

Phosphate Esters: Chemistry and Properties

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Phosphate esters are used in many textile applications because of the various surfactant properties they possess. Of the desirable surface active properties, alkali stability and wetting properties are key. This work relates the structure of a phosphate ester to these two properties.

Chemistry

Phosphate esters are part of a class of anionic surface active agents. The commercial products are complex mixtures of monoester, diester, free

Abstract

Several linear alcohol and linear alcohol ethoxylates were phosphated using P_2O_5 , and the analytical results for monoester, diester and free phosphoric acid content were determined as were wetting speed and alkali tolerance. Generally, the concentration of monoester and free phosphoric acid increased and the diester concentration decreased as the amount of ethylene oxide in the hydrophobe increased.

As the molecular weight of the hydrophobe increased, the wetting time also increased. The lowest molecular weight hydrophobe without ethylene oxide was the best wetter in the series of nonethoxylated species. As the molecular weight of the hydrophobe without ethylene oxide increased, the wetting time of the phosphated material increased.

A certain amount of ethylene oxide in the hydrophobe was necessary to give the phosphated material alkali tolerance. As the molecular weight of the hydrophobe being phosphated increases, the amount of ethylene oxide needed to develop alkali tolerance increases.

The silicone phosphate esters appeared to fit the anticipated values for alkali tolerance, when compared to the fatty phosphates, when their ethylene oxide content is considered.

KEY TERMS

Alcohol Ethoxy Phosphate
Alkali Stability
Phosphate Ester
Phosphation
Wetting

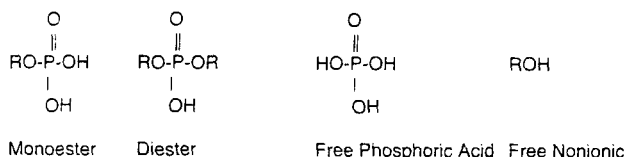


Fig. 1. Commercial products are complex mixtures of monoester, diester, free phosphoric acid and free nonionic material.

phosphoric acid and free nonionic as shown in Fig. 1.¹

Phosphating Reagent

Polyphosphoric acid and phosphorous pentoxide (P_2O_5) are generally the two different phosphating agents used commercially (Fig. 2). The selection of the phosphating reagent has an effect on the ratio of the components and on the functional properties of the finished product. Phosphorous pentoxide and a variety of linear alcohols and ethoxylates of linear fatty alcohols were chosen to determine the effect of alkyl group and amount of ethylene oxide on the resulting mono/di ratio and the amount of free phosphoric acid, as well as the effect on functional properties such as wetting and alkali tolerance.

Chemical Analysis

The phosphation product was analyzed for mono, di and free phosphoric acid concentrations using an acid value titration method. This method does not fully identify the product, but it does give valuable insights on the product's quality. The titration is run

Table I. Materials Phosphated

Fatty Alcohol	Phosphate Designation
Hexyl alcohol	Hexyl 0 EO phosphate
Octyl alcohol	Octyl 0 EO phosphate
Decyl alcohol	Decyl 0 EO
Decyl 2.5 mole ethoxylate	Decyl 2.5 EO
Decyl 6 mole ethoxylate	Decyl 6.0 EO
Decyl 8 mole ethoxylate	Decyl 8.0 EO
Tridecyl alcohol	Tridecyl 0 EO
Tridecyl 6.5 mole ethoxylate	Tridecyl 6.5 EO
Myristyl alcohol	Myristyl 0 EO phosphate
Myristyl 3 mole ethoxylate	Myristyl 3 EO phosphate
Myristyl 7 mole ethoxylate	Myristyl 7 EO phosphate
Myristyl 9 mole ethoxylate	Myristyl 9 EO phosphate
Myristyl 12 mole ethoxylate	Myristyl 12 EO phosphate
Dimethicone copolyol 3 mole ethoxylate	Silicone 3 phosphate
Dimethicone copolyol 8 mole ethoxylate	Silicone 8 phosphate

using a standardized solution of base—most commonly sodium hydroxide. There are three distinct endpoints in the titration and by evaluating each, information on product quality is obtained. Two endpoints can be deter-

Table II. Results of Acid Value Analysis for Monoester, Diester and Free Phosphoric Acid

	Monoester	Diester	Free Phosphoric Acid
Hexyl 0 EO phosphate	53.4	41.2	5.6
Octyl 0 EO phosphate	49.7	49.7	0.6
Decyl 0 EO phosphate	58.3	41.5	0.2
Decyl 2.5 EO phosphate	60.3	37.7	2.0
Decyl 6.0 EO phosphate	67.1	25.3	7.6
Decyl 8.0 EO phosphate	66.7	23.7	9.6
Tridecyl 0 EO phosphate	46.2	53.0	0.8
Tridecyl 6.5 phosphate	64.0	32.0	4.0
Myristyl 0 EO phosphate	58.2	40.7	1.1
Myristyl 3.0 EO phosphate	59.3	39.4	1.3
Myristyl 7.0 EO phosphate	59.0	36.1	4.9
Myristyl 9.0 EO phosphate	62.3	27.9	9.9
Myristyl 12.0 EO phosphate	67.7	17.8	14.5
Silicone 3 phosphate	50.3	46.7	3.0
Silicone 8 phosphate	63.4	30.9	5.7

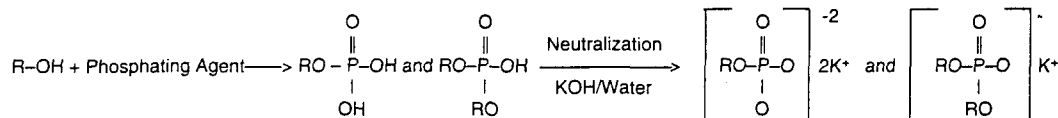


Fig. 2. Phosphation reaction.

Table III. Results of NaOH Titer Analysis

	Number of Carbons	NaOH Titer*
Hexyl 0 EO phosphate	6	Sp
Octyl 0 EO phosphate	8	Sp
Decyl 0 EO phosphate	10	Sp
Decyl 2.5 EO phosphate	10	4
Decyl 6.0 EO phosphate	10	8
Decyl 8.0 EO phosphate	10	8
Tridecyl 0 EO phosphate	13	Sp
Tridecyl 6.5 EO phosphate	13	4
Myristyl 0 EO phosphate	14	Sp
Myristyl 3.0 EO phosphate	14	Sp
Myristyl 7.0 EO phosphate	14	4
Myristyl 9.0 EO phosphate	14	4
Myristyl 12.0 EO phosphate	14	8
Silicone 3 phosphate	-	4
Silicone 8 phosphate	-	8

*Sp means split

mined directly by titration to a pH using a pH electrode. The third is determined indirectly after the addition of calcium chloride. The acid generated by the addition is titrated. The acid value (AV) calculations are shown in Eqs. 1-3.

$$AV1 = \frac{(\text{mL of NaOH to Point A})(\text{Normality})(56.1)}{(\text{Weight of sample in grams})} \quad \text{Eq. 1}$$

$$AV2 = \frac{(\text{mL of NaOH to Point B})(\text{Normality})(56.1)}{(\text{Weight of sample in grams})} \quad \text{Eq. 2}$$

$$AV3 = \frac{(\text{mL of NaOH to Point C})(\text{Normality})(56.1)}{(\text{Weight of sample in grams})} \quad \text{Eq. 3}$$

The three acid values result from the three types of phosphate protons available on each species. Species with three acid groups (i.e., phosphoric acid) have an AV1, AV2 and AV3. Those with two acid groups have an AV1 and AV2 (i.e., monoester), while those with only one acid group (i.e. diester) have only an AV1. It is then possible to calculate the monoester, diester and free phosphoric acid content. Table I summarizes phosphated

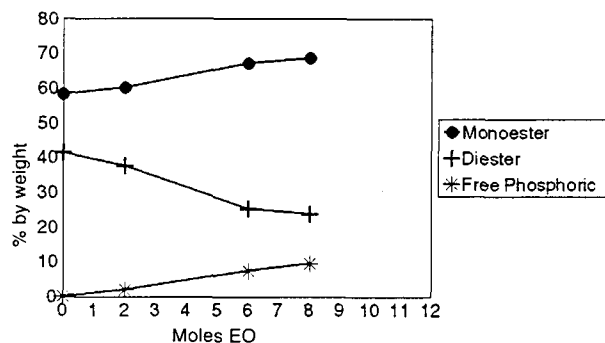


Fig. 3. Mono/diester ratio vs. moles of ethylene oxide for C₁₀ hydrophobe.

alcohols and ethoxylates, and gives the designation used to refer to the products. Table II summarizes the results of the analysis for monoester, diester and free phosphoric acid for the phosphates studied.

Properties

Alkali Stability

Alkali stability was evaluated by the NaOH titer method. The method was used to measure the concentration at which the phosphate ester remains clear in standard concentrations of NaOH. While exact numbers were not generated with this method, it served as a good screening method.

Three test solutions were prepared. NaOH was added at 4, 8 and 12% by weight. The solutions were verified by titration with standardized acid. Then, 10.0 g of each test solution was added to a test tube and 0.5 g of test phosphate ester was also added. The tubes were shaken. After 30 minutes, the tubes were observed for clarity. The highest concentration tube which remained clear was recorded as the NaOH titer. Results are presented in Table III.

Wetting Speed

The following solution was prepared and tested for wetting:

Material	% Weight
50% NaOH	8.0
Water	91.5
Test Phosphate Ester	0.5

A 0.5 cm denim disc was selected for the evaluation. Prior to the evaluation, the solution was heated to 160F. The amount of time it took for the disc to sink was recorded (Table IV). It should be noted that the test phosphate ester was placed into solution as the potassium salt.

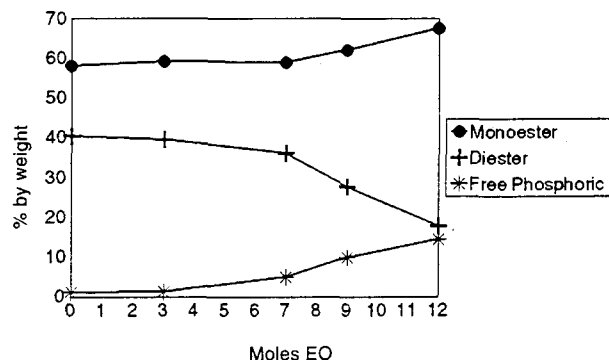


Fig. 4. Mono/diester ratio vs. moles of ethylene oxide for C₁₄ hydrophobe.

Table IV. Wetting Speed

	Carbons	Wetting Time (sec)
Hexyl 0 EO phosphate	6	5
Octyl 0 EO phosphate	8	17
Decyl 0 EO phosphate	10	28
Decyl 2.5 EO phosphate	10	8
Decyl 6.0 EO phosphate	10	23
Decyl 8.0 EO phosphate	10	33
Tridecyl 0 EO phosphate	13	34
Tridecyl 6.5 EO phosphate	13	29
Myristyl 0 EO phosphate	14	34
Myristyl 3.0 EO phosphate	14	30
Myristyl 7.0 EO phosphate	14	39
Myristyl 9.0 EO phosphate	14	49
Myristyl 12.0 EO phosphate	14	42
Silicone 8 phosphate	-	29
Silicone 4 phosphate	-	20

Results and Discussion

Product Composition

The concentration of monoester, diester and free phosphoric acid for the phosphate esters based on decyl alcohol and its ethoxylates are shown in Fig. 3. As the amount of ethylene oxide on the decyl alcohol hydrophobe was increased from zero to seven moles of ethylene oxide, the concentration of monoester and free phosphoric acid increased in an almost linear fashion. The diester content dropped as the amount of ethylene oxide on the hydrophobe increased. Since all hydrophobes were dried prior to phosphation, the increase was not attributed to the presence of water.

The concentration of monoester, diester and free phosphoric acid for the phosphate esters based on myristyl alcohol and its ethoxylates are shown in Fig. 4. As the amount of ethylene oxide on the myristyl alcohol hydrophobe was increased from zero to seven moles of ethylene oxide, the concentration of monoester and diester varied only slightly, but the trend was

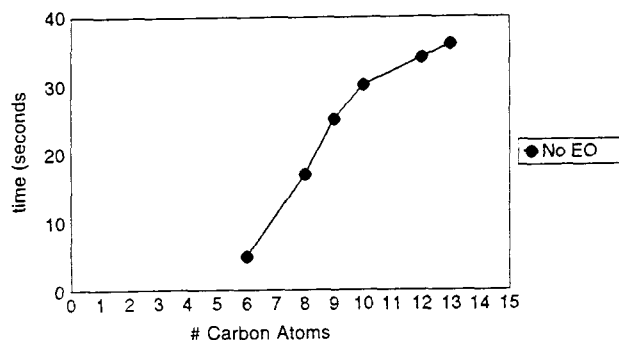


Fig. 5. Wetting speed of phosphate esters—number of carbon atoms in the hydrophobe vs. wetting time.

for less diester and more free phosphoric acid as the amount of ethylene oxide on the hydrophobe increased. Once the amount of ethylene oxide added reached over seven moles, a dramatic drop in diester and increase in monoester and free phosphoric acid resulted. Again, since all the hydrophobes were dried prior to phosphorylation, the increase was not attributed to the presence of water. It does appear however, that the more polar alcohol ethoxylates phosphate less readily, producing more monoester and free phosphoric acid than those phosphorylation reactions run using more hydrophobic fatty alcohols or fatty alcohol ethoxylates. It has been suggested that this affect may be related to steric hinderance.

Effect of Alkyl Group on Wetting Speed

As the molecular weight of the hydrophobe increased, the wetting time likewise increased. The lowest molecular weight hydrophobe (hexyl phosphate) without ethylene oxide was the best wetter in the series of nonethoxylated species. As the molecular weight of the hydrophobe without ethylene oxide was increased, the wetting time of the phosphorylated product increased (Fig. 5). This was true for hydrophobes having 6 to 14 carbon atoms.

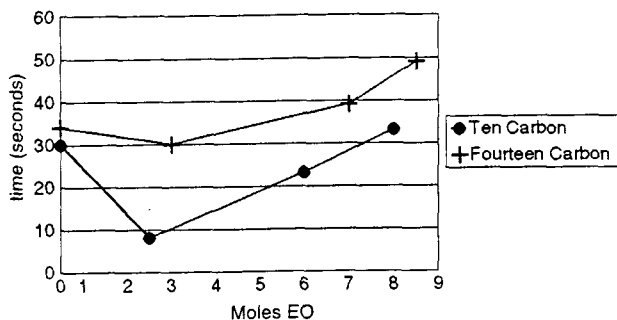


Fig. 6. Effect of ethylene oxide content on wetting speed.

Effect of Ethoxylation on Wetting Speed

The ethoxylated materials all reached their fastest wetting times with between two and three moles of ethylene oxide added within each set of hydrophobes. Two different phosphorylated hydrophobes plotted against the number of moles of ethylene oxide added to the hydrophobe, and the HLB of the alcohol ethoxylate are shown in Figs. 6 and 7, respectively. The HLB was calculated using % EO/5. The fastest wetting times fall within the same range—two to three moles of ethylene oxide. The lower the molecular weight of the hydrophobe, the faster the wetting time. What was not included in this investigation, but appears interesting, is a hexyl 2-3 mole ethylene oxide phosphate which would be predicted to have the best wetting time in the series, assuming the hexyl curve follows the decyl and myristyl curves.

The silicone phosphate esters appeared to fit the anticipated values for wetting, when compared to the fatty phosphates, when their ethylene oxide content is considered. It is anticipated that lower amounts of ethylene oxide would give improved results.

Effect of Alkyl Group on Alkali Tolerance

It appeared that a certain amount of ethylene oxide on the hydrophobe was

required to render the phosphorylated material alkali tolerant. As the molecular weight of the hydrophobe being phosphorylated increased, the amount of ethylene oxide required for alkali tolerance also increased. Decyl alcohol phosphate containing eight moles of ethylene oxide had an alkali titer of 8, while it took twelve moles of ethylene oxide on myristyl alcohol to obtain the same level of alkali tolerance (Figs. 8 and 9).

Effect of Ethoxylation on Alkali Tolerance

The greater the degree of ethoxylation, the more alkali tolerance was obtained. Few materials exhibited good alkali tolerance with less than six moles of ethylene oxide. It also appeared that as one attempts to increase the wetting speed, alkali tolerance decreased. Decyl alcohol phosphate containing six moles of ethylene oxide appeared to be a good compromise for both properties.

Alkali Tolerance of Silicone Phosphates

The silicone phosphate esters appeared to fit the anticipated values for alkali tolerance, when compared to the fatty phosphates, when their ethylene oxide content is considered.

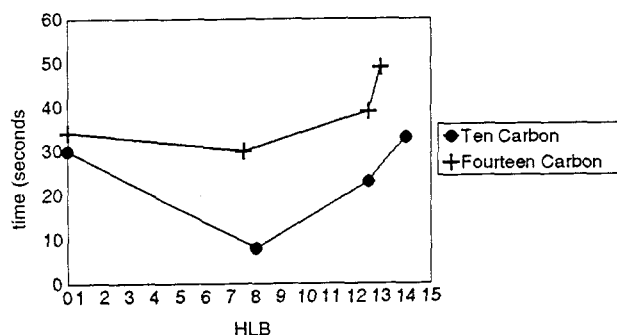


Fig. 7. Effect of HLB on wetting speed.

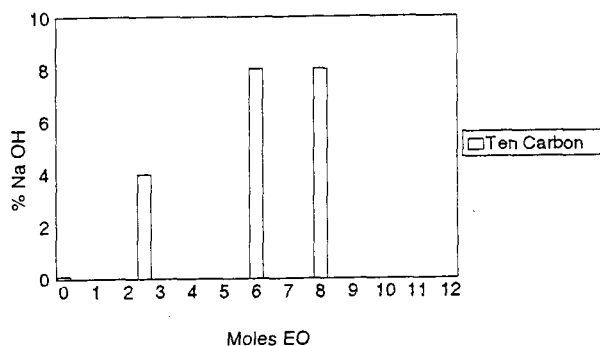


Fig. 8. Sodium hydroxide titer vs. moles of ethylene oxide in the C₁₀ starting hydrophobe.

Conclusions

The selection of a phosphate ester for a particular application depends on which properties and compromises of properties are desired. It is clear that one product does not give optimum wetting and alkali tolerance. Selection then must be based on choosing the best compromise.

Instrumental Methods

More recently, an instrumental method for the evaluation based on phosphorous NMR was used. The data provided from this technique has shed light on the structure and process control used to make phosphate esters. Not only does it give information on monoester, diester and free phosphoric acid content, it gives insight into the polymeric products which are present in low concentrations that until now were difficult to analyze. Typical values for structures are given in Table V. This technique gives a very clean first order spectra. It is believed that this technique will become very important in the future as access to the equipment and familiarity with the method become more common.

Acknowledgements

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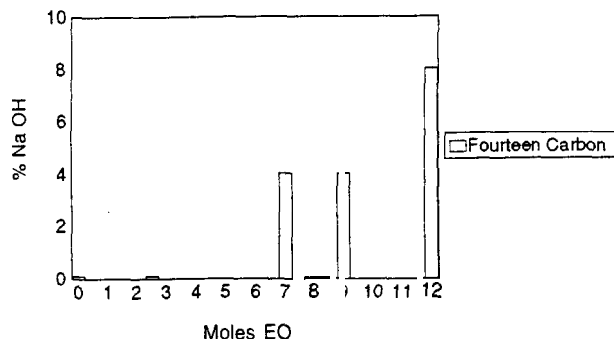


Fig. 9. Sodium hydroxide titer vs. moles of ethylene oxide in the C₁₄ starting hydrophobe.

Table V. Typical Phosphorous NMR Values for Structures

ppm	Structure	Description
2.9	$O=P(OH)_3$	Free phosphoric
1.8	$O=P(OH)_2(OR)$	Monoester
0.2	$O=P(OH)(OR)_2$	Diester
-1.1	$O=P(OR)_3$	Triester
-11.4	$\begin{array}{c} \text{HO}-\text{P}-\text{O}-\text{P}-\text{OH} \\ \quad \\ \text{OH} \quad \text{OR} \\ \text{O} \quad \text{O} \end{array}$	Polyphosphate monoester
-12.2	$\begin{array}{c} \text{HO}-\text{P}-\text{O}-\text{P}-\text{OH} \\ \quad \\ \text{OH} \quad \text{OR} \\ \text{O} \quad \text{O} \end{array}$	Polyphosphate monoester
-12.8	$\begin{array}{c} \text{RO}-\text{P}-\text{O}-\text{P}-\text{OR} \\ \quad \\ \text{OH} \quad \text{OH} \\ \text{O} \quad \text{O} \end{array}$	Polyphosphate diester
-13.5	$\begin{array}{c} \text{RO}-\text{P}-\text{O}-\text{P}-\text{OR} \\ \quad \\ \text{OH} \quad \text{OR} \end{array}$	Polyphosphate triester

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