Responsible Use of Polyphosphoric Acid (PPA) Modification of Asphalt Binders

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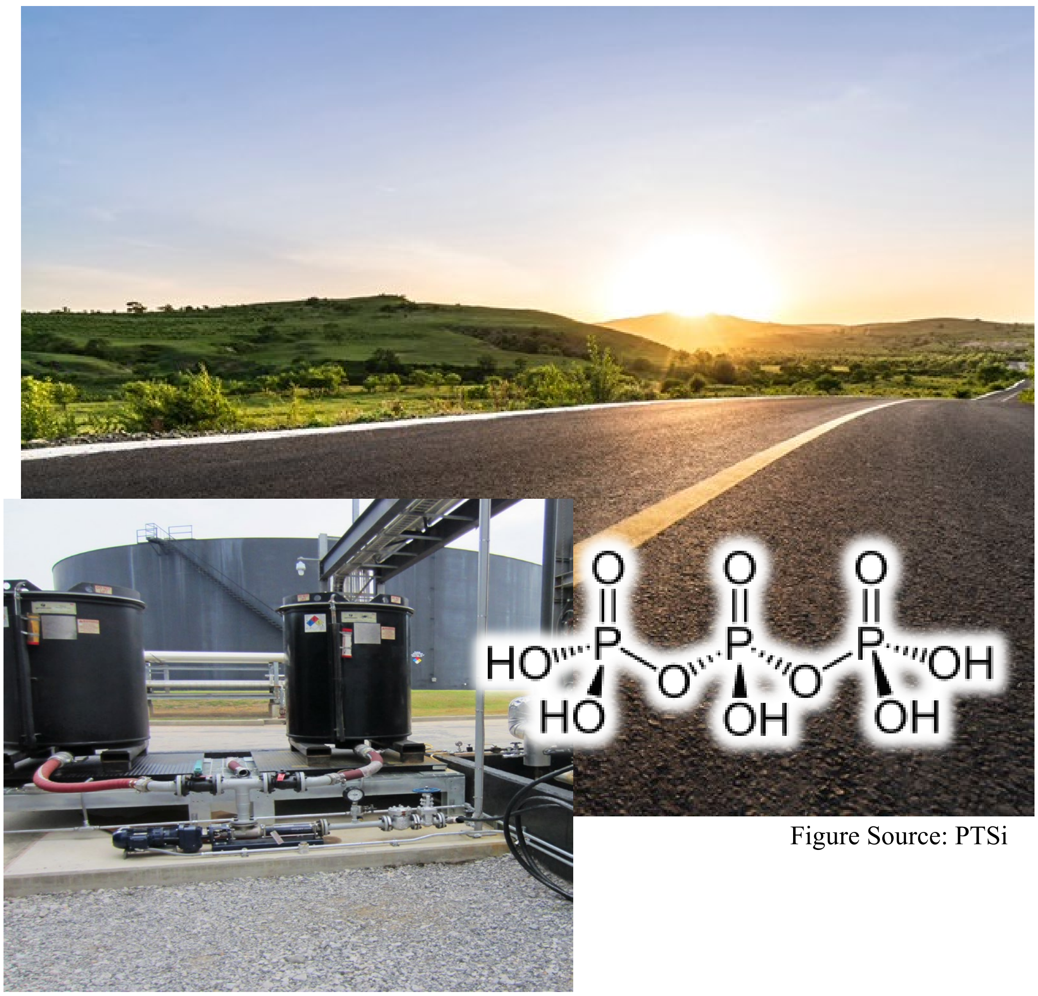

Figure Source: PTSi

U.S. Department of Transportation
Federal Highway Administration

FOREWORD

Polyphosphoric acid (PPA) has been used to chemically modify asphalt binders to improve high temperature rheological properties, without adversely affecting low temperature rheological properties, since the early 1970s.[1] Since the introduction of Superpave performance-grade (PG) binders, PPA has been used as an additive for adjusting rheological properties to meet PG specification parameters. PPA has also been used to modify asphalt binders that need an extended range between the high and low temperature performance requirements to meet PG specification limits. Since the early 1990s, PPA has also been used in combination with polymer modifiers in polymer modified asphalt binders to enhance the quality of paving grade asphalt binders. This report discusses use of PPA as an asphalt binder modifier and presents information on detection and quantification of PPA in asphalt binders.

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16. Abstract

Polyphosphoric acid (PPA) is a chemical modifier employed to improve high temperature rheological properties without adversely affecting low temperature rheological properties that has been used since the early 1970s.[1] Implementation of Superpave performance-grade (PG) asphalt binder acceptance specifications lead to use of PPA to aid in meeting rheological parameters of some polymer modified asphalt binders. PPA has also been used as a binder modifier to extend the asphalt binder range between the high and low temperature performance limits of the specification.

This report provides information to supplement existing publications communicating responsible use of Polyphosphoric Acid (PPA) in asphalt binder formulations. Information is provided on current uses of PPA, available qualitative and quantitative methods to detect presence of phosphorus in asphalt binders, and suggestions as to how phosphorus might indicate the presence and amount of PPA in asphalt binders.

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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		AREA		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		VOLUME		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
		NOTE: volumes greater than 1000 L shall be shown in m^3		
		MASS		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		TEMPERATURE (exact degrees)		
^oF	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	^oC
		ILLUMINATION		
fc	foot-candles	10.76	lux	lx
fl	foot-Lamberts	3.426	candela/m^2	cd/m^2
		FORCE and PRESSURE or STRESS		
lbf	poundforce	4.45	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
		LENGTH		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		AREA		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		VOLUME		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		MASS		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		TEMPERATURE (exact degrees)		
^oC	Celsius	1.8C+32	Fahrenheit	^oF
		ILLUMINATION		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		FORCE and PRESSURE or STRESS		
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AA	atomic absorption
AASHTO	American Association of State Highway and Transportation Officials
ASTM	ASTM International
cps	counts per second
DOT	Department of Transportation
DSR	dynamic shear rheology
EDXRF	energy dispersive X-ray fluorescence
FHWA	Federal Highway Administration
G*	complex modulus
H_3PO_4	phosphoric acid
ICP	inductively coupled plasma spectroscopy
LADOTD	Louisiana Department of Transportation and Development
$P2O_5$	phosphorus pentoxide
P_2S_5	phosphorus pentasulfide
$(P_4)_n$	red phosphorus
PAV	pressure aging vessel
PG	performance grade
PPA	polyphosphoric acid
ppm	parts per million
PTSi	Paragon Technical Services, Inc.
RTFO	rolling thin-film oven
SBS	styrene-butadiene-styrene
SHRP	Strategic Highway Research Program
TFHRC	Turner Fairbank Highway Research Center
UNR	University of Nevada, Reno
U.S.	United States
USPTO	United States Patent and Trademark Office
UTI	useful temperature interval
WDXRF	wavelength dispersive X-ray fluorescence
WYDOT	Wyoming Department of Transportation
XRF	X-ray fluorescence
ΔT_c	delta T_c
δ	phase angle

INTRODUCTION

Asphalt binder is used in more than 200 applications, including asphalt pavements.(2) Non-asphaltic additives are sometimes used in asphalt binder formulations to modify characteristics to enhance properties of end use performance. Examples of such additives include adhesion promoters, chemical additives, warm-mix additives, waxes, refined bio-oils, and polymers. Phosphorus pentoxide (P_2O_5) and polyphosphoric acid (PPA), a reactive oligomer or short chain polymer, are specific examples of non-asphaltic additives successfully used in asphalt binder formulations for more than seventy years.(1,3,4,5,6)

First use of PPA as a paving asphalt binder modifier was reported in 1973.(1) In this application, PPA modified asphalt was formulated to meet acceptance specifications set forth by the Louisiana Department of Transportation and Development (LADOTD) for a specific grade of asphalt. This specification required an asphalt having a penetration of 60–70 dmm at 25 degrees Celsius and a minimum viscosity of 3,600 poises at 60 degrees Celsius. Use of PPA modification allowed for maintaining the minimum penetration while increasing the desired viscosity.

Since the end of the Strategic Highway Research Program (SHRP)[1] in 1993 and implementation of the Superpave system performance grade (PG) binder specification in the mid 1990s, use of PPA to improve the overall properties of asphalt binders has increased.(8,9,10,11) Industry experience has shown that use of small amounts of PPA, as a tool for chemical modification of asphalt binders used alone or in conjunction with polymers, can improve high-temperature PG without adversely affecting the low-temperature PG. PPA modified asphalt binders can improve asphalt pavements performance.

Though use of PPA to enhance asphalt binder performance has a long track record, its use is often debated, possibly due to a lack of understanding of PPA benefits in improving asphalt binder performance. Some State Departments of Transportation (State DOTs) do not allow use of PPA as an asphalt binder modifier.(10) Other State DOTs have restrictions allowing use of PPA but limiting use through implementation of use levels, typically ranging for 0.25 percent to 1.5 percent. A 2022 review of published State DOT specifications showed fifteen States allowing usage or limited usage of PPA. A common maximum limit was 0.5 percent; however, some States allowed up to 0.75 and 1.0 percent maximums. Three States allowed usage with prior approval, twenty-nine States had no stated restrictions, and five States did not allow use of PPA.

BACKGROUND

Chemical modification of asphalt with phosphorus compounds like phosphorus pentoxide (P_2O_5), stable phosphorus sulfides, e.g., phosphorus pentasulfide (P_2S_5), and red phosphorus ($(P_4)_n$), was performed as early as 1948.(3) In 1973, the United States Patent and Trademark Office (USPTO) issued a patent to Stephen H. Alexander, US Patent number 3,751,278, described as, "Method of Treating Asphalt."(1) The object of the invention was to provide a treatment method to increase the viscosity of a vacuum distilled asphalt. More specifically, the object was to substantially increase viscosity of asphalt without significantly decreasing the asphalt penetration. Another object was

[1] The Strategic Highway Research Program (SHRP) was a 5-year, $150 million applied research program authorized by the Surface Transportation and Uniform Relocation Act of 1987.

to provide an asphalt composition with unique temperature susceptibility characteristics to meet the desired specification of the Louisiana State Highway Department.[1] The method describes mixtures of condensed derivatives of phosphoric acid with H_3PO_4 equivalents of greater than 100 percent used to modify asphalt binders.

Since its first reported use in the early 1970s, PPA modification has increasingly been used as a means of producing modified binders in North America. PPA provides the benefit of phosphoric acid and P_2O_5 modification without the risks associated with combining hot asphalt with water containing orthophosphoric acid, 85 percent phosphoric acid, or the handling risks associated with solid P_2O_5.[6] Similar to polymer modification, modification with PPA stiffens the asphalt at high temperature with improved resistance to permanent deformation and has no detrimental effects on low temperature properties.[6,8]

Phosphoric acid, also known as orthophosphoric acid, is typically a colorless liquid of 85 percent H_3PO_4 in water. PPA offered commercially is a mixture of orthophosphoric acid and oligomers, short chain polymers, of phosphoric acid, for example, pyrophosphoric acid, triphosphoric and higher acids and is sold on the basis of its calculated equivalent content of H_3PO_4. PPA is obtained by condensation of mono-phosphoric acid by hydration of P_2O_5. It is a viscous liquid at 25 degrees Celsius, from 840–60,000 centipoises depending on calculated equivalent content of H_3PO_4. PPA is a non-oxidant compound highly soluble in organic compounds. Asphalt applications typically use PPA with H_3PO_4 concentrations greater than 100 percent. The more common PPA used for asphalt applications, superphosphoric acid, is 105 percent. Orthophosphoric acid and PPA of H_3PO_4 concentrations less than 105 percent may be used but are generally avoided. PPA of lower H_3PO_4 than 100 percent contain water and present risk of foaming and corrosion in refinery or terminal. Table 1 presents the varied composition of mixed polyphosphoric acids which comprise mixtures having an H_3PO_4 equivalent of greater than 100 percent concentration.

Table 1. Composition of mixed polyphosphoric acids.(Table Source PTSi, Data Source (1,12))

Weight Percent		Percentage of the Strong Phosphoric Acids									
H_3PO_4	**P_2O_5**	**Ortho**	**Pyro**	**Tri-poly**	**Tetra-poly**	**Penta-poly**	**Hexa-poly**	**Hepta-poly**	**Octa-poly**	**Nona-poly**	**High-poly**
101	73.0	81.5	18.5	–	–	–	–	–	–	–	–
104	75.0	60.2	35.4	4.4	–	–	–	–	–	–	–
105.5	76.2	49.2	42.0	8.4	0.4	–	–	–	–	–	–
107	77.1	38.5	46.8	12.2	2.5	–	–	–	–	–	–
108.7	78.3	28.0	49.1	16.5	5.2	1.2	–	–	–	–	–
110	79.2	20.5	46.2	20.6	8.8	3.4	0.5	–	–	–	–
111.3	80.1	15.4	39.1	24.4	12.7	5.7	2.3	0.5	–	–	–
114.7	83.0	5.6	18.7	17.8	14.7	12.0	8.6	7.2	5.1	2.5	7.8
116.5	83.4	3.2	9.1	10.8	11.3	10.4	8.8	8.3	8.5	6.8	22.0

– not present.

Since the advent of the American Association of State Highway and Transportation Officials (AASHTO) M 320, *Standard Specification for Performance-Graded Asphalt Binder*, commonly referred to as the PG binder specification, PPA has been used in PG asphalt binders. AASHTO M 320, which is not a Federal requirement, assumes that the PG for large loads, or slow traffic, can be met by an increase in the higher temperature of the binder grade. For example, standard grade

PG64-22 for normal traffic is shifted to PG70-22 for slower heavy traffic and to PG76-22 for heavy standing or interstate conditions. With these different asphalt binder grades, the temperature range would respectively span 86, 92, and 98 degrees Celsius between the upper and lower PG limits, commonly referred to as the "Useful Temperature Interval" (UTI). Typically, PGs spanning more than 90 degrees Celsius are difficult to produce from conventional refining methods requiring asphalt binder modification. This is somewhat similar to the LADOTD AC-40 discussed in the introduction.

Polymer modification is the more common method of asphalt binder modification. However, asphalt binders that need minimal improvement of upper temperature performance limits may be modified using polyphosphoric acid (PPA) alone. The advantage of using PPA is that it improves the high temperature rheological properties without affecting the low temperature grade.

Since the implementation of the PG binder specification, PPA has also been used in combination with polymer modifiers in polymer modified asphalt binders to enhance the quality of paving grade asphalt binders.[8,9] When used in conjunction with polymer modification, PPA allows achievement of the specified acceptance limits (Dynamic Shear Rheology [DSR] parameter G*/sinδ, Elastic Recovery, etc.) while limiting the increase in asphalt binder rotational viscosity measured at 135 degrees Celsius. Results have shown an overall improvement of high temperature stiffness using a combination of PPA and SBS exceeding the additive stiffening improvement of each of the two materials.[11] Table 2 presents PG binder properties of a neat PG64-22 compared to the same base binder modified with PPA, styrene-butadiene-styrene block copolymer (SBS), and SBS plus PPA. These data show improvement in properties of the neat PG64-22 with improvements in the high, intermediate, as well as low temperature performance. The asphalt binder modified with a combination of SBS and PPA show the synergistic effect discussed as well as improvement of rotational viscosity results.

Table 2. Example of improved PG binder properties with PPA modification.(Table Source PTSi, Data Source (8,9))

Asphalt Binder	High Temperature Limit (Passing RTFO DSR G*/sinδ) (°C)	Intermediate Temperature Limit (Passing PAV DSR G*sinδ) (°C)	Low Temperature Limit (Passing m-value @ 60 sec) (°C)	Rotational Viscosity @ 135°C (Pa•s)	Elastic Recovery @ 60°C (Percent)	Useful Temperature Interval (UTI)
PG64-22 (Neat Base Binder)	66.1	26.1	–23.6	450	NT	89.7
PG67-22 (0.25 Percent PPA)	68.6	22.0	–24.1	477	NT	92.7
PG76-22 (4.75 Percent SBS)	76.8	22.0	–26.5	4,575	87.5	103.2
PG76-22 (3.4 SBS/0.25 PPA)	77.4	21.8	–27.1	2,235	85.0	104.5

Notes: DSR=dynamic shear rheometer; RTFO=rolling thin-film oven; PAV=pressure aging vessel; G*=complex modulus; δ=phase angle; NT=not tested.

COMMON CONCERNS

Some concerns about PPA are listed below and addressed in the following sections.

- What are potential adverse effects of PPA?
- How does one know if an asphalt binder contains PPA?
- How can one determine how much PPA is used in an asphalt binder?

Effects of PPA

While PPA modification has been compared to oxidation or "air blowing" of asphalt, PPA modification differs from air blowing. There is no asphalt oxidation, and PPA modified asphalt has good low temperature properties compared to air blown asphalt. Opposed to oxidation, PPA may exhibit anti-oxidative characteristics in asphalt binders.(3,4) PPA modification is a functional economic tool that can be used by binder suppliers to produce PG asphalt binders either with or without polymers depending on the specification and performance requirements. A common parameter used to identify additive effects on low temperature performance of asphalt binders is delta $T_{critical}$ or ΔT_c.(13,14) Research indicates that more negative values of ΔT_c appear to be correlated to non-load related cracking and other destresses related to poor relaxation properties.(15) Suggested considerations for potential ΔT_c specification criteria limit warning values of –2.5 degrees Celsius at 20-hour PAV aging and a failure limit value of –5 degrees Celsius at 40-hour PAV aging.(15) As previously stated, an advantage of PPA is improvement high temperature rheological properties without affecting low temperature theological properties. Therefore, addition of PPA to asphalt binders is not typically expected to have a detrimental effect on low temperature properties. Table 3 presents data from a PG64-22 asphalt binder modified with increasing levels of PPA. Table 3 indicates PPA modification can improve aging and enhance ΔT_c.

Table 3. Example of improved asphalt binder aging properties with PPA modification.(Table Source PTSi)

Asphalt Binder (PPA Dosage)	Original DSR G*/sinδ at 64°C [at 70°C] (kPa)	RTFO DSR G*/sinδ at 64°C [at 70°C] (kPa)	PAV DSR G*sinδ at 25°C (kPa)	BBR Stiffness 20 hour P/F Temp (°C)	BBR m-value 20 hour P/F Temp (°C)	ΔT_c 20 hour	BBR Stiffness 40 hour P/F Temp (°C)	BBR m-value 40 hour P/F Temp (°C)	ΔT_c 40 hour	Aging Index
PG64-22 (0.00)	1.85 [0.889]	4.12 [–]	4,470	–13.3	–14.1	0.8	–11.6	–10.7	–0.9	2.23
PG64-22 (0.25)	2.38 [1.13]	– [2.42]	4,670	–13.0	–14.7	1.7	–11.6	–10.8	–0.8	2.14
PG64-22 (0.50)	2.79 [1.33]	– [2.76]	4,500	–13.7	–15.2	1.5	–11.8	–10.8	–1.0	2.08
PG64-22 (1.00)	3.75 [1.80]	– [3.71]	4,180	–14.4	–16.0	1.6	–13.1	–12.5	–0.6	2.06

Notes: DSR=dynamic shear rheometer; BBR=bending beam rheometer RTFO=rolling thin-film oven; PAV=pressure aging vessel; G*=complex modulus; δ=phase angle; P/F=Pass/Fail; –not measured.

Data presented in Table 2 and Table 3 are in line with findings from previous laboratory studies. The stiffening effect and improved aging of PPA is crude source dependent, with anywhere from 0.5 to 3.0 percent of PPA needed to increase the binder grade.(9,10,11,16)

Increased moisture damage protentional can be of concern when PPA modified asphalt binders are used. Several laboratory studies have evaluated the moisture damage potential of mixtures produced with PPA modified asphalt binders.(9,10) Asphalt mixture testing in these studies indicated that moisture damage potential of mixtures with PPA modified asphalt binder was not noted with modification rates of 1.0 to 1.5 percent or greater for certain asphalt-aggregate combinations. Nonetheless, an increase in moisture damage potential was not noted with use levels below 1.0 percent.(16) Reported findings suggest that PPA modified asphalt binders can mitigate moisture damage potential with amine, hydrated lime, and phosphate ester anti-strips, results of which are asphalt and aggregate dependent. Field testing supports these findings with no negative performance related to PPA asphalt binder modification.(16) Typical asphalt mixture design and verification testing, including moisture damage testing, is sufficient for the PPA asphalt binder modification levels discussed. PPA asphalt binder modification levels greater than about 1.5 percent may require additional evaluation to determine adverse or deleterious effects due to interactions between PPA modified asphalt binder, aggregates, or other asphalt additives in the mixture.

PPA Detection

It is not possible to determine the presence of or measure the content of H_3PO_4 or PPA in asphalt binder.(17) However, since asphalt binder does not naturally contain phosphorus, the assumption could be made that asphalt binder containing phosphorus may contain PPA. In this case it would then be possible to calculate the theoretical content of PPA used to modify the asphalt binder.

Wet chemistry qualitative methodologies are available to determine the presence of phosphorus in organic compounds. However, these methodologies are primarily used for non-oil or non-petroleum compounds. A common method uses ammonium molybdate. In this method the organic compound is heated with an oxidizing agent, typically nitric acid, to convert the phosphate to phosphoric acid. The resulting phosphoric acid is boiled with ammonium molybdate yielding a precipitate of ammonium phosphomolybdate and a yellow coloration indicating the presence of phosphorus. It may be apparent why this method may not be particularly applicable to asphalt binder as any yellow coloration would be masked by the asphalt binder.

Asphalt researchers at the FHWA Turner-Fairbank Highway Research Center (TFHRC) developed a wet chemistry methodology to detect the presence of phosphorus in asphalt binder. This methodology was later adopted as AASHTO T 377, *Standard Method of Test for Detecting the Presence of Phosphorus in Asphalt Binder*.(18) Use of AASHTO methods and specifications are not a Federal requirement.

In this method, phosphorus present in the asphalt binder is extracted using butyl alcohol, and the extracted phosphorus is transferred to an aqueous phase. If phosphorus is present, treating this aqueous phase with ammonium molybdate, antimony potassium tartrate, and ascorbic acid will yield an antimony-phospho-molybdate complex and a blue color.

Figure 1 shows the results obtained from the AASHTO T 377 acid detection test; the control sample (a) (PG64-22) does not contain PPA. Sample (b) (PG64-22 plus 0.5 percent PPA) and sample (c) (PG64-22 plus 0.5 percent PPA and 0.5 percent liquid antistrip additive) both contain PPA, which is indicated by the blue color as described in the test method. It is of importance to note that this is not a quantitative method but a qualitative method which only determines the presence of phosphorus, it is not specific to PPA. A positive result only indicates the presence of phosphorus that may be from other sources than PPA.

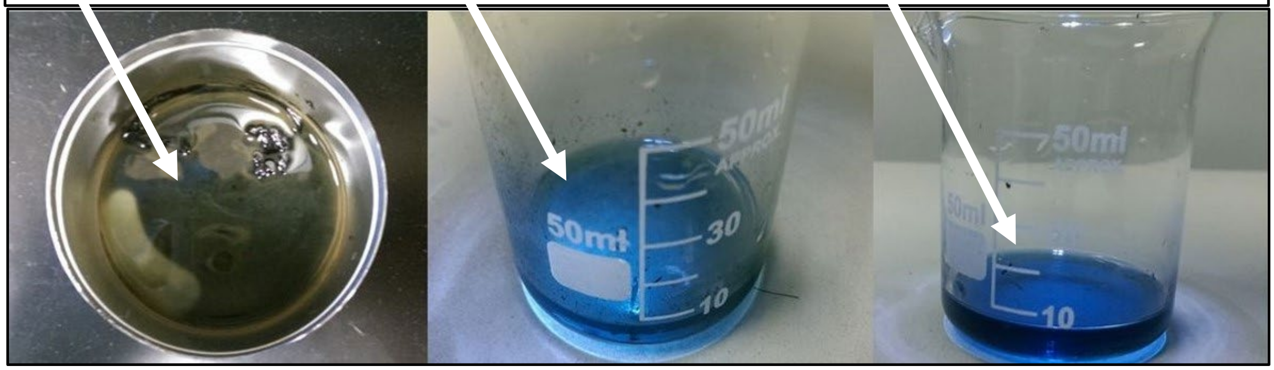

Figure 1. Phosphorus detection test results (a) negative, no phosphorus, (b) and (c) both positive detections of phosphorus. (Figure source (19))

PPA Quantification

The qualitative methods discussed have limited to no function as a quantitative tool in determining the amount of phosphorus in asphalt; however, instrumental quantitative methods for determination of phosphorus in asphalt do exist. Several instrumental analytical approaches are available for determination and quantification of phosphorous in asphalt binders. Such analytical approaches include graphite furnace atomic adsorption spectroscopy (Furnace AA),[(20)] inductively coupled plasma spectroscopy (ICP),[(,21,22)] energy dispersive x-ray fluorescence spectroscopy (EDXRF),[(23)] and wavelength dispersive x-ray fluorescence spectrometry (WDXRF).[(24)] This discussion will focus on x-ray fluorescence. EDXRF and WDXRF will be collectively referred to simply as x-ray fluorescence (XRF), both approaches can be used for asphalt binder analysis. In comparison, WDXRF instruments offer better signal intensity and resolution, however, this comes at a considerable comparative instrument investment, and longer data acquisition time that creates a risk of overheating samples. EDXRF instruments may be more suitable for asphalt binder analysis at considerable reduced investment, while providing decreased data acquisition time and reduced sample heating. EDXRF instruments are available in both benchtop and handheld versions. Handheld instruments, while unique, may not be the more practical approach for asphalt binder analysis.

All instrumental methods discussed are capable of identifying the presence of and determining phosphorous content in asphalt binders. Some may be more suitable than others. For example, sample preparation for AA and ICP requires reducing the asphalt to sufficient viscosity to be sprayed through a nebulizer into a flame. Compared to the XRF approach, this is a disadvantage as the XRF approach requires no sample preparation allowing phosphorus to be directly determined in the asphalt matrix as received. Standardized XRF methods are available for determining the amount of phosphorus in oil matrices,[(23,24)] however, there are no available standardized XRF methods for determination of phosphorus in an asphalt matrix. In fact, standardized methods for determining phosphorus in asphalt matrices with AA or ICP are non-existent as well. Some suppliers and State DOTs have developed XRF methods for determination of phosphorus in asphalt matrices.[(17,25,26)] These methods typically use existing methods for determination of phosphorus in other matrices as the starting point for preparing samples. Considering the stated disadvantages of AA and ICP and that some State DOTs and suppliers have developed analytical methods for asphalt binders, the remainder of this discussion will focus on EDXRF.

EDXRF can be used to analyze many types of matrices including solid, liquid, powder, etc. The elemental range typically includes sodium to uranium on the periodic table. The concentration range is typically from (sub) ppm levels to 100 percent. The elements with high atomic numbers have better detection limits than the lighter elements with low atomic numbers. In an EDXRF X-ray produced by the source, an X-ray tube, irradiates the sample. The elements present in the sample will emit fluorescent X-ray radiation with discrete energies that are characteristic for these elements. By measuring the sample's radiation energies, it is possible to determine which elements are present (qualitative analysis); therefore, determination of phosphorus presence in asphalt binder is a straightforward procedure. By measuring the intensities of the emitted energies, it is possible to determine how much of each element is present in the sample (quantitative analysis); nonetheless this method is somewhat more involved.

XRF instruments do not normally require frequent calibration; however, calibration for specific analysis method elements is important upon initial implementation of specific analysis methods. Instruments should be calibrated in accordance with manufacturer's recommendations. Custom prepared calibration standards for elements critical to asphalt analysis (calcium, copper, molybdenum, phosphorous, sulfur, and zinc) are readily available from commercial sources. Calibration is also important when analysis-critical components, such as X-ray source or detector, of the instrument are maintained or replaced.

In analytical chemistry, a calibration curve, also known as a standard curve, is a general method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples of known concentration. The calibration or standard curve is a plot of how the instrumental response changes with the concentration of the substance to be measured. This is the method proposed to be employed for determination of the estimated concentration of PPA in asphalt binder samples.

After ensuring instrument operation and calibration, the first step in asphalt binder analysis is preparation of an asphalt binder calibration curve specific to the element of interest. In the current case the element of interest is phosphorous or more specifically, PPA. In the asphalt binder calibration curve step PPA modified asphalt binder blends are prepared by addition of PPA to non PPA containing asphalt binder. PPA modified asphalt binders are prepared with increasing quantities of PPA ranging from zero to a desired maximum depending on asphalt binder specification limits or expected use levels. Limiting the total number of calibration samples reduces the number of XRF runs. An eleven-point calibration curve consisting of a sample of neat asphalt binder, or no PPA, and ten samples of this binder modified with equally spaced increasing loading of PPA to a target maximum is suggested. Since some State DOTs limit use levels to less than 1.0 percent, and not many asphalt binders require more than about 1.2 percent to change one full PG, an acceptable range might be 0.0 to 1.0 percent in 0.1 percent increments. Figure 2 presents a calibration curve PG64-22 modified with PPA (105 percent) with eleven-point loadings from 0.0 to 1.0 percent in 0.1 percent increments as described.

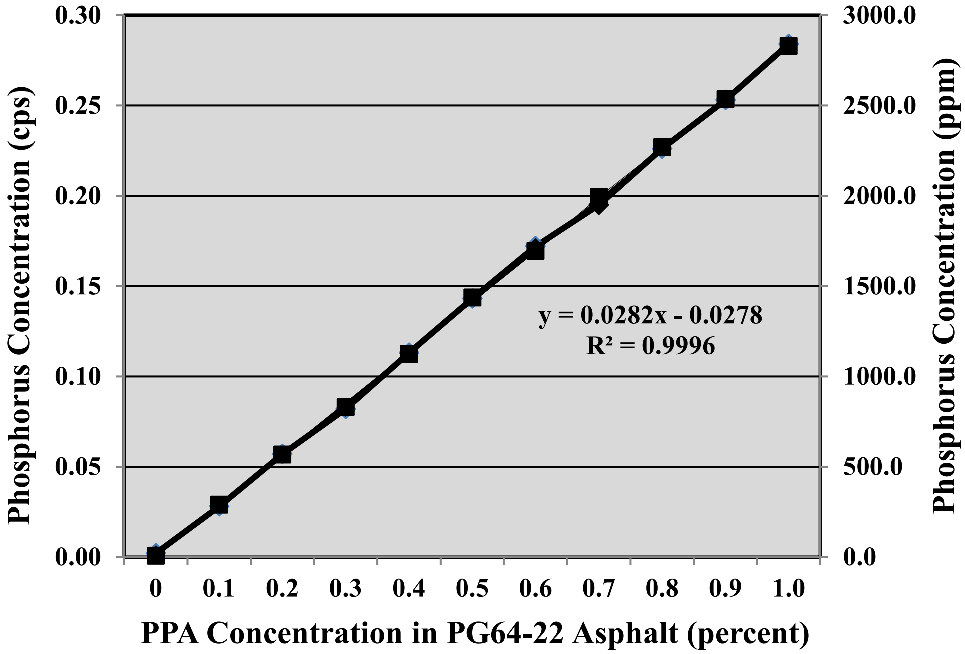

Figure 2. EDXRF calibration curve for PG64-22 asphalt binder containing PPA loadings from 0.0 to 1.0 percent. (Figure source PTSi)

To cover greater ranges, increments could be varied maintaining eleven-points of calibration. For example, 0.0 to 1.5 percent or 0.0 to 2.0 percent. Table 4 provides an example of points on an eleven-point calibration curve for a range up to 2.0 percent.

Table 4. Points of calibration curve for each base asphalt. (Table Source PTSi)

Percent PPA	Weight of Asphalt Binder (g)	Weight of PPA (g)	Total Weight (g)
0.0	100.0	0.0	100
0.1	99.9	0.1	100
0.2	99.8	0.2	100
0.3	99.7	0.3	100
0.4	99.6	0.4	100
0.6	99.4	0.6	100
0.8	99.2	0.8	100
1.0	99.0	1.0	100
1.4	98.7	1.3	100
1.6	98.4	1.6	100
2.0	98.0	2.0	100

Instrumental quantification methods are limited by the accuracy and effectiveness of the calibration generated. With any instrumental method used to quantify phosphorus and estimate PPA content in asphalt binders, it is important to consider the impact of significant changes in binder source or chemistry on the effectiveness of the calibration curve. For example, overlapping of fluorescing energies of phosphorus and sulfur caused by asphalt binders with higher concentrations of sulfur may confound or interfere with accurate determination of the amount of phosphorus in a sample.[17] Spectral overlap of sulfur on phosphorus can be lessened through use of beam filters. To address possible confounding of phosphorus concentration determination, at least four base asphalts with sulfur content ranging from 2.0 to 6.0 percent should be considered in development of calibration curves. A calibration curve using linear regression is obtained after the analysis of the prepared calibration standards in the XRF spectrometer and plotting intensity readings in terms of counts per second (cps) versus concentration in percent phosphorus as PPA. This is done for each of the base asphalt binders used in preparation of calibration samples. Accuracy is improved with a correlation coefficient of 0.9950 or better.

Evaluation of unknown samples is straightforward; the samples are analyzed in the same manner used for analyzing the samples prepared for development of calibration curves and the percent phosphorus as PPA is estimated using the prepared calibration curves.

SUMMARY

Polyphoshoric Acid (PPA) is a non-asphaltic reactive oligomer or short chain polymer that has been used in asphalt binder formulations for more than seventy years. First reported use of PPA as a paving asphalt binder modifier was in 1973. Since the end of the SHRP in 1993 and implementation of the SuperPave PG binder specification in the mid 1990s, use of PPA to improve the overall properties of asphalt binders has increased. Industry experience has shown that use of small amounts of PPA, as a tool for chemical modification of asphalt binders used alone or in conjunction with polymers, can improve high-temperature PG without adversely affecting the low-temperature PG.

Use of PPA to enhance performance of asphalt binders has a long track record; however, its use is often debated. Some State DOTs do not allow use of PPA as an asphalt binder modifier; others allow restricted use. A common maximum limit is 0.5 percent with some States allowing up to 0.75 and 1.0 percent maximums.

This report has discussed effects of PPA on asphalt binder properties and performance as well as methods to detect the presence and amount of PPA. Indications are that PPA improves high temperature performance of asphalt binder without adversely effecting asphalt low temperature properties or aging performance. In fact, use of PPA is shown to possibly provide improved binder aging performance. Presence of PPA can be indicated through chemical tests or via instrumental analysis. Instrumental methods are available to efficiently quantify dosage levels of PPA in asphalt binders.

ADDITIONAL INFORMATION

Available literature may help address issues such as use level limits in PPA modification of asphalt binders, performance characteristics of PPA modified asphalt binders with respect to multiple stress creep and recovery (MSCR) testing, and moisture sensitivity. The following list provides additional information about PPA modified asphalt binders:

- Asphalt Institute Publication IS-220: "*Polyphosphoric Acid Modification of Asphalt*"

- Association of Asphalt Paving Technologists Symposium, “Polyphosphoric Acid Modification,” March 2010
- Federal Highway Administration, TechBrief: “The Use of Performance Asphalt Binder Modified with Polyphosphoric Acid (PPA),” March 2012
- Applied Research Associates, Inc., Report No. 0001946-1: “Performance of Asphalt Mixtures Containing Polyphosphoric Acid,” September 2014
- Transportation Research Board, National Cooperative Highway Research Program (NCHRP) Synthesis 511: “Relationship Between Chemical Makeup of Binders and Engineering Performance,” (2017)

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