

# Analysis of Acid Number in Phosphate Esters by FTIR Spectroscopy

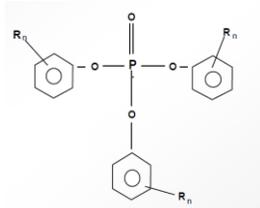
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## Introduction

In the nuclear power sector, electricity is generated from the steam generated by large turbines which are highly reliant on efficient electro-hydraulic turbine speed control systems (EHC). These systems offer a wide range of control options and operate at pressures of over 1000 psi to ensure rapid hydraulic response. At these pressures the potential for leaks of hydraulic fluid is greater as is the attendant fire hazard, leading to the use of phosphate esters as the hydraulic fluid of choice. Their selection was based on their auto-ignition temperatures being high, having a low heat of combustion which makes them self extinguishing as well as having less compressibility, making them more responsive than mineral oils. Although phosphate esters have positive attributes, in operation they have been problematic due to fluid deterioration resulting in poor fluid quality. Once phosphate esters deteriorate significantly, problems arise in the form of operating problems with the EHC, commonly caused by sticky servo valves, which makes them unable to respond to the control system commands governing the emergency and stop valves. According to a study in 1992, 240 EHC failures in the US nuclear industry over a 5 year period, with over half of those resulting in a reactor scram or manual shutdown and about one quarter in a forced power reduction. A more recent study traced these problems to hydraulic fluid quality and the few utilities which did not experience EHC problems had taken ongoing action to ensure that the phosphate ester quality was maintained.

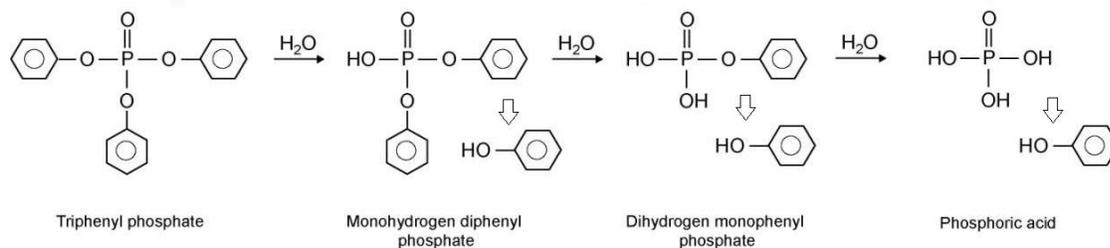
## Phosphate Ester Fluids

As noted, phosphate ester fluids are fire-resistant fluids suitable for hydraulic applications where the danger of fluid loss may result in a significant fire hazard – typical examples being compressors ranging from jet engines to nuclear plants. Although a number of fluid formulations exist, an example of a typical phosphate ester type are triaryl phosphate esters, their basic structure shown below



[1]

where R may be a methyl (XPT), isopropyl (TIPP) or tertiary butyl (TBPP) group attached somewhere on the phenyl ring and n ranging from 0-2. As noted, these fluids do undergo deterioration over time while in use for a variety of reasons. The predominant cause of ester fluid deterioration is the presence of moisture which results in hydrolysis, aggravated and accelerated by thermal stress, with oxidation being a possible adjunct mechanism. Hydrolysis results in the random and progressive release of the molecular moiety attached to the central phosphate molecule in the following manner:



[2]

As each phenyl group is released, it produces an additional ionizable acidic O=P-OH group, analogous to the ionization of phosphoric acid, their respective pka's being 2.12, 7.21 and 12.32. The loss of one phenyl group results in a very weak acid, while the loss of three phenyl groups produces phosphoric acid, which is quite strong and corrosive. Although phosphoric acid is not something which should accumulate to any significant degree, it can form if there is excessive moisture and local hot spots exist. In addition phenyl groups are lost, even the mono and di-hydrogen phenyl phosphates can chelate or react with metals to form salts that can precipitate out of solution or react with themselves to produce higher molecular weight di and tri phosphate esters which are gummy and produce varnishes. Thus over time, with moisture ingress and thermal contributions, there is a slow but steady degradation of the fluid. The most common measure of fluid degradation has been to measure the changes in acidity of the phosphate ester fluid by titration, on the assumption that as the ester linkages are broken, the acidity will rise. This is conventionally done by measuring acid number (AN) by titrating with base. The method most commonly used in the industry is ASTM 947, using standardized KOH and phenolphthalein as the indicator and reporting the acidity in mg KOH/g oil. Historically, it has been demonstrated that if the AN rises to above 0.2 mg KOH/g, the potential for problems is increased significantly in terms of EHC systems. Because of fluid replacement costs, phosphate ester hydraulic fluids were treated to remove acidity, the initial techniques making use of Fullers earth which was very efficient in removing acidity. It has since been determined that, although it removes acidity, it also participated in deposit formation due to calcium and magnesium soap formation, these elements arising from the Fullers earth. This acid reduction procedure has been largely replaced by ion exchange, which removes acid, but does not contribute metals which can precipitate, replacing them with sodium. A problem associated with this is that the resin used contains moisture and the sodium salts can cause foaming and hence air entrainment. The foaming issue is of some significance as during the compression cycle, the adiabatic compression of air causing localized rises in temperature at the bubble/liquid interface, leading to hydrolysis, oxidation and possible polymerization. Aside from removing H<sup>+</sup> and phenol, the resins also remove Ca and Mg, which breaks the degradation cycle, but which eventually cause fouling of the resin. The general experience has been that resin re-processing of phosphate esters is an improvement over Fullers earth and that it can be used successfully to extend the life of phosphate ester fluids, minimize corrosion and fouling due to deposit and/or varnish formation.

Central to maintaining the quality of phosphate ester fluids used for EHC systems is ensuring that their acidity levels are <0.1 AN. There are relatively low levels and places heavy reliance on the

accurate monitoring and determination of their AN values. The methodology used for this purpose was designed for mineral based lubricants and is not noted for its speed, accuracy, reproducibility or sensitivity. Because phosphate ester fluids are relatively clear and colorless, a colorimetric procedure can be used, however, this approach becomes problematic as the fluid darkens. The norm in the lubricant sector, where this methodology is derived from tends to be potentiometric, which is both automatable and does not rely on a subjective endpoint. Generally speaking, few in the nuclear sector have moved to this approach as the results are not identical, largely as a result of differences as to how the endpoint is determined by each method. From the perspective of the industry, the information garnered, is simply acidity, without differentiation of whether the acidity is either weak or strong. This is because the base used (KOH) is strong enough to measure all three forms of the "acids" formed in [2], the di and mono-phenol as well as the free phosphoric acid. From the standpoint of acidity or reactivity, they are far from equal and it would be helpful to differentiate between them if possible, as they have distinctly different meaning in terms of reactivity.

FTIR spectroscopy has been developed as an alternative means of measuring acid number (AN), or more specifically acid content (AC). This methodology is based on similar chemistry as titrimetric procedures, but uses spectrally active bases to measure the acid present. The other important aspect of this approach is the ability to use bases having varying pKa's which target distinctly different categories of acids. For example, a strong base with a pKa of 10, can measure acids with a pKa of >2, while a base having a pKa of 13.5 can measure all bases having a pKa of <2. If one were to determine the acidity using these two bases, the first would be considered representative of all the total acidity (TA), while the second, only of the strong acids (SA), e.g, phosphoric acid. The difference (TA-SA) would be equal to the weak acids (di, mono and possibly phenols). Thus this approach would lead to a differentiation of the acidity, providing guidance to the quality of the phosphate ester fluid and its condition. One could expand on this concept by also determining the base number, which would be an indication of accumulating soaps. Here one would react the solution with TFA to determine bases present, which may provide another quality measurement.....