PHOSPHORIC ANHYDRIDE & POLYPHOSPHORIC ACID IN THE MANUFACTURE OF PHOSPHORIC ACID ESTERS

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Introduction

Phosphate esters (phosphoric acid esters) are a useful range of products derived by reacting phosphoric anhydride or polyphosphoric acid with various alcohols. This technical information bulletin describes the use of phosphoric anhydride, polyphosphoric acid and hypophosphorous acid in the production of these products.

Phosphoric anhydride, polyphosphoric acid and hypophosphorous acid are products of Innophos. They are all manufactured in Nashville, TN. Polyphosphoric acid is also produced in Morrisville, PA. Information on these products may be obtained from Innophos Customer or Technical Service organizations, and by reading the following Innophos publications:

<table>
<thead>
<tr>
<th>Phosphoric Anhydride Brochure</th>
<th>Phosphoric Acid Brochure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product Data Sheets</td>
<td>Material Safety Data Sheets</td>
</tr>
<tr>
<td>Phosphoric Anhydride</td>
<td>Phosphoric Anhydride</td>
</tr>
<tr>
<td>Polyphosphoric Acid</td>
<td>Polyphosphoric Acid</td>
</tr>
<tr>
<td>Hypophosphorous Acid</td>
<td>Hypophosphorous Acid</td>
</tr>
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</table>

Phosphoric Anhydride and Polyphosphoric Acid

Phosphoric Anhydride

Phosphoric anhydride (or phosphorus pentoxide, P$_2$O$_5$) is a white granular powder consisting mainly of the hexagonal form of the oxide. Although P$_4$O$_{10}$ better represents the actual molecular formula of phosphorus pentoxide, P$_2$O$_5$ is the traditional and common representation. At atmospheric pressure, P$_2$O$_5$ sublimes at about 360°C. It is extremely hygroscopic and dissolves readily in water with the release of large amounts of heat, forming phosphoric acid (H$_3$PO$_4$).

For more information on phosphoric anhydride, refer to the Innophos Technical Bulletin (TIR 26) for this product.
REACTIONS

Phosphoric Anhydride and Polyphosphoric Acid in the Manufacture of Phosphoric Acid Esters

Reactions Phosphoric

Anhydride and Alcohols

Phosphoric anhydride has a tetrahedron like molecular structure, with six P - O - P bonds and four P=O bonds. It is generally described as having a cage structure as illustrated in Figure (1) below.

The reactivity of phosphoric anhydride is discussed in some detail in the bulletin TIR 26, "Phosphoric Anhydride", available from Innophos. In this Technical Information Bulletin we will expand on phosphoric anhydride's reactivity with alcohols.

An alcohol, ROH reacting with $\text{P}_4\text{O}_{10}$, splits one of the six P-O-P bonds as in Equation (1),

$$ (\text{P}_2\text{O}_7) + \text{ROH} \rightarrow (\text{P}_2\text{O}_7)\text{P-O-R}$$

splitting off the hydrogen atom from the organic radical and forming P-O-R and P-OH bonds. This is further illustrated in Figure (2) below.
A second alcohol radical may react with this molecule in one of several ways. The RO group may bond to a phosphorus (P) atom already bonded to an RO group, to one bonded to an (OH) group, or it may split an as yet unbroken P-O-P bond. Each of these reactions occurs, however the unbroken P-O-P group is attacked preferentially. This reaction may continue until all six P-O-P bonds are broken, when the product is essentially an equimolar mixture of mono- and dialkyl acid phosphates, as in Equation (2).

$$\text{P}_4\text{O}_{10} + 6 \text{ROH} \rightarrow 2 \text{(RO)}_2\text{POH} + 2\text{(RO)P(OH)}_2$$

Figure 2. The reaction of phosphoric anhydride and alcohol

<table>
<thead>
<tr>
<th>Dialkyl acid phosphate</th>
<th>Monoalkyl acid phosphate</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Dialkyl acid phosphate</th>
<th>Monoalkyl acid phosphate</th>
</tr>
</thead>
</table>
The Polyphosphate Content of Polyphosphoric Acid (PPA)

Phosphoric Anhydride and Polyphosphoric Acid in the Manufacture of Phosphoric Acid Esters

The Polyphosphate Content of Polyphosphoric Acid (PPA)

To be useful in these reactions, the phosphate must be present in the polyphosphate form. Since a portion of the phosphate content of polyphosphoric acid may be in the ortho form, when PPA issued in the production of phosphoric acid esters, we need to calculate the percentage of the polyphosphate in the acid (as % $P_4O_{10}$).

PPA strengths are usually expressed in terms of their percentage phosphoric acid (% $H_3PO_4$) content, and we can use this knowledge, coupled with Table (1) showing the orthophosphate content of PPA at various % $H_3PO_4$ strengths, to determine the actual polyphosphate ($P_4O_{10}$) content of the acid. Once this is done we can use Table (2), to calculate the mass of the hydroxyl [OH] radical needed to react with the polyphosphate.

It should be understood that it is common practice to add an excess of alcohol in order to drive this reaction to its completion.

There are three steps to calculating the $P_4O_{10}$ content of PPA:

Step (1) **Calculate the actual polyphosphoric acid content of the PPA, as % $H_3PO_4$.** This is done using Table (1) on page 2, subtracting the percent orthophosphoric acid content from the total per cent phosphoric acid content of the PPA. That is,

$$\% \text{ Polyphosphoric acids} = \% \text{ Total } H_3PO_4 - \% \text{ Orthophosphoric acid}$$

Step (2) **Convert the % Polyphosphoric acid expressed as % $H_3PO_4$ into its $P_4O_{10}$ equivalent.** This is done using the molecular weights of the $H_3PO_4$ (97.972) and $P_4O_{10}$ (283.89). It is given by the formula

$$\% P_4O_{10} = \frac{\% H_3PO_4 \times 283.89}{4 \times 97.972}$$

Step (3) **Determine the actual mass of $P_4O_{10}$ to be reacted.** This may be calculated using the following formula.

$$\text{Mass of } P_4O_{10} = \frac{\text{Mass of PPA} \times \% P_4O_{10}}{100}$$

**Example:** Assume 1000 pounds of 116% polyphosphoric acid is to be reacted. How much $P_4O_{10}$ is this equivalent to?

Step (1) $\%$ Total $H_3PO_4 - \%$ Orthophosphoric acid = $\%$ Polyphosphoric acids

Step (2) Converting 116% $H_3PO_4$ polyphosphoric acid to its $P_4O_{10}$ equivalent, we can use the equation in step (2):

$$\% P_4O_{10} = \frac{116 \times 283.89}{4 \times 97.972}$$

$$\% P_4O_{10} = 112.08\%$$

Step (3) Determining the actual mass of $P_4O_{10}$ to be reacted,

$$\text{Mass of } P_4O_{10} = \frac{1000 \times 112.08}{100} = 1120.80 \text{ pounds of } P_4O_{10}$$
\[
\%P_4O_{10} = \frac{\%H_3PO_4 \times 283.89}{4 \times 97.972} = 81.1926\% \ P_4O_{10}
\]

Step (3) Calculating the actual mass of $P_4O_{10}$ using step (3) and assuming 1000 pounds of $P_4O_{10}$,

\[
(Mass \ of \ P_4O_{10}) = \frac{(Mass \ of \ PPA) \times (\% \ P_4O_{10})}{100} = \frac{1000 \times 81.1926}{100} = 811.926 \text{ pounds}
\]

Once the mass of $P_4O_{10}$ has been determined we can use Table (2) to calculate the quantity of [OH] needed to perform the reaction.
REACTION CONDITIONS

Reaction Conditions

The presence of water as an impurity may lead to difficulties in phosphate ester production. For example, to the extent that water is present, reactions with $\text{P}_4\text{O}_{10}$ increase the monoalkyl production. With PPA, increased orthophosphate production occurs, and yields drop. To avoid these problems, extreme care should be taken to ensure that the equipment is free from water. Nitrogen purging of the pipes drums and valves is a common practice.

The reaction of either the anhydride or acid, is usually conducted between 35°C and 60°C. A major side reaction is the formation of olefins as in Equation (7).

\begin{equation}
6R_n\text{OH} + \text{P}_4\text{O}_{10} \rightarrow 6R_{n-2}\text{CH} = \text{CH}_2 + 4\text{H}_3\text{PO}_4
\end{equation}

Olefin

The temperature limits of the reaction are related to the ease of dehydration of the alcohol at the upper end, and the rate of reaction at the lower end. Primary alcohols may be reacted at temperatures of 60°C or higher, while secondary alcohols should be reacted at lower temperatures. Tertiary alcohols often dehydrate to olefins, even at temperatures below ambient. Generally, alcohols with the lowest available water content should be selected.

In actual practice, the acid or anhydride is added to the agitated, cooled reactor at a rate sufficient to control the temperature within the desired limits. In addition the anhydride must be added slowly enough to prevent clumping in the reactor. Once the components are substantially reacted, it is common practice to heat the batch for several hours to drive it towards completion.

Completion of the reaction is usually determined by the stability of the "Acid Number" to the first and second inflection points. The Acid Number is determined by titrating a sample of the reacting mix with sodium hydroxide according to the method outlined on page 11 of this bulletin. A description of Acid Numbers and their significance in phosphate ester production may be found on pages 8 and 9.
Hypophosphorous Acid and Color Formation

Phosphoric Anhydride and Polyphosphoric Acid in the Manufacture of Phosphoric Acid Esters

Hypophosphorous Acid and Color Formation

An additional limit on the reaction temperature is color formation. Higher temperatures may yield a darker colored product. The optimum reaction temperatures are those that offer the best compromise between color formation and reaction rate.

During the synthesis of phosphate esters using phosphoric anhydride and polyphosphoric acid, the use of hypophosphorous acid within a closed system will prevent or reduce discoloration, permit higher operating temperatures and allow faster reaction rates.

Generally between 0.03% to 0.50% hypophosphorous acid is used based on the batch weight. Lower molecular weight alcohols require more than those of higher molecular weight, and alcohols require more than ethoxylates.

When hypophosphorous acid is used, the reactor must be inerted with nitrogen, and a small purge maintained. The order of addition of the reactants should be alcohol, hypophosphorous acid (H$_3$PO$_2$) and lastly phosphoric anhydride. When the phosphoric anhydride is added, trace (in the low parts per million) quantities of phosphine (PH$_3$) will occur in the headspace and vent gases. The addition of a small quantity of hydrogen peroxide (a few tenths of a percent of the total batch weight) approximately one hour after the addition of the P$_4$O$_{10}$ is complete will oxidize any remaining phosphine.

Since phosphine is both toxic and spontaneously flammable, care should be taken to prevent any exposure to, or contact with, the gas vented during the process. The purge gases can be passed through a scrubber using a dilute solution of hydrogen peroxide to remove any residual phosphine before venting.

Alternatively, a vent gas incinerator may be utilized, along with a scrubber using water to remove the resulting acids.

Materials of Construction

Reactor

- 316L Stainless steel (SS), welding to be done with 316 ELCrods

Piping

- 316L SS, welded and flanged construction

Gaskets

- PTFE (polytetrafluoroethylene) sandwich type such as Envelon®
- PTFE envelope (jacketed) gasket such as Chemiseal® A-F, both manufactured by Garlock

Valves

- 316 SS body ball or plug-type, Teflon™ sleeve, seats and seals
Pumps

- Cenrifugal, 316, SS or Worthite®

Trade Names

Chemiseal®: Garlock, Mechanical Packing Div., Palmyra, NY.
Envelon®: Garlock, Mechanical Packing Div., Palmyra, NY.
Teflon®™: E.I. duPont Nemours & Co., Wilmington, DE.
Worthite®: Worthington Corp., Harrison, NJ.

DOT Rating

Because of their corrosive and strongly dehydrating nature, both phosphoric anhydride and polyphosphoric acid are classified as hazardous chemicals by the Department of Transportation. Product Safety Data Sheets detailing the hazards and recommending safe handling procedures are available from Innophos.
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Phosphate Esters and Their Acid Values (AV)*

Phosphate esters, as we have seen earlier in this bulletin, consist of mixtures of monoalkyl esters, dialkyl esters, phosphoric acid and unreacted alcohols. Both the type of alcohol (nonionic component) and the phosphorus product used in the preparation of the phosphate ester play a key role in determining its composition and function.

The titration of phosphate esters with an alkali such as caustic soda (NaOH), plotting pH against the addition of alkali, gives valuable information on the properties and composition of phosphate esters. This titration is known as the "Acid Value", and a method of determining it is given on pages 9 and 10 of this bulletin.

The acid value titration is in effect, a titration of the "phosphoric acid" which would result from the hydrolysis of the unreacted or partially unreacted polyphosphoric acid or phosphoric anhydride used in the reaction. In plotting the chart, three distinct end points become apparent (the inflection points of the pH titration curve). Two of the end points can be determined directly using a pH electrode. The third is determined indirectly after the addition of calcium chloride, when the acid generated by this, is titrated (see Chart 1).

The Acid Values, (#1, #2, or #3) are calculated by the equation:

\[ \text{Acid Value} = \frac{\text{ml NaOH} \times \text{Normality NaOH} \times 56.1}{\text{Weight of sample in grams}} \]

Each acid value (AV) results from the neutralization of one of the three acid groups (protons) of phosphoric acid. Phosphoric acid with three available protons would have all three acid values (see Chart 1). The monoalkyl ester will have acid values for #1 and #2, and the dialkyl ester only for #1.

Using this information, the mono-(MAE) and dialkyl ester (DAE) composition of the sample can be calculated as follows:

\[ \% H_3PO_4 = (AV_3 - AV_2) \times 0.00175 \]

\[ \% \text{Diester (DAE)} = 2(AV_1 - AV_2) \times (\text{MW DAE}) \times 0.0178 \]

\[ \% \text{Monoester (MAE)} = 0.0356 (AV_1 - AV_2 - AV_3) \times (\text{MW MAE}) \]
Analytical Procedures

The Determination of the Acid Number and the Percent Phosphoric Acid, Monoester and Diester in Phosphate Ester

Scope: This method is applicable to most phosphate esters, however, modification of pretreatments may be necessary.

Theory: A solution of the sample is titrated potentiometrically with a solution of sodium hydroxide, plotting a chart showing pH against ml of NaOH added. After the second inflection point on a chart is reached, a solution of calcium chloride is added and the solution is titrated to the third inflection point.

1. At the first inflection point, one H⁺ each from the free acid, the monoester and the diester has been titrated.
2. At the second inflection point, a second H⁺ from the free acid and the monoester, has been titrated.
3. At the third inflection point, the balance of the H⁺ from the free phosphoric acid has been titrated.

Inference: All other acids will interfere with this titration. Neutralization with base will interfere with quantification.

Apparatus:    Autotitrator
              Analytical Balance
              Standard Laboratory Glassware

Reagents: Sodium hydroxide (0.5N.).

Procedure:

1. Accurately weigh 5g ± 0.5g phosphate ester into a 250 ml beaker.
2. Add 100 ml of the appropriate solvent and stir to dissolve.
3. Titrte with 0.5N. sodium hydroxide to the second inflection point. (plotting pH against ml of NaOH added)
4. Add 5 ml of a 10% solution of calcium chloride.
5. Titrate to the third inflection point.
Table 1. The hydrolysis products of phosphoric anhydride.

<table>
<thead>
<tr>
<th>$\text{H}_3\text{PO}_4$ (%)</th>
<th>$\text{P}_2\text{O}_5$ (%)</th>
<th>Percentage Composition in Terms of the Constituent Polyphosphoric Acids**</th>
<th>High Poly</th>
<th>Tri-Meta</th>
<th>Tetra-Teta-Meta</th>
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<tbody>
<tr>
<td>93.0</td>
<td>67.4</td>
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<td>94.8</td>
<td>68.7</td>
<td>99.7, 0.3</td>
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<td></td>
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<tr>
<td>97.2</td>
<td>70.4</td>
<td>96.2, 3.8</td>
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<td>112.1</td>
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<td>1.46, 2.8, 3.74</td>
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<td>120.2</td>
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<td>121.3</td>
<td>87.9</td>
<td>0.50, 0.8, 1.56</td>
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</table>
**Phosphoric Acid Esters and Their Uses**

One of the important uses of polyphosphoric acid and phosphoric anhydride is in their reactions with alcohols, to form phosphoric acid esters (phosphate esters). Phosphate esters are mixtures of mono- and dialkyl phosphates together with various amounts of free alcohol and free phosphoric acid. The wide range of alcohols and reaction conditions possible in these processes, enables the production of numerous and diverse products, whose most common applications are listed below.

- Fiber and metal lubricants
- Pesticide emulsifiers
- Textile wet processing
- Cosmetic emulsifiers
- Flame proofing
- Corrosion inhibition
- Uranium recovery
- Sequestering agents in peracetic acid production
- Vinyl stabilizers (alkali metal salts)
- Antifreeze liquid components
- Industrial, household and dry cleaning detergents and surfactants (alkali metal or amine salts)

* Prepared by dehydration orthophosphoric acid; \(^b\) prepared by dissolving phosphoric anhydride in orthophosphoric acid.

** 1 = ortho-, 2 = pyrophosphate, etc.; high-poly. = material retained by resin and includes the 15-phosphoric acid when this was separated.
**Phosphoric Anhydride and Polyphosphoric Acid in the Manufacture of Phosphoric Acid Esters**

**Table 2.** Molar equivalent masses, Phosphoric anhydride: [OH]

<table>
<thead>
<tr>
<th>Mass P₄O₁₀</th>
<th>Number of Molar Equivalents of [OH]</th>
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<tbody>
<tr>
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<td>1</td>
</tr>
<tr>
<td>1</td>
<td>0.060</td>
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<tr>
<td>2</td>
<td>0.120</td>
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<tr>
<td>3</td>
<td>0.180</td>
</tr>
<tr>
<td>4</td>
<td>0.240</td>
</tr>
<tr>
<td>5</td>
<td>0.300</td>
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<tr>
<td>6</td>
<td>0.360</td>
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<tr>
<td>7</td>
<td>0.420</td>
</tr>
<tr>
<td>8</td>
<td>0.481</td>
</tr>
<tr>
<td>9</td>
<td>0.541</td>
</tr>
<tr>
<td>10</td>
<td>0.601</td>
</tr>
</tbody>
</table>

The mass of P₄O₁₀ reacting with an alcohol (in any unit of mass) is shown in the first column. The number of moles of [OH] radicals reacting with the P₄O₁₀ are listed at the head of the remaining columns. The equivalent mass of [OH] corresponding to the mass of P₄O₁₀ reacting and the number of molar equivalents of [OH] selected may be determined from the intersection of the appropriate row and column.

For example, suppose that you wish to react 500 pounds of P₄O₁₀ with three moles equivalent of [OH]. The intersection of the row representing 5 mass units of P₄O₁₀ and the column for 3 moles of [OH] shows that you need 0.901 mass units of [OH]. Multiplying this value by 100 would indicate that you need 90.1 pounds of [OH] for 500 lb. P₄O₁₀.

The exact amount of actual alcohol required can be determined by dividing this number by the decimal percentage (i.e. percent/100) of the [OH] in the alcohol you wish to use.

For example, with ethanol (C₂H₅OH,MW = 46), [OH] = 36.96% of the alcohol. Dividing 90.1 pounds by 0.3696 = 243.78, showing that 243.78 pounds of 100% ethanol is needed for this reaction.

**Reaction Conditions**

The presence of water as an impurity may lead to difficulties in phosphate ester production. For example, to the extent that water is present, reactions with P₄O₁₀ increase the monoalkyl production. With PPA, increased orthophosphate production occurs, and yields drop. To avoid these problems, extreme care should be taken to ensure that the equipment is free from water. Nitrogen purging of the pipes drums and valves is a common practice.

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Olefin

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The reactivity of phosphoric anhydride is discussed in some detail in the bulletin TIR 26, "Phosphoric Anhydride", available from Innophos. In this Technical Information Bulletin we will expand on phosphoric anhydride’s reactivity with alcohols.

An alcohol, ROH reacting with $P_4O_{10}$, splits one of the six P-O-P bonds as in Equation (1).

$$\begin{align*}
(P_2O_7) & \xrightarrow{\text{ROH}} (P_2O_7) \\
\text{O} & \xrightarrow{\text{P=O}} \text{O} \\
\text{P} & \xrightarrow{\text{P=O}} \text{P} \\
\text{O} & \xrightarrow{\text{P=O}} \text{O}
\end{align*}$$

splitting off the hydrogen atom from the organic radical and forming P-O-R and P-OH bonds. This is further illustrated in Figure (2) below.
A second alcohol radical may react with this molecule in one of several ways. The RO group may bond to a phosphorus (P) atom already bonded to an RO group, to one bonded to an (OH) group, or it may split an as yet unbroken P-O-P bond. Each of these reactions occurs, however the unbroken P-O-P group is attacked preferentially. This reaction may continue until all six P-O-P bonds are broken, when the product is essentially an equimolar mixture of mono- and dialkyl acid phosphates, as in Equation (2).

\[
(2) \ P_4O_{10} + 6 \ ROH \rightarrow 2 (RO)_2POH + 2(RO)P(OH)_2
\]

Figure 2. The reaction of phosphoric anhydride and alcohol.
**Phosphoric Anhydride and Polyphosphoric Acid in the Manufacture of Phosphoric Acid Esters**

**Figure 3.** Chromatoographic apparatus for the determination of total nonionics by ion exchange.

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Phosphoric Anhydride and Polyphosphoric Acid in the Manufacture of Phosphoric Acid Esters

Chart 1. Typical pH curves in the acid value titration of phosphate esters.

Phosphate Esters and Their Acid Values (AV)*

Phosphate esters, as we have seen earlier in this bulletin, consist of mixtures of monoalkyl esters, dialkyl esters, phosphoric acid and unreacted alcohols. Both the type of alcohol (nonionic component) and the phosphorus product used in the preparation of the phosphate ester play a key role in determining its composition and function.

The titration of phosphate esters with an alkali such as caustic soda (NaOH), plotting pH against the addition of alkali, gives valuable information on the properties and composition of phosphate esters. This titration is known as the "Acid Value", and a method of determining it is given on pages 9 and 10 of this bulletin.

The acid value titration is in effect, a titration of the "phosphoric acid" which would result from the hydrolysis of the unreacted or partially unreacted polyphosphoric acid or phosphoric anhydride used in the reaction. In plotting the chart, three distinct end points become apparent (the inflection points of the pH titration curve). Two of the end points can be determined directly using a pH electrode. The third is determined indirectly after the addition of calcium chloride, when the acid generated by this, is titrated (see Chart 1).

The Acid Values, (#1, #2, or #3) are calculated by the equation:

\[
(8) \quad \text{Acid Value} + \frac{(\text{ml NaOH}) \times (\text{Normality NaOH}) \times (56.1)}{(\text{Weight of sample in grams})}
\]

Each acid value (AV) results from the neutralization of one of the three acid groups (protons) of phosphoric acid. Phosphoric acid with three available protons would have all three acid values (see Chart 1). The monoalkyl ester will have acid values for #1 and #2, and the dialkyl ester only for #1.

Using this information, the mono-(MAE) and dialkyl ester (DAE) composition of the sample can be calculated as follows:

\[
(9) \quad \% H_3PO_4 = (AV3 - AV2) \times 0.00175
\]
(10)  % Diester (DAE) = 2(AV1 - AV2) x (MW DAE) x 0.0178

(11)  % Monoester (MAE) = 0.0356 (AV1 - AV2 - AV3) x (MW MAE)