, the hydraulic fluid continuously absorbs water from the environment, and water levels that exceed the capacity of the acid control additive are not uncommon. For example, most aircraft manufacturers allow operation with up to 0.8% water in the hydraulic system. This is based on the expectation that high levels of strong acidity will not occur before the next sampling of the fluid due to normal make-up with new fluid and the typically low hydrolysis rate at the moderate temperatures encountered in hydraulic systems.

To protect against damage from high acidity, aircraft manufacturers typically recommend a maximum acid number of 1.5, beyond which the fluid should be replaced. The time it takes a fluid to reach an acid number of 1.5 can be considered the in-service life of the fluid. The acid number limit of 1.5 does contain a safety factor against aircraft system damage. Serious damage would start occurring at acid numbers above 5 and the extent of damage would depend on the magnitude of the acid number, duration, and temperature of the exposure.

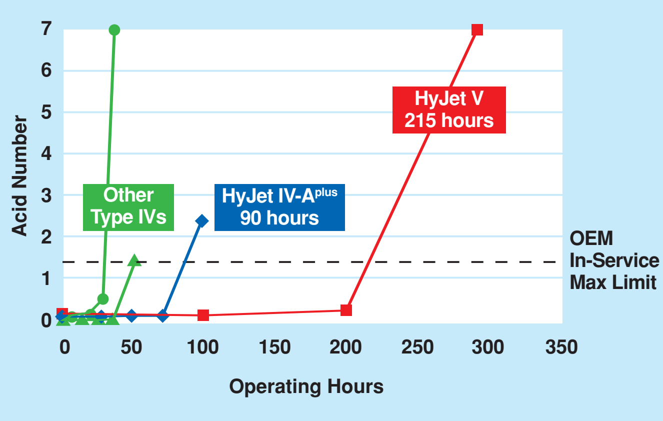
Ampoule Stability Test

The method we use to evaluate comparative hydrolysis resistance of various fluids is the Ampoule Stability test. The test is designed to measure the hydrolytic and thermal stability of phosphate ester aviation hydraulic fluids. The fluids are contaminated with precise water concentrations and sealed in glass tubes in which small strips of steel and copper wire are used to simulate the metals in hydraulic systems that would tend to catalyze the hydrolysis reactions. The glass tubes are kept in a controlled-temperature oven for very long time periods. At regular intervals the fluid is tested to determine whether it has exceeded an acid number of 1.5, at which point the end of fluid life has been reached.

Ampoule Stability @ 0.5% Water, 125°C, 50 ppm chlorine



Ampoule Stability @ 0.5% Water, 150°C, 50 ppm chlorine



Fluid Life Curves

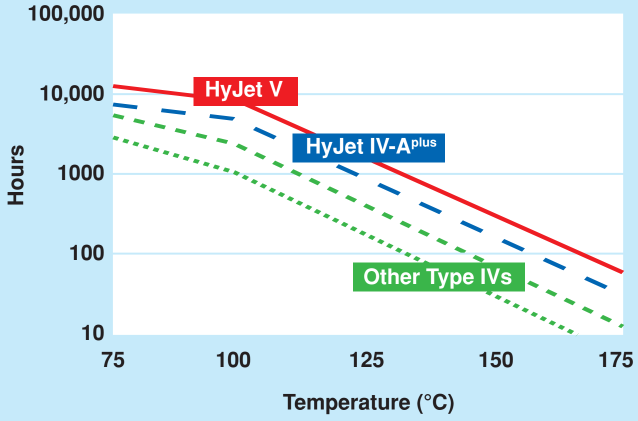
The Ampoule Stability test can be run in a range of temperatures and water concentrations to produce “Fluid Life” curves. Hydrolysis is the main degradation mechanism in tests run with water contents of 0.5% and higher. Thermal stability of the base oils and fluid degradation products become a factor at low (for example, 0.2%) water content and high temperature.

By combining results obtained at a constant water content, but at different temperatures, we can build the Fluid Life curves that relate to a particular hydraulic system temperature.

The comparison of HyJet V, HyJet IV-A^{plus}, and other competitive fluids in the chart at right is based on side-by-side testing of samples. It demonstrates the superiority of HyJet V at 0.5% water and a range of temperatures chosen to replicate aircraft in service conditions. The same conclusion is reached from testing conducted at other water concentrations.

- The fluid life for HyJet V as a function of temperature in these test conditions is about twice that of HyJet IV-A^{plus} and several times that of other commercial Type IV fluids.
- Experience with fluid samples taken from several aircraft fleets corroborates the superior performance of HyJet IV-A^{plus} observed in these laboratory experiments compared to other commercial Type IV fluids.

Fluid Life Curves at 0.5% Water Contamination



A Final Point

All acidity measured in an aircraft’s fluids is not necessarily “strong” acidity caused by the decomposition of phosphate esters, which is the type that may cause serious damage to aircraft hydraulic system materials. The fluid also contains weak acids (such as carboxylic acids) formed by the degradation of the additives in the fluid. In fact, acidity measured in aircraft hydraulic systems with acid numbers below 1.5 is primarily due to weak acids which build up gradually and are not neutralized by acid control additives. Weak acids are not very harmful. They are formed at the same time as strong acids. While the strong acids are neutralized by the acid control additive, weak acids tend to accumulate. Weak acids are therefore an indication of the extent of fluid degradation. By the time you reach an acid number of 1.5, even if this acidity is not coming primarily from strong acids, the fluid is ripe for a sudden increase of strong acidity, thus it is time for a change in the hydraulic fluid.