

# The Use of Phosphoric Acid to Stiffen Asphalt Binders

PUBLICATION NO. FHWA-HRT-14-086

NOVEMBER 2014



U.S. Department of Transportation  
**Federal Highway Administration**

Research, Development, and Technology  
Turner-Fairbank Highway Research Center  
6300 Georgetown Pike  
McLean, VA 22101-2296

## FOREWORD

*The Use of Phosphoric Acid to Stiffen Hot Mix Asphalt Binders* provides guidelines for the use of the different commercially available grades of phosphoric acid to enhance the high temperature performance grade of asphalt binders derived from different crude oil sources for use in hot mix paving applications. The expected effect on pavement life, in terms of oxidative aging, moisture resistance, fatigue, rutting, and use with different types of aggregates are presented. Analytical procedures for detecting the presence of phosphoric acid using X-ray fluorescence spectroscopy as well as a simple rapid test method are included.

The guidelines presented in this report will be useful to producers of asphalt binders, hot mix paving contractors, State departments of transportation, and local highway agencies.

Jorge E. Pagán-Ortiz  
Director, Office of Infrastructure  
Research and Development

### Notice

This document is disseminated under the sponsorship of the U.S. Department of Transportation in the interest of information exchange. The U.S. Government assumes no liability for the use of the information contained in this document.

The U.S. Government does not endorse products or manufacturers. Trademarks or manufacturers' names appear in this report only because they are considered essential to the objective of the document.

### Quality Assurance Statement

The Federal Highway Administration (FHWA) provides high-quality information to serve Government, industry, and the public in a manner that promotes public understanding. Standards and policies are used to ensure and maximize the quality, objectivity, utility, and integrity of its information. FHWA periodically reviews quality issues and adjusts its programs and processes to ensure continuous quality improvement.

## TECHNICAL REPORT DOCUMENTATION PAGE

1. Report No. FHWA-HRT-14-086	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle The Use of Phosphoric Acid to Stiffen Hot Mix Asphalt Binders		5. Report Date November 2014	
		6. Performing Organization Code	
7. Author(s) Terence Stanley Arnold CChem FRIC		8. Performing Organization Report No.	
9. Performing Organization Name and Address Federal Highway Administration Pavement Materials Team (HRDI-10) 6300 Georgetown Pike McLean, VA 22101-2296		10. Work Unit No.	
		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address Office of Infrastructure Research and Development Federal Highway Administration 6300 Georgetown Pike McLean, VA 22101-2296		13. Type of Report and Period	
		14. Sponsoring Agency Code HRDI-10	
15. Supplementary Notes			
16. Abstract This document offers guidelines for the use of phosphoric acid to stiffen asphalt binders for hot mix paving applications. Data are presented on the likely effect on pavement life, moisture resistance, and use with limestone aggregates and liquid amine antistripping additives. Analytical methods for the detection of phosphoric acid in asphalt binders are also presented. Asphalt producers, hot-mix paving contractors, and State departments of transportation are the main audiences.			
17. Key Words Asphalt, aggregate, phosphoric acid, superphosphoric acid, polyphosphoric acid, lime, antistripping additives, X-ray fluorescence spectroscopy		18. Distribution Statement No restrictions. This document is available to the public through the National Technical Information Service, Springfield, VA 22161. <a href="http://www.ntis.gov">http://www.ntis.gov</a>	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 87	22. Price

Form DOT F 1700.7 (8-72)

Reproduction of completed page authorized

## SI\* (MODERN METRIC) CONVERSION FACTORS

### APPROXIMATE CONVERSIONS TO SI UNITS

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

### APPROXIMATE CONVERSIONS FROM SI UNITS

Symbol	When You Know	Multiply By	To Find	Symbol
<b>LENGTH</b>				
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
<b>AREA</b>				
mm <sup>2</sup>	square millimeters	0.0016	square inches	in <sup>2</sup>
m <sup>2</sup>	square meters	10.764	square feet	ft <sup>2</sup>
m <sup>2</sup>	square meters	1.195	square yards	yd <sup>2</sup>
ha	hectares	2.47	acres	ac
km <sup>2</sup>	square kilometers	0.386	square miles	mi <sup>2</sup>
<b>VOLUME</b>				
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m <sup>3</sup>	cubic meters	35.314	cubic feet	ft <sup>3</sup>
m <sup>3</sup>	cubic meters	1.307	cubic yards	yd <sup>3</sup>
<b>MASS</b>				
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
<b>TEMPERATURE (exact degrees)</b>				
°C	Celsius	1.8C+32	Fahrenheit	°F
<b>ILLUMINATION</b>				
lx	lux	0.0929	foot-candles	fc
cd/m <sup>2</sup>	candela/m <sup>2</sup>	0.2919	foot-Lamberts	fl
<b>FORCE and PRESSURE or STRESS</b>				
N	newtons	0.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in <sup>2</sup>

\*SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380.  
(Revised March 2003)

## TABLE OF CONTENTS

<b>CHAPTER 1. INTRODUCTION</b> .....	1
<b>BACKGROUND</b> .....	1
<b>SOME PHOSPHORIC ACID CHEMISTRY</b> .....	2
<b>HOW PHOSPHORIC ACID IS USED TO MODIFY ASPHALT BINDERS</b> .....	3
<b>RESEARCH PLAN</b> .....	3
Analysis.....	3
Effect of Acid Grade and Binder Types .....	4
Aging.....	4
Reaction With Lime and Limestone Aggregates .....	4
Moisture .....	4
<b>CHAPTER 2. ANALYTICAL METHODS</b> .....	7
<b>QUANTITATIVE ANALYSIS OF ASPHALT BINDERS FOR PHOSPHORIC ACID</b> .....	7
<b>A SIMPLE QUALITATIVE TEST TO DETECT THE PRESENCE OF PHOSPHORIC ACID IN ASPHALT BINDERS</b> .....	12
Reagents .....	12
Procedure .....	13
<b>SATURATE, AROMATIC, RESIN, AND ASPHALTENE ANALYSIS OF ASPHALT BINDERS MODIFIED WITH PHOSPHORIC ACID</b> .....	14
Findings.....	19
<b>HOW DOES THE PHOSPHORIC ACID REACT WITH THE BINDER?</b> .....	21
<b>MAJOR CONCLUSIONS FROM CHAPTER 2, ANALYTICAL METHODS</b> .....	22
<b>CHAPTER 3. EFFECT OF ACID GRADE AND BINDER TYPE</b> .....	23
<b>EFFECT OF ASPHALT TYPE</b> .....	23
<b>EFFECT OF PHOSPHORIC ACID GRADE</b> .....	24
<b>EFFECT OF TANK AGING AT 165 °C</b> .....	26
<b>CONCLUSIONS</b> .....	28
<b>CHAPTER 4. AGING</b> .....	29
<b>DOES PHOSPHORIC ACID CATALYZE ASPHALT OXIDATION IN HOT MIX ASPHALT BINDERS?</b> .....	29
<b>CONCLUSIONS</b> .....	33
<b>CHAPTER 5. LIME AND LIMESTONE AGGREGATES</b> .....	35
<b>LIME</b> .....	35
<b>LIMESTONE</b> .....	38
<b>CONCLUSIONS</b> .....	41
<b>CHAPTER 6. MOISTURE</b> .....	43
<b>EFFECT OF WATER ON ASPHALT MASTICS WITH AND WITHOUT PHOSPHORIC ACID</b> .....	43
Conclusions.....	45
<b>EFFECT OF WATER ON NEAT ASPHALT BINDERS</b> .....	46
Conclusions.....	52

<b>EFFECT OF PHOSPHORIC ACID MODIFICATION IN THE USE OF ANTISTRIP ADDITIVES .....</b>	<b>52</b>
Conclusions .....	61
<b>APPENDIX .....</b>	<b>65</b>
<b>IATROSCAN® TEST METHOD FOR SARA ANALYSIS OF ASPHALT     BINDERS.....</b>	<b>65</b>
Apparatus .....	65
Asphaltene/Material Separation .....	65
Iatroscan® TH-10 Procedure .....	66
Report.....	67
<b>EFFECT OF OVEN AGING 12 DAYS AT 165 °C ON ASPHALT STIFFNESS.....</b>	<b>68</b>
<b>DOES PHOSPHORIC ACID CAUSE OXIDATION IN ASPHALT BINDERS? .....</b>	<b>72</b>
<b>REFERENCES.....</b>	<b>75</b>
<b>ADDITIONAL READING.....</b>	<b>77</b>

## LIST OF FIGURES

Figure 1. Photo. XRF cup (inverted) with plastic membrane. ....	7
Figure 2. Photo. XRF cup (inverted) filled with asphalt.....	8
Figure 3. Photo. Steel XRF cup holder. ....	8
Figure 4. Photo. Interior of XRF spectrometer. ....	8
Figure 5. Chart. XRF spectrum of asphalt AAB-1 modified with 1 percent of 105-percent phosphoric acid. ....	9
Figure 6. Chart. XRF spectrum of asphalt AAB-1. ....	10
Figure 7. Chart. XRF Calibration chart for phosphoric acid. ....	10
Figure 8. Chart. Plot of XRF signal of SHRP reference asphalts modified with superphosphoric acid content.....	11
Figure 9. Chart. X-ray fluorescence of SHRP reference asphalts modified with superphosphoric acid corrected for baseline fluorescence.....	11
Figure 10. Chart. Accuracy of PPA analysis using XRF.....	12
Figure 11. Photo. Phosphoric acid detected by the blue color developed in the Susan P. Needham test.....	13
Figure 12. Chart. Results of SARA fractionation of AAD-1 and AAD-1 modified with 1 percent of 105-percent phosphoric acid or 0.75-percent phosphorus pentoxide. ....	15
Figure 13. Chart. Results of SARA fractionation of asphalt AAK-1 modified with 1 percent of 105-percent phosphoric acid or 0.75-percent phosphorus pentoxide.....	15
Figure 14. Chart. Results of SARA fractionation of asphalt AAM-1 modified with 1 percent of 115-percent phosphoric acid , 1 percent of 105-percent phosphoric acid, or 0.75-percent phosphorus pentoxide.....	16
Figure 15. Chart. Results of SARA fractionation of asphalt ABM-1 modified with 1 percent of 115-percent phosphoric acid or 0.75-percent phosphorus pentoxide. ....	16
Figure 16. Chart. Results of SARA separation of asphalt AAD-1 modified with 115-percent phosphoric acid. ....	17
Figure 17. Chart. Results of SARA separation of asphalt AAK-1 modified with 115-percent phosphoric acid. ....	18
Figure 18. Chart. Results SARA separation of asphalt AAM-1 modified with 115-percent phosphoric acid . ....	18
Figure 19. Chart. Results of SARA separation of asphalt ABM-1 modified with 115-percent phosphoric acid. ....	19
Figure 20. Chart. Results of SARA separation of B6317 Venezuelan asphalt modified with 115-percent phosphoric acid. ....	19
Figure 21. Chart. NMR spectrum of heptane-insoluble fraction of phosphoric acid-modified asphalt. ....	21
Figure 22. Chart. NMR spectrum of heptane soluble fraction of phosphoric acid-modified asphalt. ....	22
Figure 23. Chart. Initial stiffness of SHRP reference binders modified with 115-percent phosphoric acid. ....	24
Figure 24. Chart. Effect of phosphoric acid grade on the stiffness of asphalt AAD-1. ....	25
Figure 25. Chart. Effect of phosphoric acid grade on the stiffness of asphalt AAK-1. ....	25
Figure 26. Chart. Effect of phosphoric acid grade on the stiffness of asphalt AAM-1. ....	26
Figure 27. Chart. Effect of phosphoric acid grade on the stiffness of asphalt ABM-1. ....	26

Figure 28. Chart. Simulated tank aging of binders modified with 1 percent of 105-percent phosphoric acid. ....	27
Figure 29. Chart. PAV aging of asphalt AAD-1 modified with 1-percent phosphoric acid at 100 °C under air. ....	29
Figure 30. Chart. PAV aging of asphalt AAK-1 modified with 1-percent phosphoric acid at 100 °C under air. ....	30
Figure 31. Chart. PAV aging of asphalt AAM-1 modified with 1-percent phosphoric acid at 100 °C under air. ....	30
Figure 32. Chart. PAV aging of asphalt ABM-1 modified with 1-percent phosphoric acid at 100 °C under air. ....	31
Figure 33. Chart. PAV aging of asphalt AAD-1 modified with 1-percent phosphoric acid at 100 °C under nitrogen. ....	31
Figure 34. Chart. PAV aging of asphalt AAK-1 modified with 1-percent phosphoric acid at 100 °C under nitrogen. ....	32
Figure 35. Chart. PAV aging of asphalt AAM-1 modified with 1-percent phosphoric acid at 100 °C under nitrogen. ....	32
Figure 36. Chart. PAV aging of asphalt ABM-1 modified with 1-percent phosphoric acid, at 100 °C under nitrogen. ....	33
Figure 37. Chart. Performance grades of binders after treatment with lime. ....	36
Figure 38. Chart. Effect of lime content on asphalt stiffness. ....	37
Figure 39. Chart. Flow number for the mixture modified with binder from Lion Oil. ....	37
Figure 40. Chart. Flow number for the mixture modified with binder from HollyFrontier® asphalt. ....	38
Figure 41. Chart. PGs of phosphoric acid-modified binders recovered from limestone mixes. ....	40
Figure 42. Chart. Plot of moisture absorption of Citgo® 50-percent asphalt/sand mastic modified with 115-percent phosphoric acid. ....	43
Figure 43. Chart. Plot of moisture absorption of Citgo® 50-percent asphalt/diabase mastic modified with 115-percent phosphoric acid. ....	44
Figure 44. Chart. Moisture absorption of Venezuelan 50-percent asphalt/gravel mastic modified with 115-percent phosphoric acid. ....	44
Figure 45. Chart. Moisture absorption of Citgo® 50-percent asphalt/montmorillonite mastic modified with 115-percent phosphoric acid. ....	45
Figure 46. Chart. Fifty-percent montmorillonite asphalt binder mastic after water immersion for 105 days. ....	46
Figure 47. Chart. Plot of water absorption of Venezuelan asphalt beams modified with 115-percent phosphoric acid. ....	47
Figure 48. Chart. Plot of stiffness of phosphoric acid modified Citgo® asphalt after 245 days of water immersion. ....	47
Figure 49. Chart. Plot of phosphate extracted from Lion Oil binder diabase aggregate gyratory specimen. ....	49
Figure 50. Chart. Plot of phosphate extracted from BP Whiting binder diabase aggregate gyratory specimen. ....	49
Figure 51. Chart. Plot of phosphate extracted from Lion Oil binder granite aggregate gyratory specimen. ....	50
Figure 52. Chart. Plot of phosphate extracted from BP Whiting binder granite aggregate gyratory specimen. ....	50



Figure 53. Chart. Plot of phosphate extracted from Lion Oil binder diabase aggregate loose mix.....	51
Figure 54. Chart. Plot of phosphate extracted from BP Whiting binder diabase aggregate loose mix.....	52
Figure 55. Chart. Hamburg rut test of Citgo® asphalt sandstone aggregate. ....	53
Figure 56. Chart. Hamburg rut test of Citgo® asphalt limestone aggregate. ....	54
Figure 57. Chart. Hamburg rut test of Citgo® asphalt granite aggregate.....	54
Figure 58. Chart. Hamburg rut test of Citgo® asphalt lime-treated sandstone aggregate.....	55
Figure 59. Chart. Hamburg rut test of Citgo® asphalt lime-treated limestone aggregate. ....	55
Figure 60. Chart. Hamburg rut test of Citgo® asphalt lime-treated granite aggregate.....	56
Figure 61. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LA-2 antistrip-treated sandstone aggregate. ....	56
Figure 62. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LA-2 antistrip-treated limestone aggregate. ....	57
Figure 63. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LA-2 antistrip-treated granite aggregate.....	57
Figure 64. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LOF 65-00 antistrip-treated sandstone aggregate.....	58
Figure 65. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LOF 65-00 antistrip-treated limestone aggregate. ....	58
Figure 66. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LOF 65-00 antistrip-treated granite aggregate.....	59
Figure 67. Chart. Hamburg rut test of Citgo® asphalt Innovalt®-W antistrip-treated sandstone aggregate. ....	59
Figure 68. Chart. Hamburg rut test of Citgo® asphalt Innovalt®-W antistrip-treated limestone aggregate. ....	60
Figure 69. Chart. Hamburg rut test of Citgo® asphalt Innovalt®-W antistrip-treated granite aggregate. ....	60
Figure 70. Equation. Calculation of maltene concentration .....	66
Figure 71. Equation. Calculation of n-heptane filtrate .....	66

## LIST OF TABLES

Table 1. History of State regulations on the use of phosphoric acid to modify asphalt. ....	2
Table 2. Materials used in the study. ....	5
Table 3. Properties of the SHRP asphalt binders. ....	23
Table 4. Commercial grades of phosphoric acid used. ....	23
Table 5. Stiffness ( $ G^* /\text{Sin}\delta$ ) of simulated tank-aged binders modified with 105-percent phosphoric acid. ....	27
Table 6. Stiffness sensitivity of reference binders to PPA modification. ....	28
Table 7. Limestone mix designs. ....	39
Table 8. Phosphorus in recovered asphalt binders. ....	39
Table 9. High temperature PGs of phosphoric acid-modified binders recovered from limestone mixes. ....	40
Table 10. Percentage of the added phosphoric acid extracted after 245 days of immersion in water. ....	51
Table 11. Summary of Hamburg rut testing results with antistrip additives. ....	61
Table 12. Change in stiffness of asphalt AAD-1 with phosphoric acid modification immediately after mixing and after 24 h at 165 °C. ....	67
Table 13. Change in stiffness of asphalt AAM-1 with phosphoric acid modification immediately after mixing and after 24 h at 165 °C. ....	67
Table 14. Change in stiffness of asphalt AAK-1 with phosphoric acid modification immediately after mixing and after 24 h at 165 °C. ....	68
Table 15. Change in stiffness of asphalt ABM-1 with phosphoric acid modification immediately after mixing and after 24 hours at 165 °C. ....	68
Table 16. Oven aging at 165 °C asphalt AAD-1 modified with 115-percent phosphoric acid . ...	68
Table 17. Oven aging at 165 °C asphalt AAD-1 modified with 105-percent phosphoric acid. ....	68
Table 18. Oven aging at 165 °C asphalt AAD-1 modified with 85-percent phosphoric acid. ....	69
Table 19. Oven aging at 165 °C asphalt AAD-1 modified with 75-percent phosphoric acid. ....	69
Table 20. Oven aging at 165 °C asphalt AAD-1 modified with 50-percent “green” phosphoric acid. ....	69
Table 21. Oven aging at 165 °C asphalt AAK-1 modified with 115-percent phosphoric acid . ...	69
Table 22. Oven aging at 165 °C asphalt AAK-1 modified with 105-percent phosphoric acid. ....	69
Table 23. Oven aging at 165 °C asphalt AAK-1 modified with 85-percent phosphoric acid. ....	70
Table 24. Oven aging at 165 °C asphalt AAK-1 modified with 75-percent phosphoric acid. ....	70
Table 25. Oven aging at 165 °C asphalt AAK-1 modified with 50-percent “green” phosphoric acid. ....	70
Table 26. Oven aging at 165 °C asphalt AAM-1 modified with 115-percent phosphoric acid. ....	70
Table 27. Oven aging at 165 °C asphalt AAM-1 modified with 105-percent phosphoric acid. ....	71
Table 28. Oven aging at 165 °C asphalt AAM-1 modified with 85-percent phosphoric acid. ....	71
Table 29. Oven aging at 165 °C asphalt AAM-1 modified with 75-percent phosphoric acid. ....	71
Table 30. Oven aging at 165 °C asphalt AAM-1 modified with 50-percent “green” phosphoric acid. ....	71
Table 31. Oven aging at 165 °C asphalt ABM-1 modified with 115-percent phosphoric acid. ....	71
Table 32. Oven aging at 165 °C asphalt ABM-1 modified with 105-percent phosphoric acid. ....	72
Table 33. Oven aging at 165 °C asphalt ABM-1 modified with 85-percent phosphoric acid. ....	72
Table 34. Oven aging at 165 °C asphalt ABM-1 modified with 75-percent phosphoric acid. ....	72

Table 35. Oven aging at 165 °C asphalt ABM-1 modified with 50-percent “green” phosphoric acid. ....	72
Table 36. PAV aging asphalt ABM-1 under air pressure at 100 °C. ....	72
Table 37. PAV aging asphalt AAD-1 under air pressure at 100 °C. ....	73
Table 38. PAV aging asphalt AAK-1 under air pressure at 100 °C. ....	73
Table 39. PAV aging asphalt AAM-1 under air pressure at 100 °C. ....	73
Table 40. PAV aging asphalt ABM-1 under nitrogen pressure at 100 °C. ....	73
Table 41. PAV aging asphalt AAD-1 under nitrogen pressure at 100 °C. ....	73
Table 42. PAV aging asphalt AAK-1 under nitrogen pressure at 100 °C. ....	73
Table 43. PAV aging asphalt AAM-1 under nitrogen pressure at 100 °C. ....	74

## LIST OF ACRONYMS AND ABBREVIATIONS

AASHTO	American Association of State Highway and Transportation Officials
BBR	Bending Beam Rheometer
DSR	Dynamic Shear Rheometer
FID	Flame Ionized Detection
HDPE	High Density Polyethylene
HMA	Hot Mix Asphalt
NMR	Nuclear Magnetic Resonance
NYSDOT	New York State Department of Transportation
PAV	Pressure Aging Vessel
PG	Performance Grade
PPA	Polyphosphoric Acid
RH	Relative Humidity
RTFOT	Rolling Thin Film Oven Test
SARA	Saturate, Aromatic, Resin, and Asphaltene
SBS	Styrene–Butadiene–Styrene
SHRP	Strategic Highway Research Program
TCE	Trichloroethylene
TFHRC	Turner Fairbank Highway Research Center
XRF	X-Ray Fluorescence Spectroscopy

## CHAPTER 1. INTRODUCTION

### BACKGROUND

An unsolved mystery regarding the premature failure of I-80 in Nebraska led in part to this study. The transverse cracking problems that occurred there, as well as highway performance problems in other States attributed to the use of phosphoric acid but without forensic support, caused State agencies to question the use of phosphoric acid as an asphalt modifier despite its use for 30 years. A number of preconceived objections exist. These include the following:

- Phosphoric acid is used as a blowing additive to make roofing asphalt. It will cause premature aging in paving asphalt.
- Phosphoric acid is an acid; it will react with limestone aggregates.
- Phosphoric acid is an acid; it will react with lime anti-strip additives.
- Phosphoric acid is an acid; it will react with liquid amine antistrip additives (which are alkaline).
- Phosphoric acid is very hydrophilic; it will promote moisture damage.
- Phosphoric acid is very hydrophilic; it will be leached from asphalt pavements and could pollute the surrounding ground water.

The American Association of State Highway and Transportation Officials (AASHTO) carried out surveys in December 2005 and again in October 2008. States were asked, “Do you allow the use of acid-modified binders?”

The 2005 survey went out to the 50 States as well as the Canadian provinces. Of 31 respondents, 11 allowed phosphoric acid, 16 banned it, 1 restricted its use, and 3 did not specifically address the issue. Because the Superpave specification is supposed to be blind to additives, it is likely that phosphoric acid would have been allowed in the latter three States.

In the 2008 follow-up survey, five States specifically allowed phosphoric acid, eight States banned it, four placed restrictions on its use, and three had a specification for elastic recovery or phase angle, which would preclude the use of phosphoric acid as the sole modifier. Ten States did not address the issue. Twenty-three States did not respond to the survey.

The more recent 2009–2010 survey conducted by the Asphalt Institute indicated that the use of phosphoric acid is banned by 16 States. Thirty-two States do not specifically address the issue, which would imply that it is allowed, although 20 of these States have either an elastic recovery or phase angle specification, (which would preclude the use of phosphoric acid or merely force the inclusion of polymers), leaving 12 States that would allow phosphoric acid as the sole modifier. One State, Minnesota, has a requirement to carry out the binder tests out after the addition of 0.5-percent liquid amine antistrip additives. Because amines are alkaline, phosphoric acid would be expected to react with the amines and might preclude the use of phosphoric acid. Binder tests are usually carried out before the addition of amine antistrip additives.

The results of these three surveys are summarized in table 1.

**Table 1. History of State regulations on the use of phosphoric acid to modify asphalt.**

Status	AASHTO 2005	AASHTO 2008	AI 2009/2010
Allowed	11	5	3
Banned	16	8	16
Not Addressed	3	10	12
Restricted	1	4	0
With Polymers	0	3	20
No Response	21	23	0
Undecided	1	0	0
Total Responses	53	53	51

AASHTO = American Association of Highway and Transportation Officials

AI = Asphalt Institute

### SOME PHOSPHORIC ACID CHEMISTRY

Phosphoric acid exists in different strengths or concentrations, with physical forms ranging from a clear odorless colorless liquid or a transparent solid, depending on the concentration and temperature.

The most common form is orthophosphoric acid ( $H_3PO_4$ ). It is commonly called phosphoric acid, and is one of the oldest known and most important phosphorous compounds. It is made in vast quantities, usually as an 85-percent acid, by the direct reaction of ground phosphate rock (calcium phosphate or apatite) with sulfuric acid. This yields “green acid,” which contains typically 25- to 50-percent  $H_3PO_4$  and is heavily contaminated with impurities, including anions such as chloride and sulfate (likely an excess of sulfuric acid), which might be expected to cause equipment corrosion problems if used to modify asphalt. Green acid is mainly used to produce fertilizer; some is further refined to phosphoric acid of food-grade quality.

Phosphoric acid is also made by the direct burning of phosphorus and subsequent hydration of the oxide commonly known as  $P_2O_5$ . (Its actual chemical formula is  $P_4O_{10}$  but for historical reasons, it is still called  $P_2O_5$ .)

The pure acid is crystalline, and the hydrates have tetrahedral  $PO_4$  groups connected by hydrogen bonds. These persist in the concentrated solutions and are responsible for its syrupy nature.

The grades of phosphoric acid (i.e., orthophosphoric acid ( $H_3PO_4$ )) available commercially have acid concentrations of 50, 75, 85, 100, 105, and 115 percent.

Polyphosphoric acids (PPA) exist and have the general formula  $H_{n+2}P_nO_{3n+1}$  for  $n > 1$ . They range from pyrophosphoric acid ( $H_4P_2O_7$  ( $n=2$ )) through the metaphosphoric acid (large values of  $n$ ).

Although pyrophosphoric acid may be crystallized in several forms, other grades of phosphoric acid all have equilibrium distributions of molecules and are known only in liquid or glassy form. The viscosity of these acids increases greatly as  $n$  becomes large.

The PPA offered commercially is a mixture of orthophosphoric acid with pyrophosphoric acid, triphosphoric acid, and higher acids, and is sold on the basis of its calculated content of  $H_3PO_4$ .

## **HOW PHOSPHORIC ACID IS USED TO MODIFY ASPHALT BINDERS**

There are three uses for phosphoric acid in the modification of asphalt binders:

- As an additive: Polymers are often used to improve the performance grade (PG) of asphalt binders. Some of these polymers are difficult to disperse in asphalt. For example, U.S. Patents 6,117,926 and 6,399,680 (Engberger and Reinke) describe the use of phosphoric acid to facilitate the dispersion of these polymers in asphalt binders.<sup>(1,2)</sup>
- Synergistic effect with polymers: The most common use is to allow the reduction in the amount of styrene–butadiene–styrene (SBS) polymer so that the pressure aging vessel (PAV) dynamic shear rheometer (DSR) value of  $\leq 5,000$  KPa can be achieved and still meet the elastic recovery requirements of the other Strategic Highway Research Program (SHRP) Superpave Plus specifications. It is also used as a supplemental additive to SBS-modified asphalt that is marginal on the rolling thin film oven test (RTFOT). This test is intended to mimic the aging of asphalt that occurs in a hot mix plant. The test requires the dynamic shear ( $|G^*|/\sin\delta$ ) to increase from a minimum of 1.00 kPa to 2.20 kPa after the test. Polymer-modified asphalts that are marginal will usually pass the test if stiffened with small amounts of phosphoric acid.
- Grade bumping: Phosphoric acid is the sole asphalt modifier used to deliberately alter the asphalt PG.

## **RESEARCH PLAN**

The plan objective is to develop a best practices guide for the use of phosphoric acid as an asphalt modifier and to address the industry perceptions such as effect on aging, moisture damage, and reaction with limestone aggregates. Elements of the plan include the analysis, effect of acid grade and binder types, aging, reaction with limestone aggregates, and moisture, as described below.

### **Analysis**

Analysis will focus on the following tasks:

- Develop quantitative and qualitative analytical methods for detecting the presence of phosphoric acid in asphalt.
- Determine the effect on key asphalt binder components (e.g., the saturate, asphaltene, resin and aromatics content).

## **Effect of Acid Grade and Binder Types**

In this area, researchers will determine the following:

- Stiffening effect of phosphoric acid added to asphalt from different crude oil sources and determine if the effect changes during tank storage.
- Effect of different grades of phosphoric acid.

## **Aging**

Researchers will determine whether phosphoric acid increases the aging rate of asphalt binders. Some concerns have been expressed on this issue because phosphoric acid is used as a blowing catalyst in the production of roofing asphalt.

## **Reaction With Lime and Limestone Aggregates**

Some State agencies treat their aggregates with lime (calcium hydroxide) to improve the moisture resistance of their asphalt mixes. Lime is a strong alkali and might be expected to react with phosphoric acid in the mix. Limestone (calcium carbonate) is not an alkali but is readily attacked by acids. In either case, if the phosphoric acid is effectively removed from the binder by chemical reaction, it could result in softening of the binder. Testing will determine whether phosphoric acid-modified asphalt will soften if used with limestone aggregates in asphalt mixes.

## **Moisture**

Most liquid antistripping additives are alkaline amines, which might be expected to react with phosphoric acid. This could result in change in binder stiffness. Tests will be carried out to determine whether this is the case.

Because phosphoric acid is very hydrophilic, there is a possibility that it would increase the sensitivity of the mix to moisture damage. Mixes made with aggregates known to be nonstripping and stripping will be tested for moisture damage using the Hamburg wheel tracker.

The team will determine whether the benefits obtain by modification are permanent. In particular, phosphoric acid is very soluble in water—is it leached from the mix by rain?

Table 2 lists the materials used in the study.



**Table 2. Materials used in the study.**

<b>Supplier</b>	<b>Name</b>	<b>TFHRC Reference</b>	<b>Description</b>
SHRP	AAD-1	—	Asphalt Binder California Coastal
SHRP	AAM-1	—	Asphalt Binder West Texas Intermediate
SHRP	AAK-1	—	Asphalt Binder Boscan
SHRP	ABM-1	—	Asphalt Binder California Valley
Citgo®	—	B6362	Asphalt Binder Venezuela 94-Percent Bachaquero-13, 6-Percent Mery-16
BP Whiting	—	B6364	Asphalt Binder Canadian Crude and Gulf Coast Sour
Ergon®/Lion Oil	—	B6367	Asphalt Binder Saudi and Arkansas Crudes
Various	Phosphoric Acid	—	Phosphoric Acid 115-, 105-, 75-, and 50-percent grades
Keystone Aggregates MD	—	—	Sandstone Aggregate
Mellot Company MD	—	—	Limestone Aggregate
Arr-Maz	AD-HERE® LOF65-00	—	Amine Antistrip Additive
Arr-Mazz	AD-HERE® LA2	—	Amine Antistrip Additive
Innophos	Innovalt®	—	2-Ethylhexyl Phosphate Antistrip Additive
Chemical Lime Company	Lime	—	Calcium Hydroxide

— Indicates not applicable

TFHRC = Turner Fairbank Highway Research Center

SHRP = Strategic Highway Research Program



## CHAPTER 2. ANALYTICAL METHODS

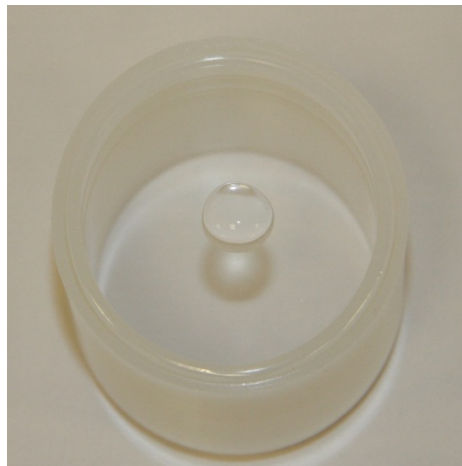
### QUANTITATIVE ANALYSIS OF ASPHALT BINDERS FOR PHOSPHORIC ACID

X-ray fluorescence spectroscopy (XRF) is an analytical technique by which all the elements in the periodic table from sodium to uranium can be quantitatively and rapidly detected with minimal sample preparation. Test samples are irradiated with an X-ray beam, and the resulting spectrum can be used to provide quantitative information on each element present.

The use of XRF to quantitatively determine the amount of phosphoric acid contained in asphalt binders was developed by Puzic et al.<sup>(3)</sup> The method has been refined by Reinke et al.<sup>(4)</sup>

Samples are placed in cups consisting of two concentric polypropylene rings over which a thin plastic film is stretched like a drum skin. The X rays are able penetrate the film with no attenuation of the beam. Initially, 6-micron Mylar® polyester film was chosen for its strength. It was discovered that it contains the equivalent 0.1-percent phosphoric acid and was discarded in favor of polypropylene, which contains none. Pictures of the inverted cups are shown in figure 1 and figure 2. A drop of water has been placed on the film of the empty cup in figure 1 to make the film visible. Warm asphalt is poured into the empty cup while it is sitting on a ¼-inch thick aluminum plate. The plate acts as a heat sink and prevents the heat of the asphalt from melting the plastic film. The asphalt temperature is not critical; the asphalt just needs to be molten. Typical pouring temperatures are 140 °C.

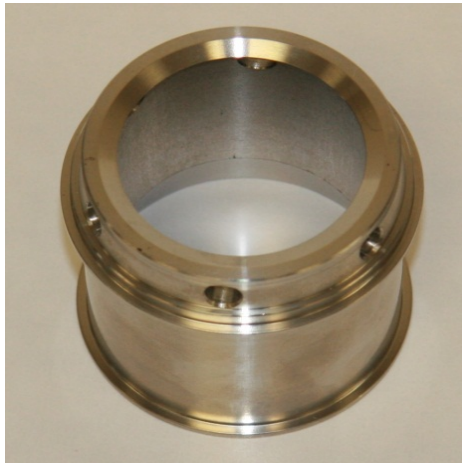
The plastic cup, filled with asphalt, is then placed inside a stainless steel cup holder (figure 3), which is placed inside the spectrometer (figure 4). Each sample takes 20 to 25 min to run. The program runs automatically, and the spectrometer is capable of analyzing up to 52 samples unattended.



**Figure 1. Photo. XRF cup (inverted) with plastic membrane.**



**Figure 2. Photo. XRF cup (inverted) filled with asphalt.**



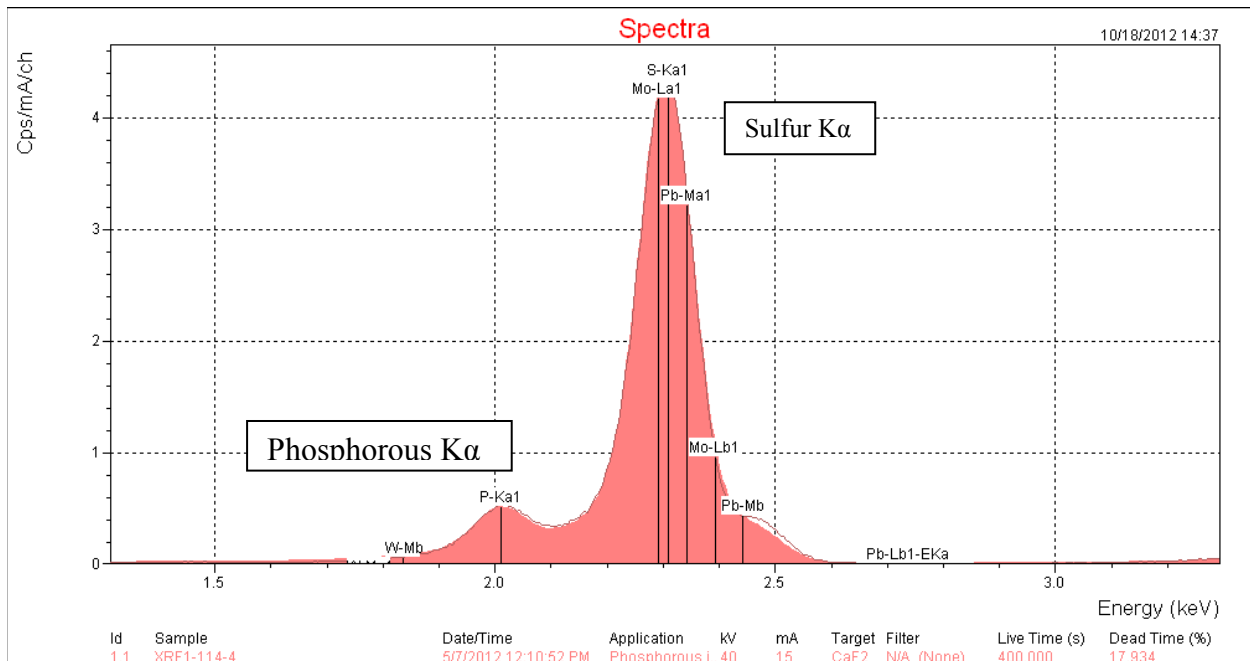
**Figure 3. Photo. Steel XRF cup holder.**



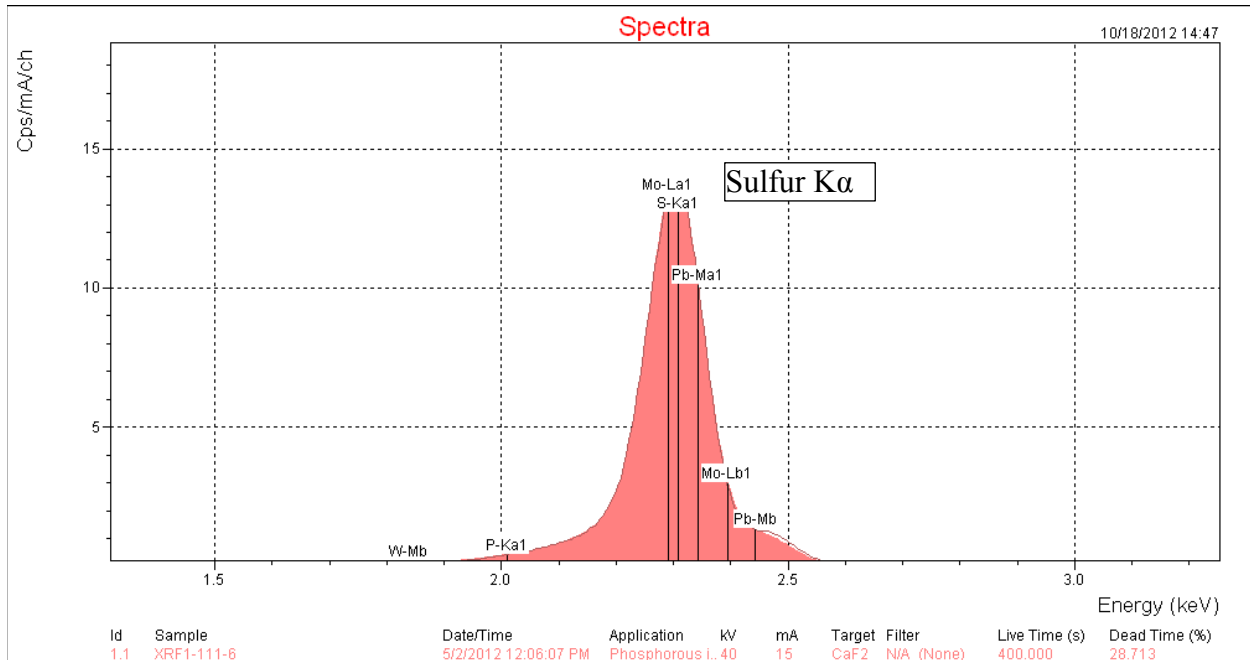
**Figure 4. Photo. Interior of XRF spectrometer.**

All asphalt binders contain a significant amount of sulfur; they do not contain phosphorus. Because sulfur and phosphorus are next to each other in the periodic table they have very similar XRF energies. The major  $K\alpha$  peak energy for phosphorus is 2.013 KeV and for sulfur 2.307 KeV. This proximity causes the peaks in the XRF spectrum from these two elements to overlap. Because the amount of sulfur in asphalt is very much higher than the amounts of phosphoric acid typically used for modification, the sulfur peak is very much larger. It overwhelms the phosphorus peak. This negatively affects the accuracy of the analysis. The XRF spectrometer software “sees” a phosphorus peak when none may be present. This phenomenon is clearly shown in figure 6, the XRF spectrum of asphalt AAB-1. At the energy level of approximately 2.0 KeV on the x-axis, the software has labeled the spectrum P-Ka1 indicating a phosphorus  $K\alpha$  peak when none is present. The software is using the intensity of the first part of the sulfur peak and interprets it incorrectly. Ninety samples of unmodified asphalt binders showed a phosphoric acid level of 0 to 0.2 percent when we know that none was actually present. Compare this with figure 5, the XRF spectrum of the same asphalt, AAB-1, modified with 1 percent of 105-percent phosphoric acid where the phosphorus peak can be clearly seen. There is no fixed detection limit. The results may also depend on the spectrometer used; however, these results suggest that XRF analyses indicating the presence of low levels of approximately 0.2 percent or less might be misleading.

The accuracy of the phosphoric acid analysis was improved markedly by entering into the spectrometer software phosphoric acid calibration standards, the known sulfur content of the binder used. The sulfur levels in the binders were determined using XRF. Accuracy was improved further by using the published sulfur contents of the SHRP reference binders.<sup>(5)</sup>

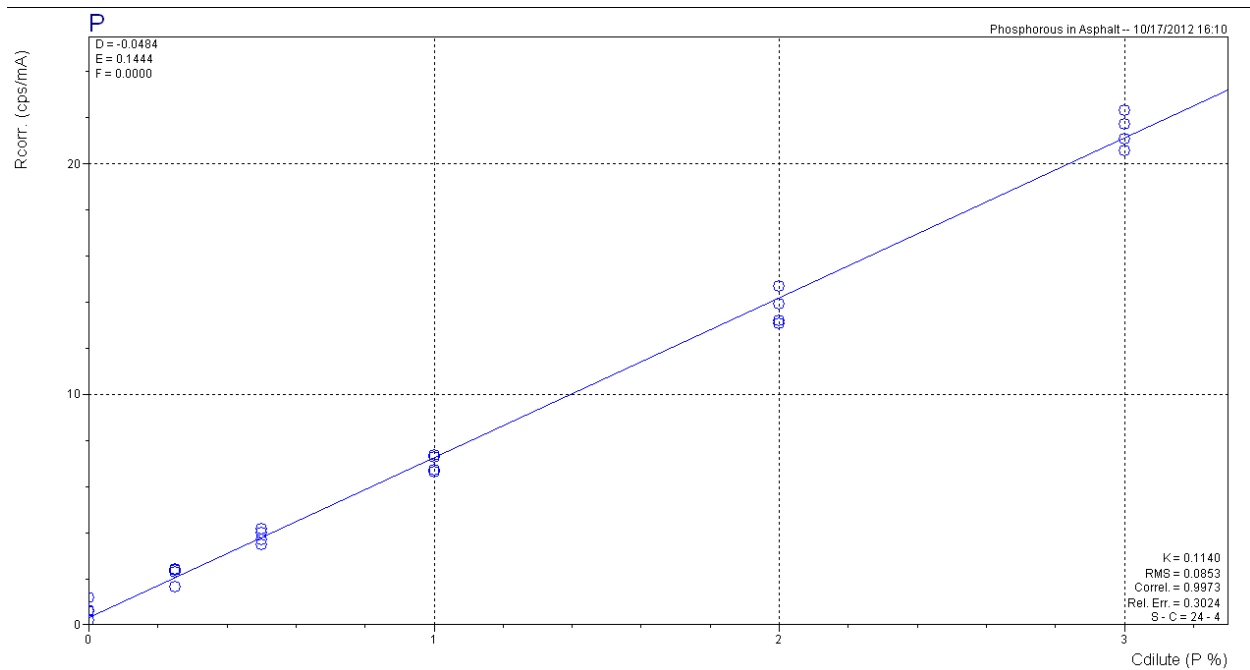


**Figure 5. Chart. XRF spectrum of asphalt AAB-1 modified with 1 percent of 105-percent phosphoric acid.**



**Figure 6. Chart. XRF spectrum of asphalt AAB-1.**

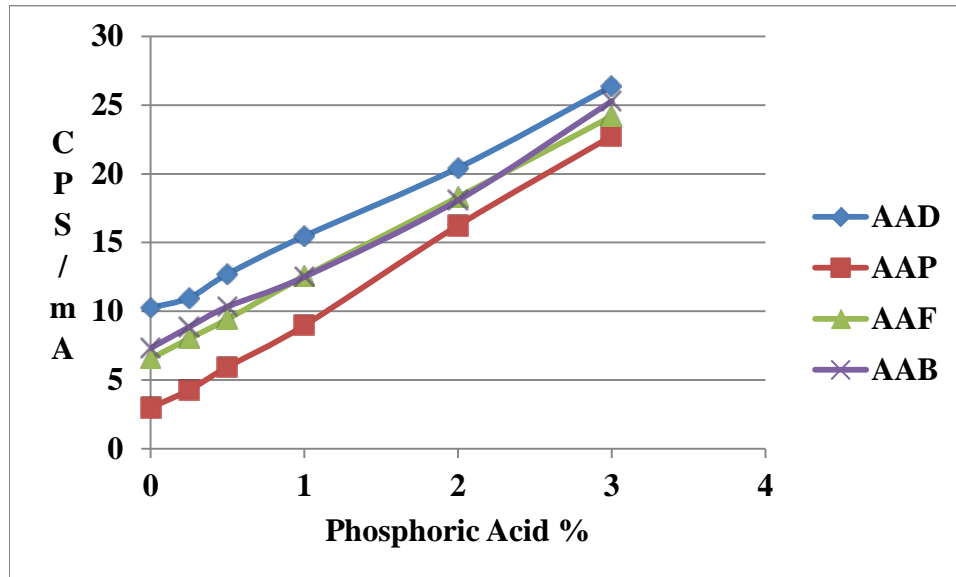
Reference standards for the XRF analyses were prepared by blending 105-percent phosphoric acid in asphalt at 165 °C while stirring briskly with a propeller stirrer under air for 30 min. The hot asphalt was then poured into XRF cups for analysis. Addition levels of superphosphoric acid used were 0.25, 0.5, 1.0, 2.0, and 3.0 percent. The correlation chart showing phosphoric acid concentration plotted against the XRF intensity (measured in counts per second per milliamp of current), taken from the spectrometer is shown in figure 7. The  $R^2$  correlation is 0.9973.



**Figure 7. Chart. XRF Calibration chart for phosphoric acid.**

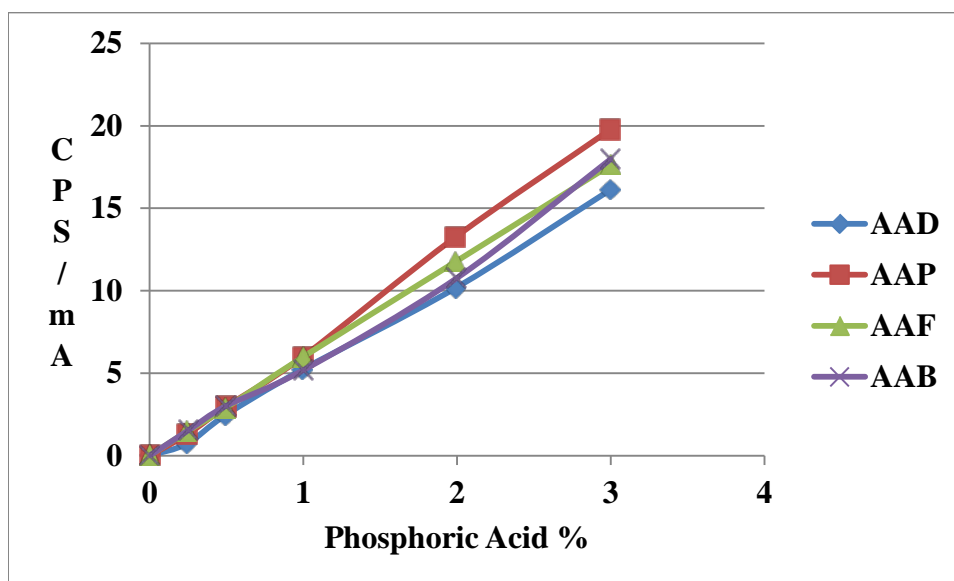
Figure 8 shows that the XRF signals of the four SHRP reference asphalts at zero phosphoric acid addition differ slightly.

Figure 9 shows the same data corrected for the difference in zero acid addition.

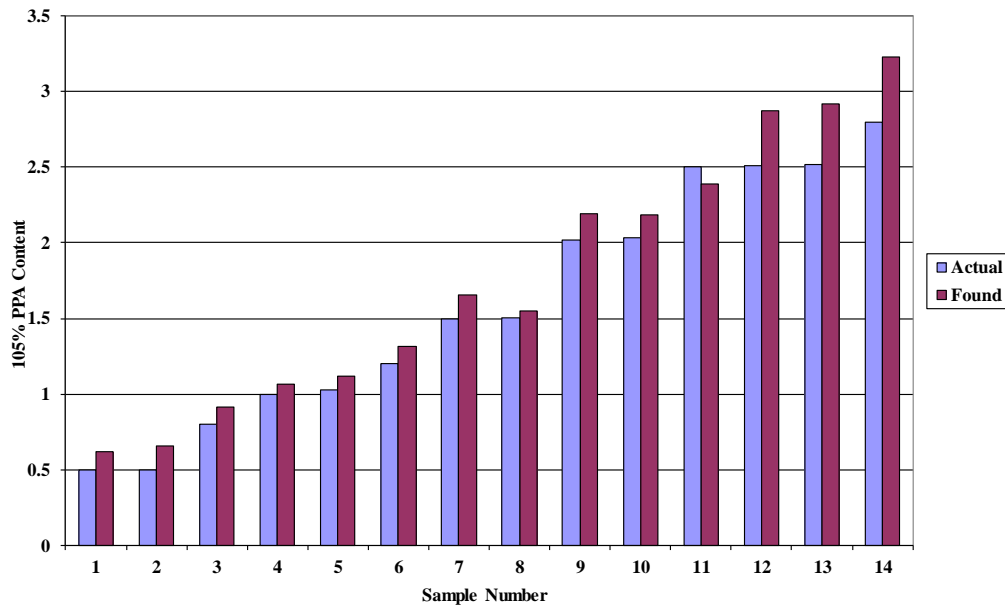


**Figure 8. Chart. Plot of XRF signal of SHRP reference asphalts modified with superphosphoric acid content.**

The XRF up to 1-percent acid modification is the same for the four asphalts. However, at higher modification levels, the curves diverge, indicating some asphalt dependency. Test results were found to be less accurate at higher modification levels as shown in figure 10.



**Figure 9. Chart. X-ray fluorescence of SHRP reference asphalts modified with superphosphoric acid corrected for baseline fluorescence.**



**Figure 10. Chart. Accuracy of PPA analysis using XRF.**

### **A SIMPLE QUALITATIVE TEST TO DETECT THE PRESENCE OF PHOSPHORIC ACID IN ASPHALT BINDERS**

Because not all State agencies have access to XRF spectrometers, a simple procedure, the “Susan P. Needham Test,” was developed. It is a very simple technique; it requires no special equipment—just the use of a few simple chemicals. The test is very sensitive, and care must be taken that the equipment used and chemical used do not contain phosphates. This is particularly true for the use of metal cans that contain a phosphate film on the surface because they will give a positive result. The test has been submitted to AASHTO and is published as provisional test method TP 78-09, “Detecting the Presence of Phosphorus in Asphalt Binder.” The following describes the reagents and procedures used in the test method.

#### **Reagents**

- Antimonyl Tartrate/Ammonium Molybdate Solution: Dissolve 0.13 g of potassium antimonyl tartrate hydrate [C<sub>8</sub>H<sub>4</sub>K<sub>2</sub>O<sub>12</sub>Sb<sub>2</sub>·H<sub>2</sub>O] in 50 mL of distilled water. Add 5.6 g of ammonium molybdate [(NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4 H<sub>2</sub>O] and swirl until dissolved.
- 1N Sulfuric Acid Solution (H<sub>2</sub>SO<sub>4</sub>): This can be purchased in 1-L polyethylene bottles.
- Stock Solution Mixture: Mix (solution 1) and approximately 950 mL of (solution 2) above. This can be done by adding solution 1 to the 1 L of solution 2 if there is sufficient space in the bottle. The exact amount of solution 2 is not critical. This stock solution is stable for 1 year.



- Ascorbic Acid Color Reagent: Dissolve 0.50 g of L-Ascorbic Acid [C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>] in 100 mL of solution 3. This reagent is stable for a week if stored at 4 °C; otherwise, prepare the reagent fresh daily or as needed.
- Iso Butanol ((CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>OH) (n-butanol can also be used).

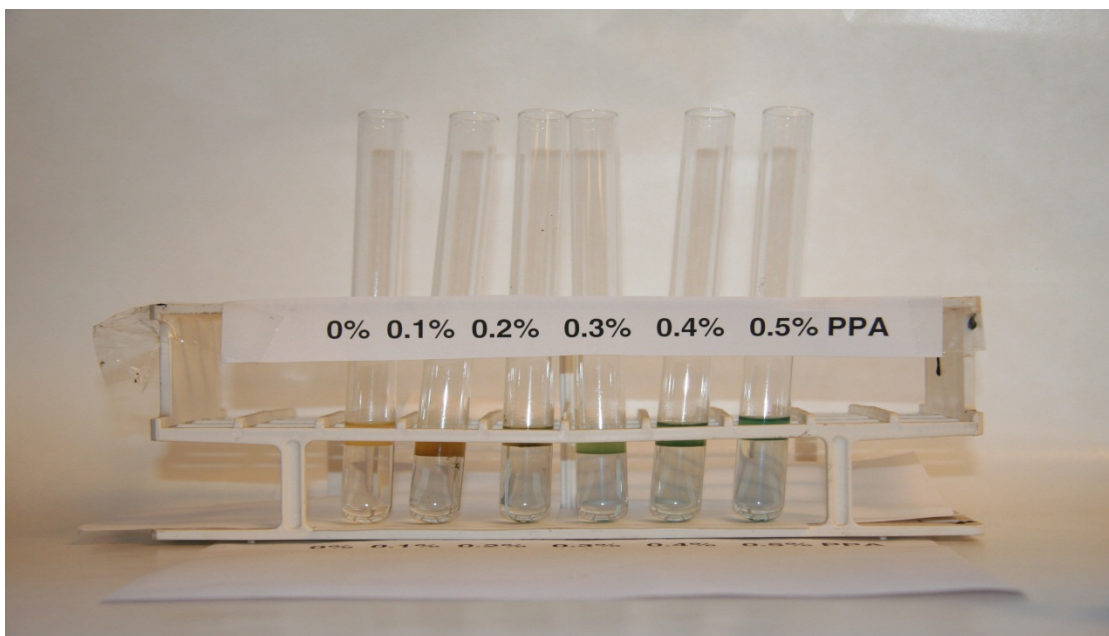
## Procedure

### *Description:*

- Heat the asphalt and pour 1 to 2 g into a small container, glass beaker, or test tube.
- Place the container in an oven for 10 min to ensure the asphalt is fluid.
- Remove the container and immediately add 2 mL of solution 5 while swirling the container.
- Continue to swirl the container and add 2 mL of distilled water.
- While still swirling the container, add 2 mL of solution 4.

### *Identification:*

- If phosphoric acid is present in the asphalt, a blue color (figure 11) will develop at the bottom of the tube within 5 to 10 min. (Decant into a second 1 oz can/glass tube if unable to see color.)



**Figure 11. Photo. Phosphoric acid detected by the blue color developed in the Susan P. Needham test.**

## **SATURATE, AROMATIC, RESIN, AND ASPHALTENE ANALYSIS OF ASPHALT BINDERS MODIFIED WITH PHOSPHORIC ACID**

Solvent separation of asphalt binders (saturate, aromatic, resin, and asphaltene (SARA) analysis) was accomplished using Chromarods® (thin layer chromatography) run on the Iatroscan® TH-10 hydrocarbon analyzer. This method results in the separation of the four operationally defined fractions inherently present in all petroleum-derived asphalt and asphaltic residuals, namely are asphaltenes, resins, aromatics, and saturates.

Asphaltenes are the viscosity builders in asphalt. They are black amorphous solids that contain the bulk of the heteroatoms (nitrogen, sulfur, and oxygen) found in asphalt. Trace elements, such as nickel and vanadium, are also present. Asphaltenes are highly polar aromatic materials of aggregated molecular weights of 750 (number average), and constitute approximately 5 to 25 percent of the weight of asphalt.

Resins (polar aromatics) are dark-colored, solid or semi-solid, very adhesive fractions of relatively high molecular weight present in the maltenes. They are the dispersing agents or peptizers for the asphaltenes, and the ratio of resins to asphaltenes governs, to a degree, the sol- or gel-type character of asphalts. Resins separated from bitumen are found to have molecular weights of 800 to 2,000 (number average) but there is a wide molecular distribution. This component constitutes 15 to 25 percent of the weight of asphalts.

Cyclics (naphthenic aromatics) comprise the compounds of lowest molecular weight in bitumen and represent the major portion of the dispersion medium for the peptized asphaltenes. They constitute 45 to 60 percent by weight of the total asphalt and are dark viscous liquids. They are compounds with aromatic and naphthenic aromatic nuclei with side chain constituents and have molecular weights of 500 to 900 (number average).

Saturates comprise predominately the straight-and-branched-chain aliphatic hydrocarbons present in bitumen, together with alkyl naphthenes and some alkyl aromatics. The average molecular weight range is approximately similar to that of the cyclics, and the components include the waxy and non-waxy saturates. This fraction forms 5 to 20 percent of the weight of asphalts.

The test method used was kindly provided by Dr. Gaylon Baumgardner of Ergon® Inc. A copy of the method is provided in the appendix.

The four test asphalts, AAD-1, AAK-1, AAM-1, and ABM-1 were dosed with the equivalent of 1-percent acid. For phosphorus pentoxide, the stoichiometry calculates to 0.75 percent. The samples were conditioned overnight at 165 °C. Separation was carried out according the aforementioned procedure. The results are shown in figure 12 to figure 15.

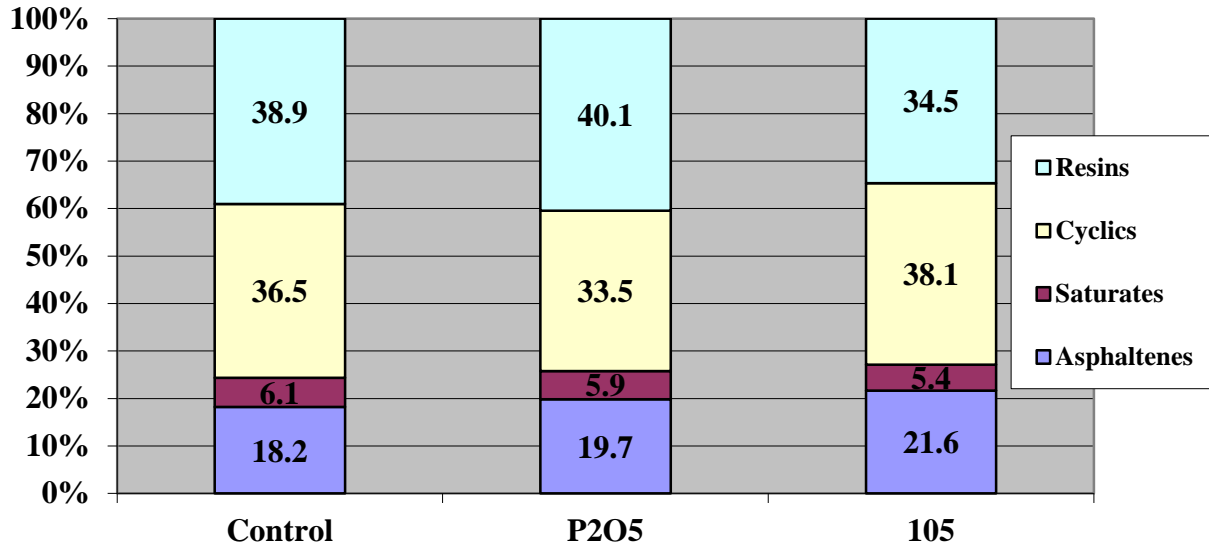


Figure 12. Chart. Results of SARA fractionation of AAD-1 and AAD-1 modified with 1 percent of 105-percent phosphoric acid or 0.75-percent phosphorus pentoxide.

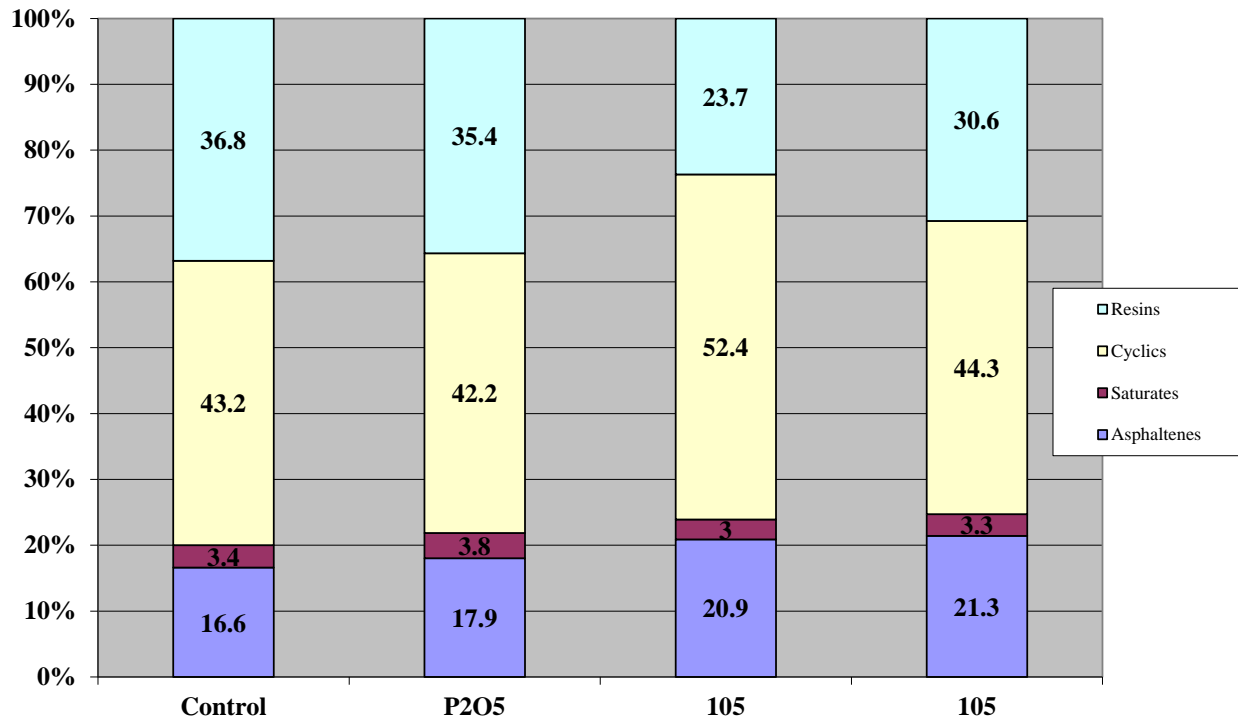
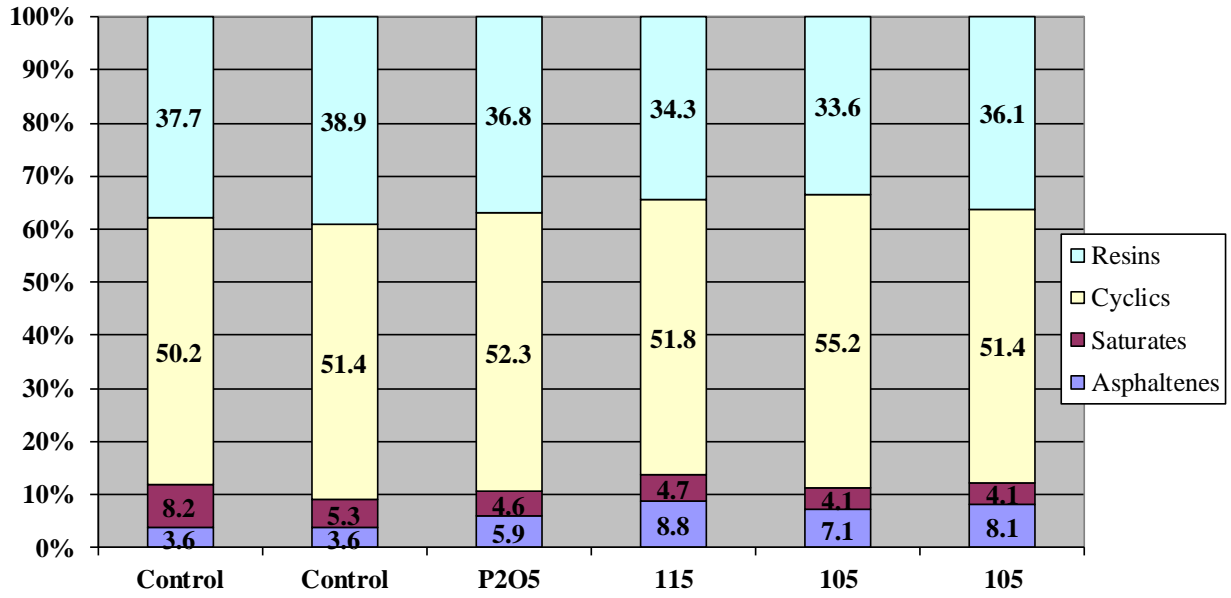
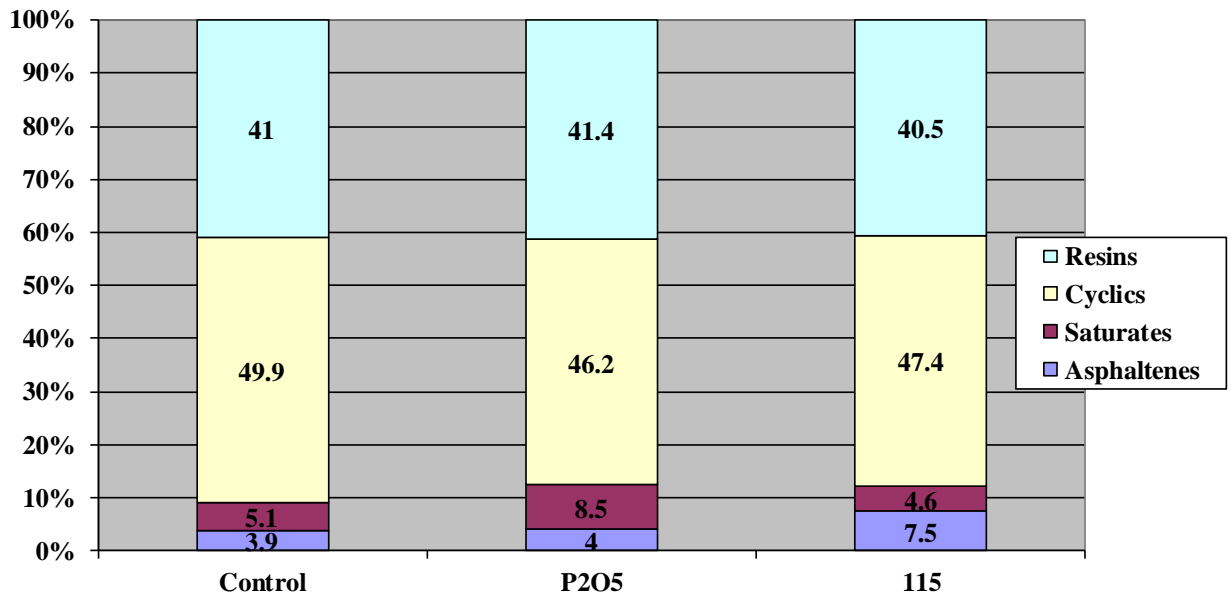


Figure 13. Chart. Results of SARA fractionation of asphalt AAK-1 modified with 1 percent of 105-percent phosphoric acid or 0.75-percent phosphorus pentoxide.



**Figure 14. Chart. Results of SARA fractionation of asphalt AAM-1 modified with 1 percent of 115-percent phosphoric acid , 1 percent of 105-percent phosphoric acid, or 0.75-percent phosphorus pentoxide.**

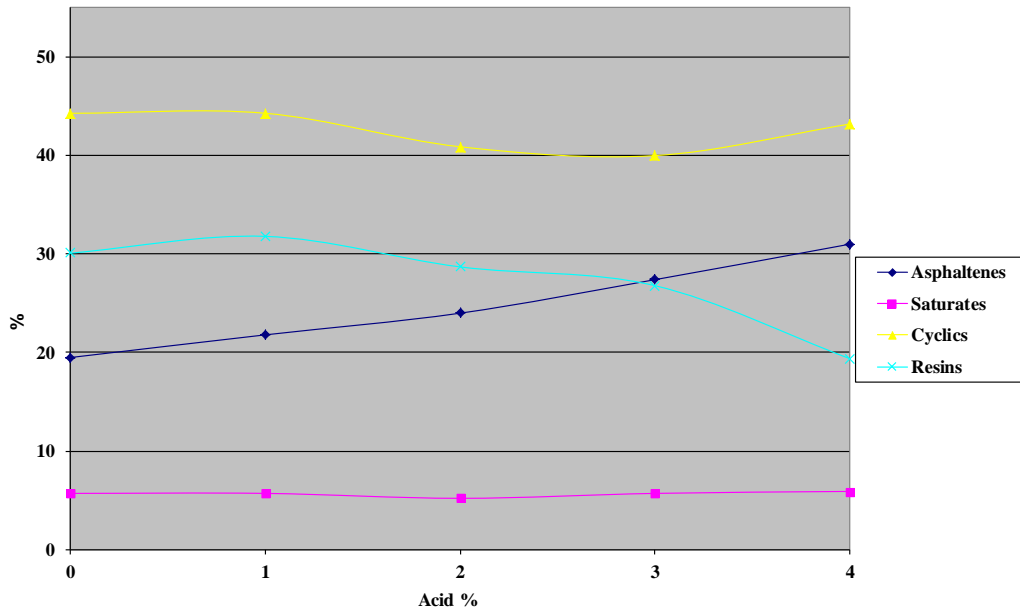


**Figure 15. Chart. Results of SARA fractionation of asphalt ABM-1 modified with 1 percent of 115-percent phosphoric acid or 0.75-percent phosphorus pentoxide.**

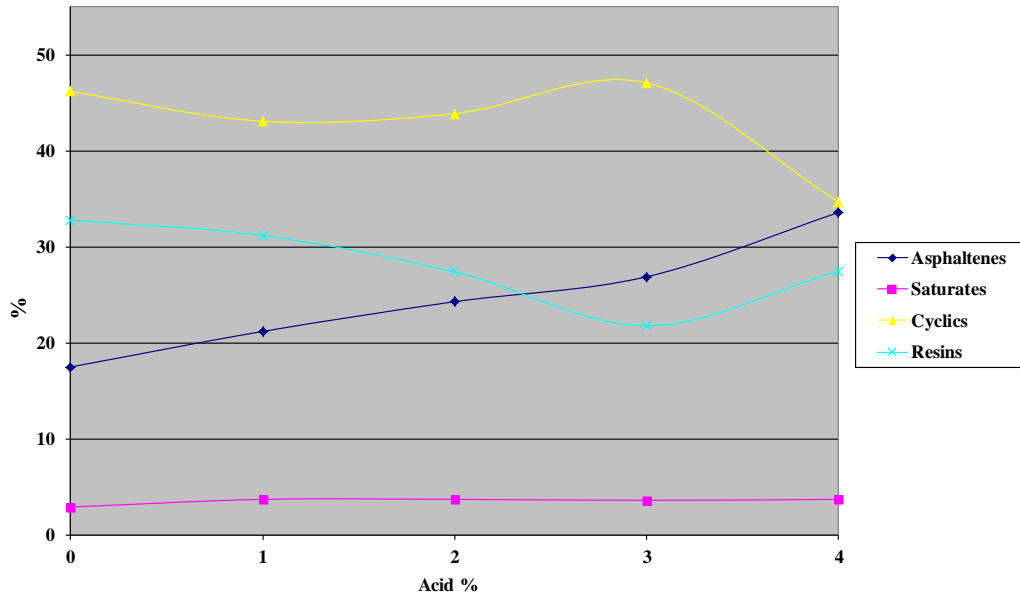
The Iatroscan® technique is very sensitive to temperature, humidity, and time. Test results in the Turner Fairbank Highway Research Center (TFHRC) chemistry laboratory showed a high degree of variability because, at the time of this research, the building temperature and humidity were not well controlled. This variability precluded the detection of any trend at low levels of acid modification in the components separated by the technique. The tests were repeated, with higher

levels of acid than would be expected to be used in practice, to see whether a definite trend could be determined.

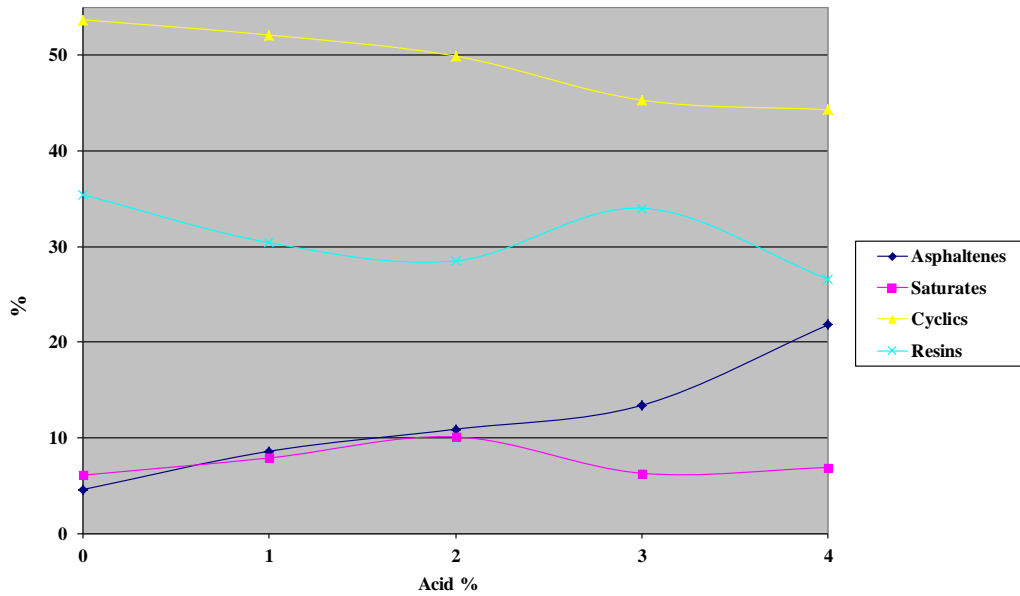
Samples of the four SHRP test asphalts were dosed with 115-percent phosphoric acid at acid levels from 1 to 4 percent (based on 100-percent acid) and the samples aged overnight at 165 °C. The variability of the technique is evident from the shapes of the curves shown in the following four charts (figure 16 through figure 20). The data do, however, illustrate trends.



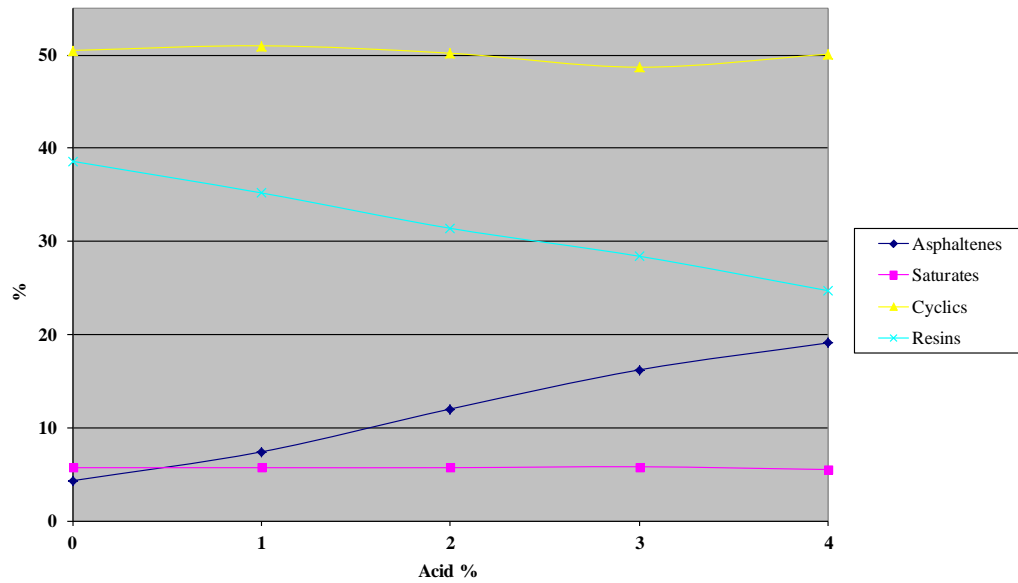
**Figure 16. Chart. Results of SARA separation of asphalt AAD-1 modified with 115-percent phosphoric acid.**



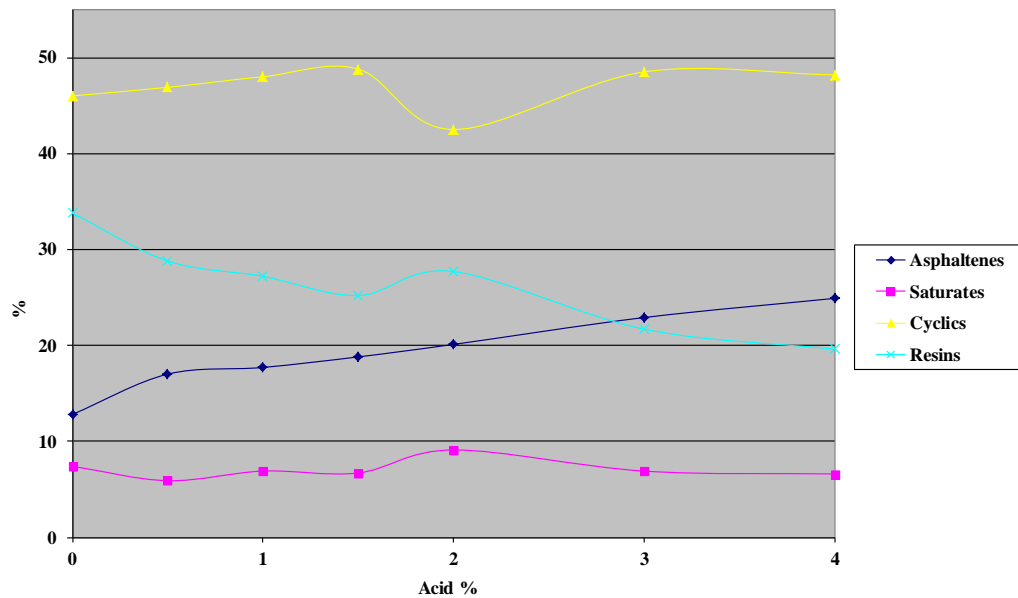
**Figure 17. Chart. Results of SARA separation of asphalt AAK-1 modified with 115-percent phosphoric acid.**



**Figure 18. Chart. Results SARA separation of asphalt AAM-1 modified with 115-percent phosphoric acid .**



**Figure 19. Chart. Results of SARA separation of asphalt ABM-1 modified with 115-percent phosphoric acid.**



**Figure 20. Chart. Results of SARA separation of B6317 Venezuelan asphalt modified with 115-percent phosphoric acid.**

### Findings

The following findings resulted from the SARA analysis:

1. Phosphorus pentoxide has less effect on the SARA fractions than does phosphoric acid.

2. The heptane insoluble fractions (labeled as asphaltenes), of all five asphalt samples increased with increasing acid content.
3. The increase in the heptane insoluble fraction with increasing acid content was accompanied by a decrease in one or more of the other fractions:
  - a. AAD-1: The increase in the heptane insoluble fraction from 19.5 to 31 percent was accompanied by an almost equal decrease in the level of the resin fraction from 31 to 19.4 percent. The cyclic fraction varied a little but was basically unchanged while the saturate fraction level did not change at all.
  - b. AAK-1: The increase in the heptane insoluble fraction from 17.5 to 33.6 percent was accompanied by a decrease in the resin content up to the 3-percent acid level when the resin content then increased up to the 4-percent acid level. This increase in the resin fraction was accompanied by a decrease in the cyclic fraction, which was constant up to the 3-percent acid level and then declined. The amount of saturates was unchanged.
  - c. AAM-1: The heptane insoluble fraction showed an increase from 4.6 to 21.8 percent. This was accompanied by an overall decrease in resin content from 35.4 to 26.6 percent although the curve shows an inflexion point at 2- to 3-percent acid. The content of cyclics shows a steady decline from 53.7 to 44.3 percent. There is some fluctuation in the level of saturates but overall, these remain almost unchanged.
  - d. ABM-1: There is a 14.85-percent straight line increase in the heptane insoluble fraction from 4.3 to 19.15 percent. This is accompanied by a straight line decrease of 13.9 percent in the resin content from 38.6 to 24.7 percent. The levels of saturates and cyclics remain unchanged.
  - e. B6317 Venezuelan Asphalt: The heptane insoluble fraction shows a steady increase from 12.8 to 24.9 percent. The resin content declined from 33.8 to 19.6 percent and showed a small inflection point at the 2-percent acid level.
  - f. Four of the charts show a positive inflection point in the resin content, and this is accompanied by a negative inflection in the level of cyclics. Our experience with the Iatroscan® chromatographic technique has shown that the separation of saturates is straightforward and very reproducible. The separation of the cyclics and resins is much more difficult and subject to variation. Each data point in the charts is the average result of reading 10 Iatroscan® rods and so could reasonably be expected to show the true picture. Although four of the five charts show a decline in the level of cyclics with increasing acid, it cannot be assumed that they do actually decline. It may be some quirk with the technique. The level of the heptane insoluble fraction is not affected because it is not determined with the Iatroscan®. This fraction is removed before the Iatroscan® step and determined gravimetrically.
4. The increase in the amount of heptane insoluble fraction is not necessarily accompanied by an equivalent increase in viscosity. ABM-1, which shows no increase in stiffness when modified with up to 1-percent of 115 percent phosphoric acid, also shows the same rate of increase in heptane insoluble fraction as the other asphalts but, up to the 1-percent acid



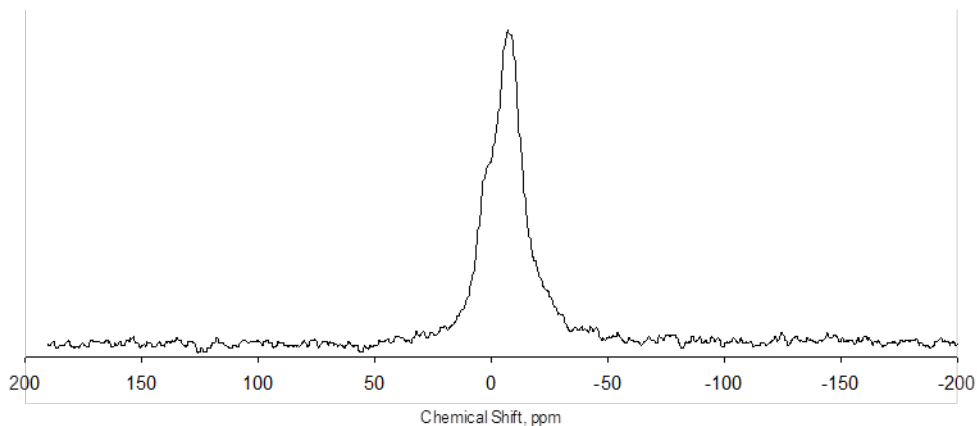
modification level, at least this was found to be actually accompanied by a slight decrease in stiffness (figure 15 and chapter 3).

5. The change in stiffness of the four SHRP reference binders when modified with phosphoric acid is shown in chapter 3. The sensitivity of the stiffness change to phosphoric acid addition found was AAK-1 > AAM-1 > AAD-1 > ABM-1. No correlation could be found between this phosphoric acid/stiffness sensitivity to any of the chemical characteristics published in SHRP-A-645 "SHRP Materials Reference Library: Asphalt Cements: A Concise Data Compilation."<sup>(5)</sup>

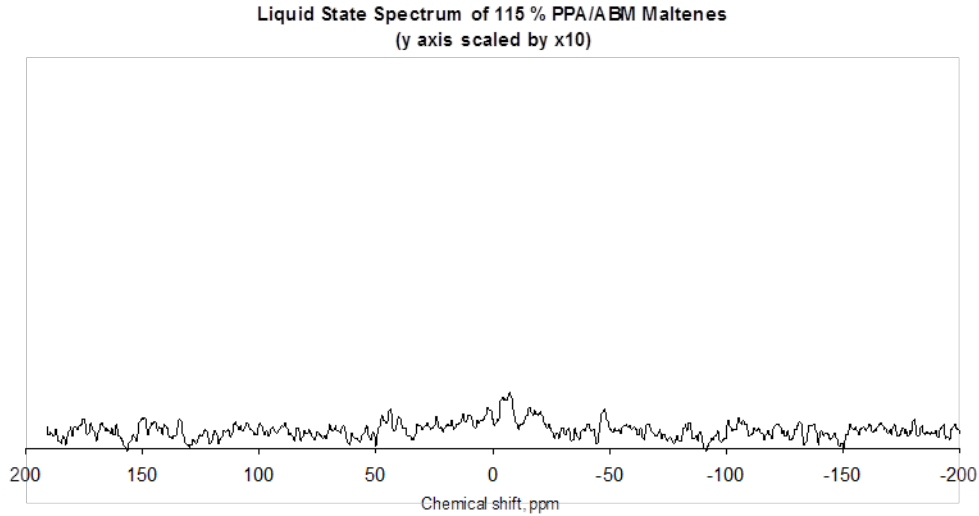
### **HOW DOES THE PHOSPHORIC ACID REACT WITH THE BINDER?**

A small amount of the asphaltenes and heptane-insoluble fractions from the initial solvent separations was analyzed using the energy dispersive spectrometry attachment to the Amray scanning electron microscope. This is purely a qualitative test. It showed that the heptane-insoluble fraction contained phosphorus while the heptane-soluble maltene fraction contained none.

This was confirmed by Liquid State <sup>31</sup>P nuclear magnetic resonance (NMR) spectra. The spectrum for the heptane-insoluble fraction (asphaltenes) shown in figure 21 clearly shows the peak due to the presence of phosphorus. In figure 22, the NMR spectrum for the heptane-soluble fraction (maltenes) has no phosphorus peak.



**Figure 21. Chart. NMR spectrum of heptane-insoluble fraction of phosphoric acid-modified asphalt.**



**Figure 22. Chart. NMR spectrum of heptane soluble fraction of phosphoric acid-modified asphalt.**

#### **MAJOR CONCLUSIONS FROM CHAPTER 2, ANALYTICAL METHODS**

- With proper calibration, the phosphoric acid content of asphalt binders can be readily measured using XRF spectroscopy.
- The Susan P. Needham test, which requires no specialized equipment, can be used to detect the presence of phosphoric acid in asphalt binders.
- Addition of phosphoric acid to asphalt binders causes an increase in the heptane-insoluble fraction, which is not necessarily accompanied by a corresponding increase in binder stiffness.
- The phosphorus from the acid all ends up in the heptane-insoluble phase.
- The increase in the heptane-insoluble fraction is generally accompanied by a decrease in the resin fraction. With some binders, there may have been a change in the level of cyclics although variability in the method makes this uncertain. The level of saturates is unaffected by the use of phosphoric acid.

### CHAPTER 3. EFFECT OF ACID GRADE AND BINDER TYPE

This chapter addresses the issue of acid grade, that is, can all of the commercially available grades of phosphoric acid be used, how does their effect vary with asphalt from different crude oil sources, and how does the rheology of the modified binders change following addition.

When polymers such as SBS are added to asphalt binders, it usually takes several hours before the full stiffening effect is achieved. To determine whether this is the case with phosphoric acid, the stiffness ( $|G^*|/\sin\delta$  at 64 °C) was first measured immediately after mixing. Samples were then oven aged, in air tight containers to minimize oxidation, at 165 °C to determine whether the stiffness would be likely to change after 12 days in a storage tank.

The four SHRP reference asphalts used are shown in table 3, and the five grades of commercially available phosphoric acid grades in table 4.

**Table 3. Properties of the SHRP asphalt binders.**

	Origin	Grade	Asphaltenes (percent)	Polar Aromatics (percent)	Napthenic Aromatics (percent)	Saturates (percent)
AAD-1	CA Coastal	58-28	20.5	41.3	25.1	8.6
AAK-1	Venezuelan	64-22	20.1	41.8	30.0	5.1
AAM-1	West TX Int.	64-16	4.0	50.3	41.9	1.9
ABM-1	CA Valley	58-10	7.1	52.4	29.6	9.0

**Table 4. Commercial grades of phosphoric acid used.**

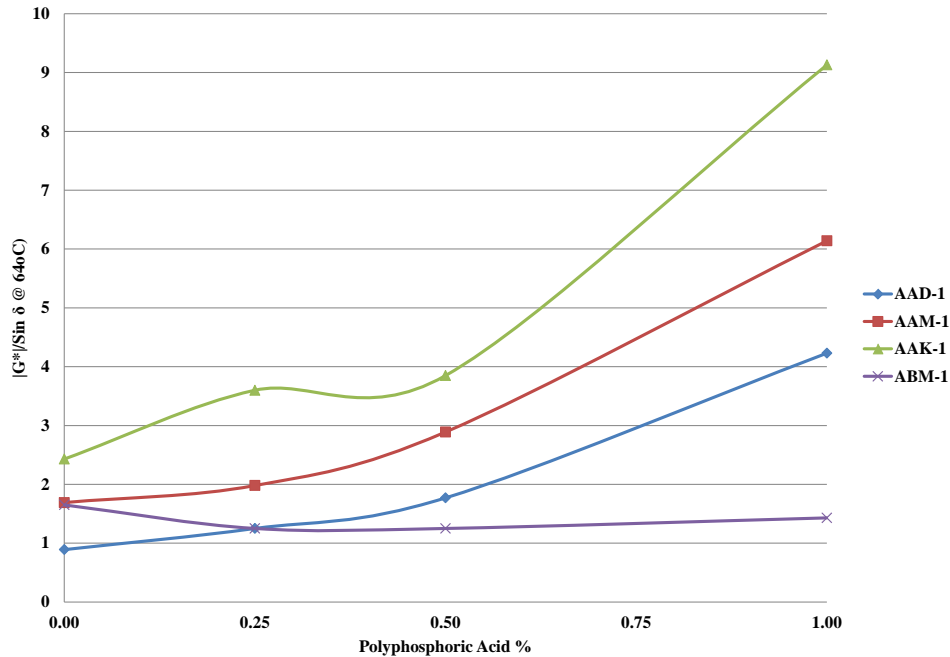
Name	Acid Strength (percent)	Water Content (percent)
Polyphosphoric Acid	115	0
Superphosphoric Acid	105	0
Phosphoric Acid	85	15
Phosphoric Acid	75	25
Green Acid	50	50

Addition levels were 0.25, 0.5, and 1.0 percent normalized to 100-percent phosphoric acid. (For example, in the case of 50-percent green acid, the actual weight of acid would be doubled.)

The samples were prepared by adding acid to the asphalt at 165 °C while mixing with a mechanical stirrer running at 450 rpm. Mixing was continued for 20 min after addition. The binder stiffness, ( $|G^*|/\sin\delta$  at 64 °C) was measured using AASHTO test method T315.

#### EFFECT OF ASPHALT TYPE

The results shown in figure 23 indicate the change in stiffness is asphalt dependent. Asphalt AAK-1 showed the greatest stiffness increase while ABM-1 was hardly affected by PPA addition.



**Figure 23. Chart. Initial stiffness of SHRP reference binders modified with 115-percent phosphoric acid.**

### EFFECT OF PHOSPHORIC ACID GRADE

The results for each of the SHRP asphalts are shown in figure 24 to figure 27. Note that the stiffness scales on each chart are different. The stiffening effect was generally greater with the green acid, possibly because it contains some very strong acidic impurities such as sulfuric and hydrofluoric acids, which might be expected to increase the stiffening effect compared with phosphoric acid, which is a relatively weak acid. The other grades of acid showed similar effects with some minor differences. The test results indicate that any grade could be used to modify asphalt although the green acid might cause corrosion problems and the more dilute grades might cause foaming as the inherent water boils off on contact with the hot asphalt.

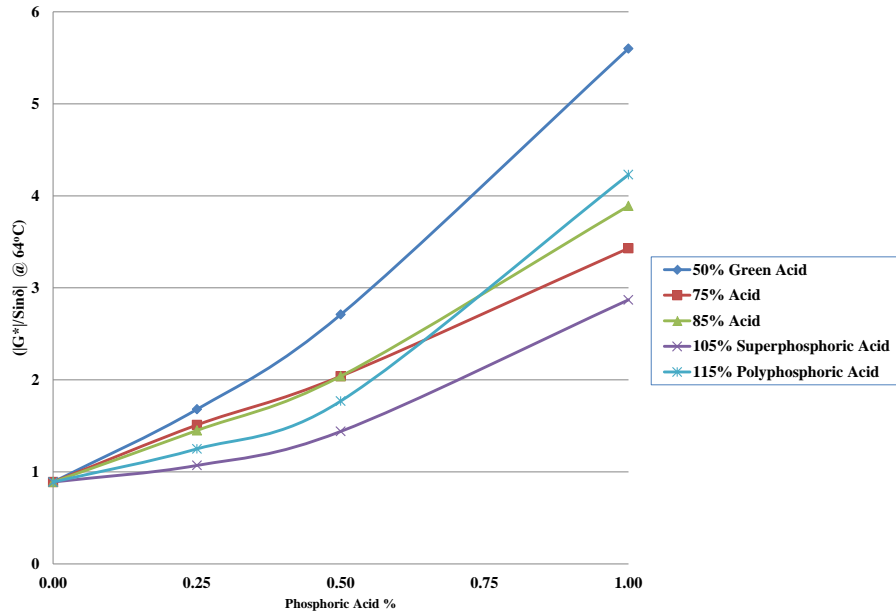


Figure 24. Chart. Effect of phosphoric acid grade on the stiffness of asphalt AAD-1.

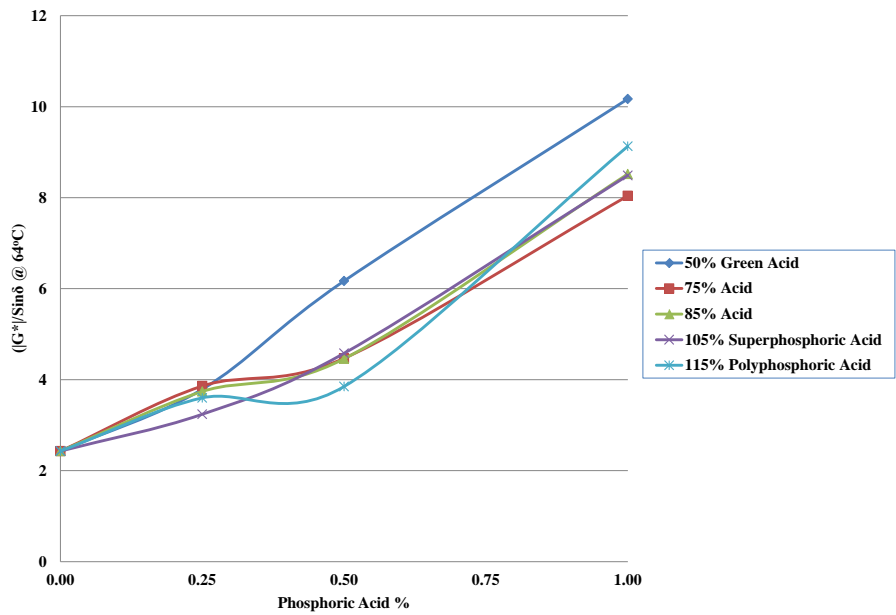


Figure 25. Chart. Effect of phosphoric acid grade on the stiffness of asphalt AAK-1.

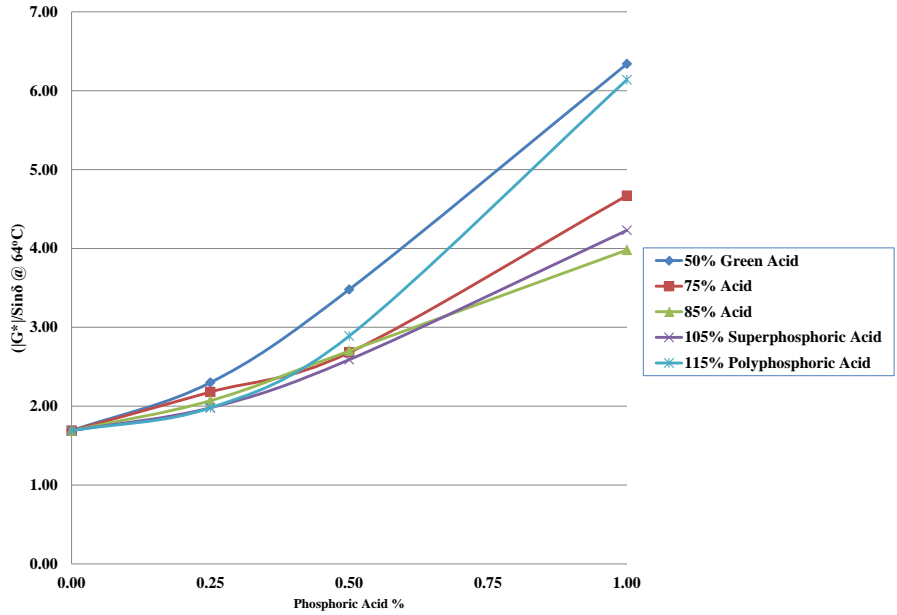


Figure 26. Chart. Effect of phosphoric acid grade on the stiffness of asphalt AAM-1.

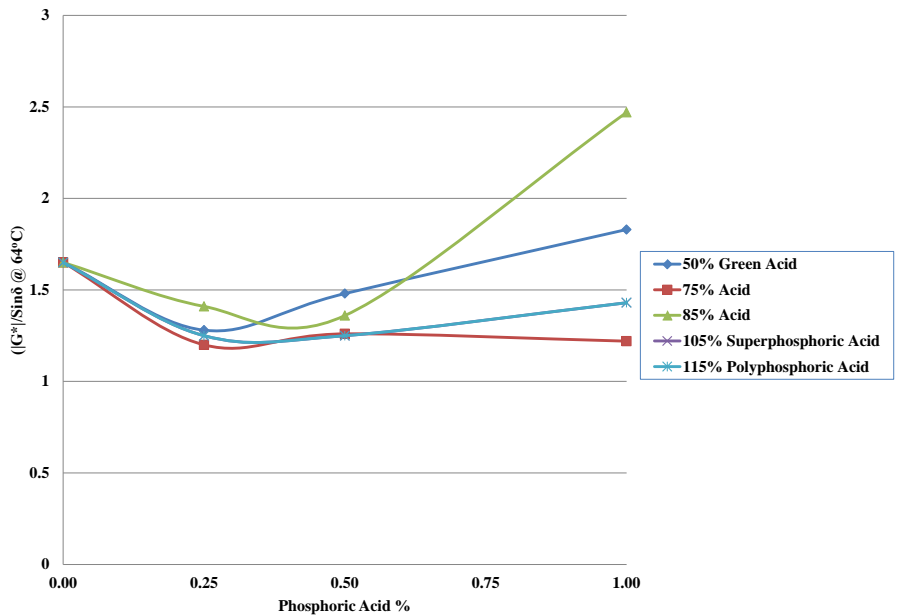


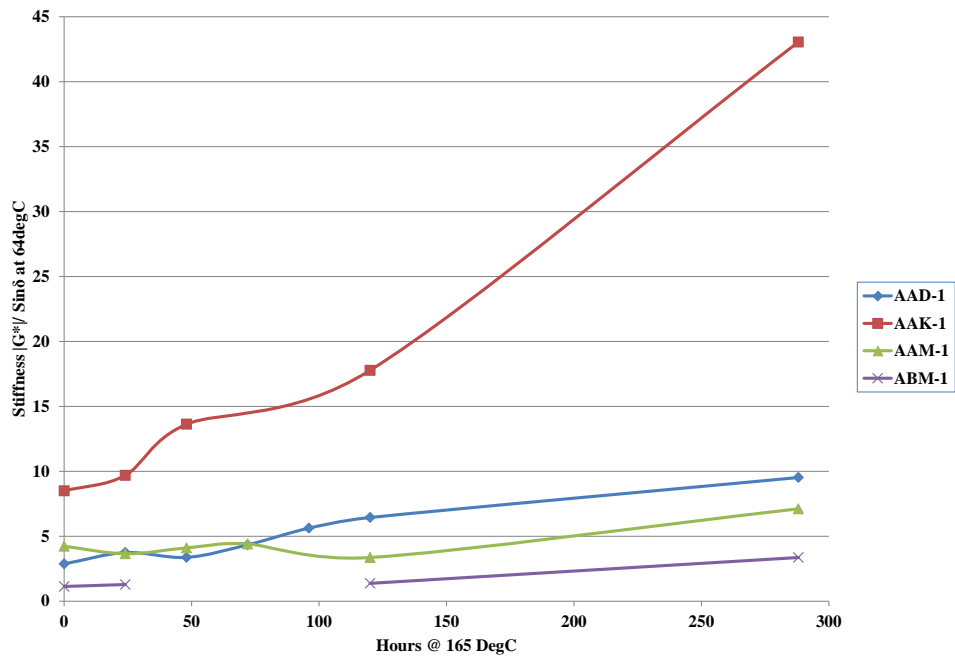
Figure 27. Chart. Effect of phosphoric acid grade on the stiffness of asphalt ABM-1.

### EFFECT OF TANK AGING AT 165 °C

The purpose of this test was to determine whether the stiffness of PPA-modified asphalts was likely to increase if stored in a heated tank for extended periods of time. Asphalt in storage tanks generally has a small exposed surface area to volume ratio, essentially an anaerobic condition. To simulate this condition on a small scale, samples of the four SHRP reference binders were placed in 1/4-pint cans fitted with lever lids and oven aged at 165 °C. Stiffness was measured as  $|G^*|/\text{Sin}\delta$  at 64 °C. Tests were run with all five grades of phosphoric acid and addition levels of

0, 0.25, 0.5, and 1 percent. The results for all 20 of these combinations are given in the appendix in table 16 through table 35. To simplify this report, only the case for 1-percent superphosphoric acid is presented here in figure 28. The numerical data for this case are presented in table 5, which include the control data for zero acid modification. All unmodified binders exhibited some increase in stiffness except ABM-1, which remained almost unchanged. The modified binders all increased in stiffness; asphalt AAK-1 showed the largest change. In this case, the unmodified binder stiffness changed from 2.43 to 12.9, and the 1-percent acid modified material increased from 8.59 to 43.05. A summary chart showing the case for 1-percent superphosphoric acid is shown in table 5.

The numerical data are shown in the appendix.



**Figure 28. Chart. Simulated tank aging of binders modified with 1 percent of 105-percent phosphoric acid.**

**Table 5. Stiffness ( $G^*/\text{Sin}\delta$ ) of simulated tank-aged binders modified with 105-percent phosphoric acid.**

Hours	AAD-1		AAK-1		AAM-1		ABM-1	
	0-percent Acid	1-percent Acid	0-percent Acid	1-percent Acid	0-percent Acid	1-percent Acid	0-percent Acid	1-percent Acid
0	0.89	2.87	2.43	8.49	1.69	4.23	1.65	1.13
24	—	3.74	2.80	9.69	—	3.65	—	1.28
48	—	3.37	—	13.63	—	4.1	—	—
72	—	4.34	—	—	—	4.41	—	—
96	—	5.62	—	—	—	—	—	—
120	1.33	6.44	10.5	17.77	1.96	3.36	1.52	1.37
288	5.92	9.52	12.9	43.05	11.68	7.11	1.81	3.36

— Indicates not measured.

## CONCLUSIONS

The following conclusions can be drawn:

- The stiffening effect of phosphoric acid is asphalt dependent; AAK-1 showed the greatest stiffness response. ABM-1 stiffness was hardly affected by acid modification. Both AAD-1 and AAM-1 gave very similar stiffness values on modification with acid. For these reference binders in these tests, no real correlation could be found between their published properties<sup>(5)</sup> and their stiffness sensitivity to phosphoric acid modification. This ranking is shown in table 6.

**Table 6. Stiffness sensitivity of reference binders to PPA modification.**

	<b>Origin</b>	<b>Grade</b>	<b>Stiffening Rank</b>	<b>Asphaltenes (percent)</b>	<b>Polar Aromatics (percent)</b>	<b>Napthenic Aromatics (percent)</b>	<b>Saturates (percent)</b>
AAD-1	CA Coastal	58-28	2	20.5	41.3	25.1	8.6
AAK-1	Venezuelan	64-22	1	20.1	41.8	30.0	5.1
AAM-1	West TX Int.	64-16	3	4.0	50.3	41.9	1.9
ABM-1	CA Valley	58-10	4	7.1	52.4	29.6	9.0

- There was some increase in stiffness after oven aging for at 165 °C, especially for asphalt AAK-1. This suggests that the stiffness of asphalt like AAK-1 might increase if stored molten in a tank for extended periods of time.
- Any grade of phosphoric acid can be used. The impurities in green acid may cause some equipment corrosion.



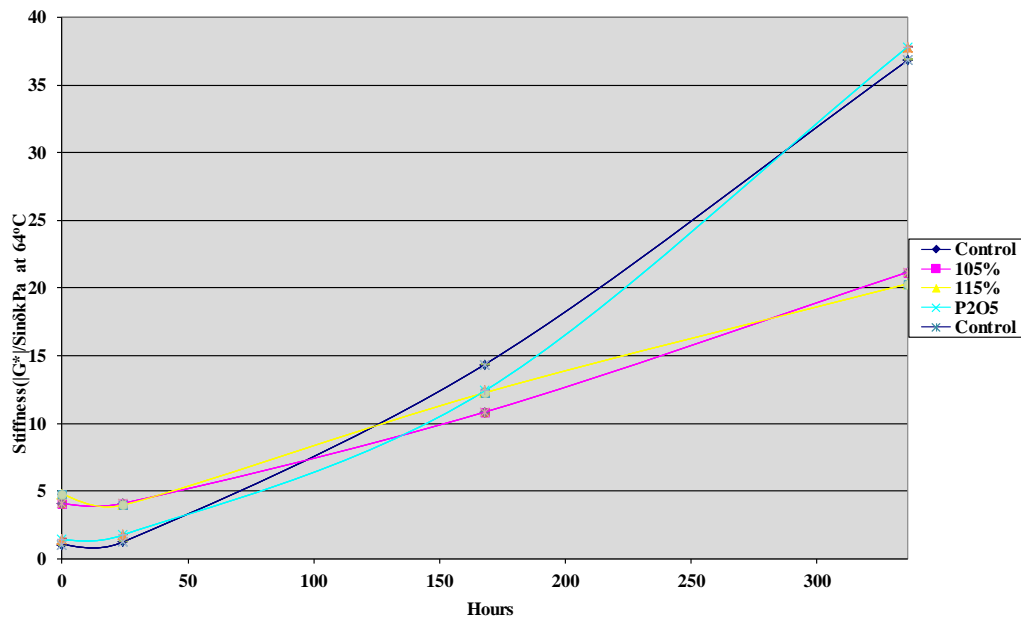
## CHAPTER 4. AGING

### DOES PHOSPHORIC ACID CATALYZE ASPHALT OXIDATION IN HOT MIX ASPHALT BINDERS?

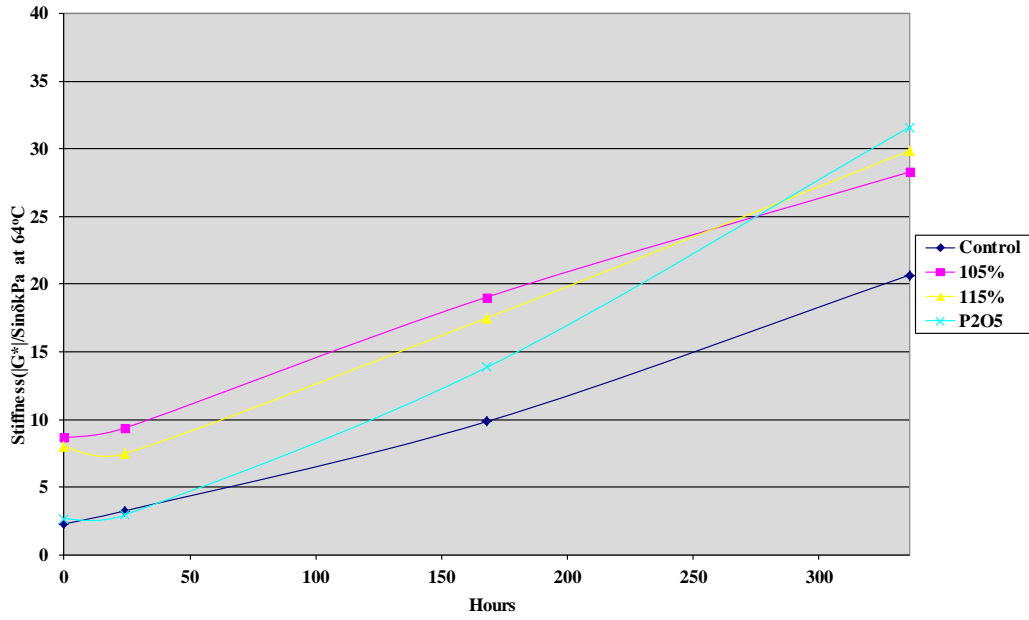
Phosphoric acid is used as a blowing catalyst in producing asphalt for roofing; consequently, fears have been expressed that its use as a binder modifier will cause premature aging of paving asphalts. To test this concern, samples were modified with 105- and 115-percent phosphoric acid and aged at 100 °C in the PAV under air pressure. Because phosphorus pentoxide has been used as a blowing catalyst, it was included in the study.

Samples were stored in open ¼-pint cans. The level of acid used was 1 percent (calculated as 100-percent acid). The stiffness was measured as  $|G^*|/\sin\delta$  at 64 °C. The results are shown in figure 29 to figure 32, and the numerical data are shown in the appendix in table 36 through table 39.

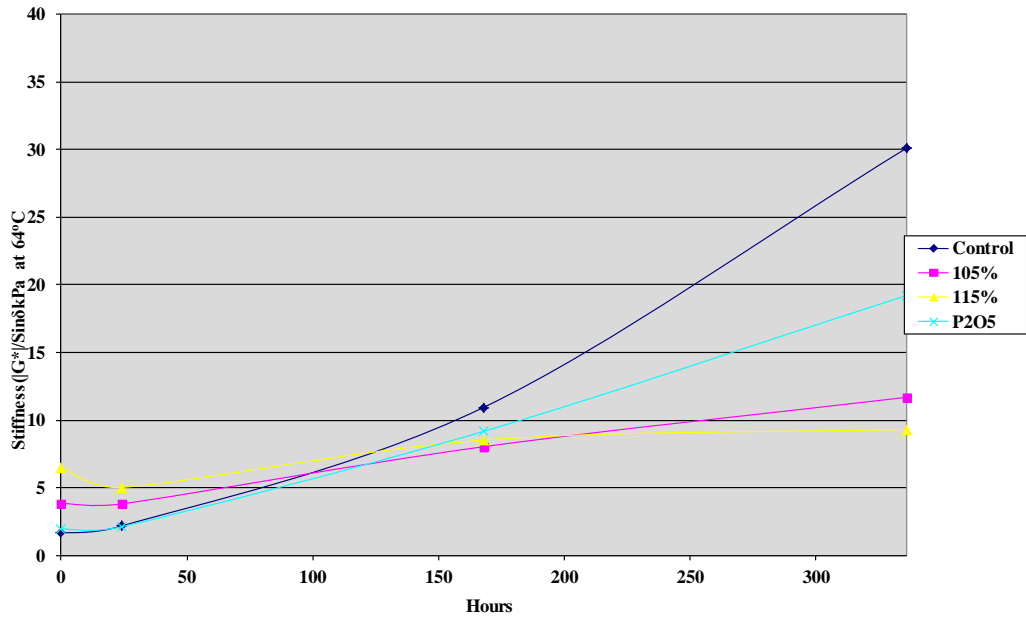
To determine whether any stiffness change was due to oxidation or simple the result of exposure to 100 °C temperature for 300 hours, the tests were repeated under nitrogen pressure instead of air. Figure 33 to figure 36 show the data graphically; the numerical results are in table 40 through table 43.



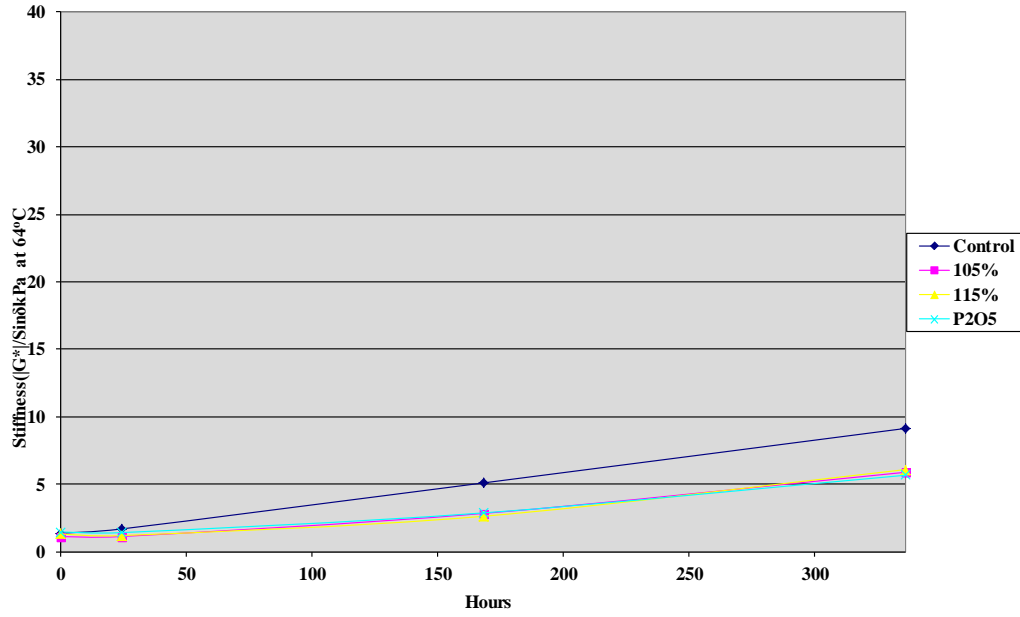
**Figure 29. Chart. PAV aging of asphalt AAD-1 modified with 1-percent phosphoric acid at 100 °C under air.**



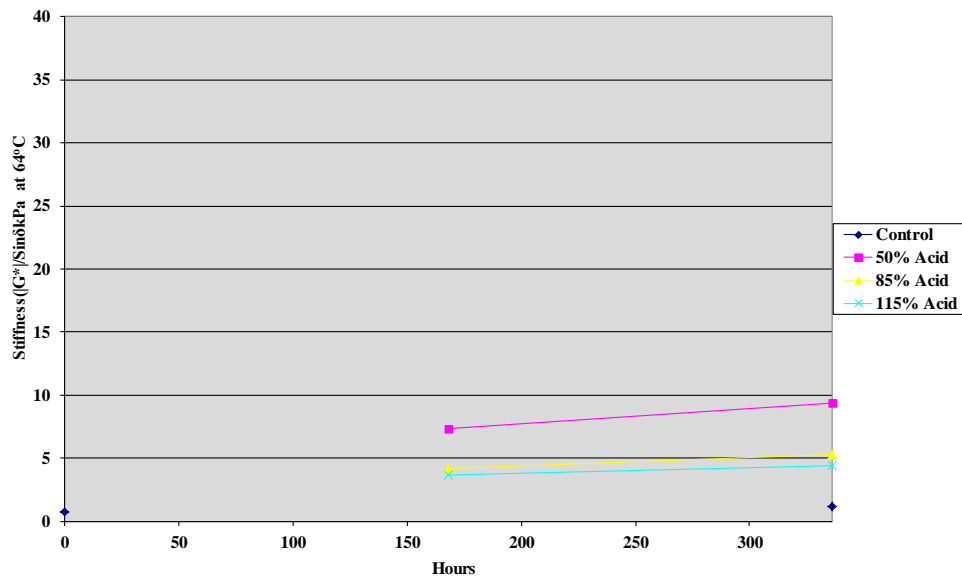
**Figure 30. Chart. PAV aging of asphalt AAK-1 modified with 1-percent phosphoric acid at 100 °C under air.**



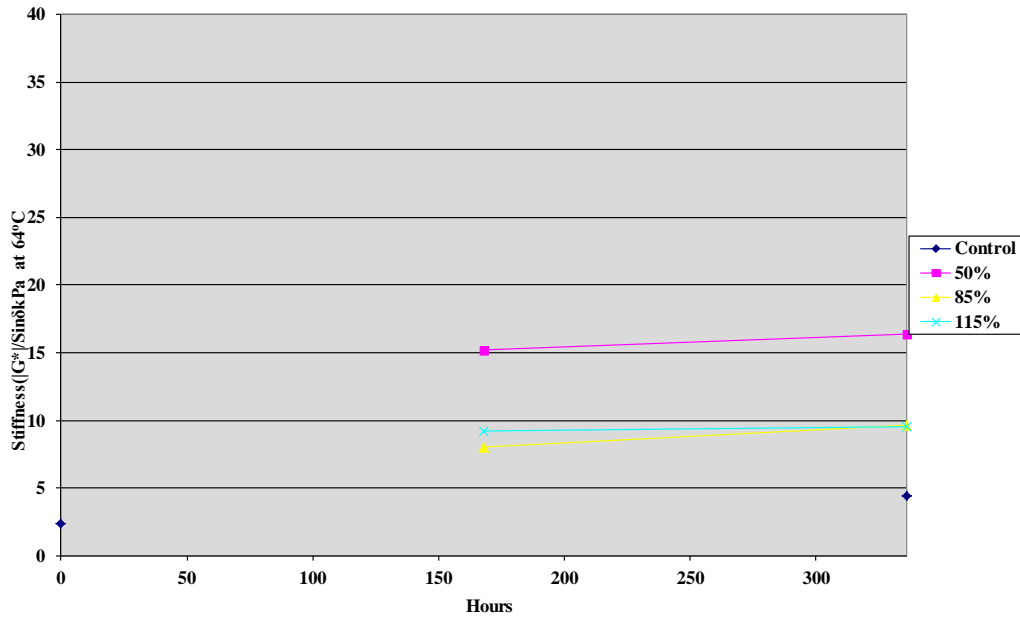
**Figure 31. Chart. PAV aging of asphalt AAM-1 modified with 1-percent phosphoric acid at 100 °C under air.**



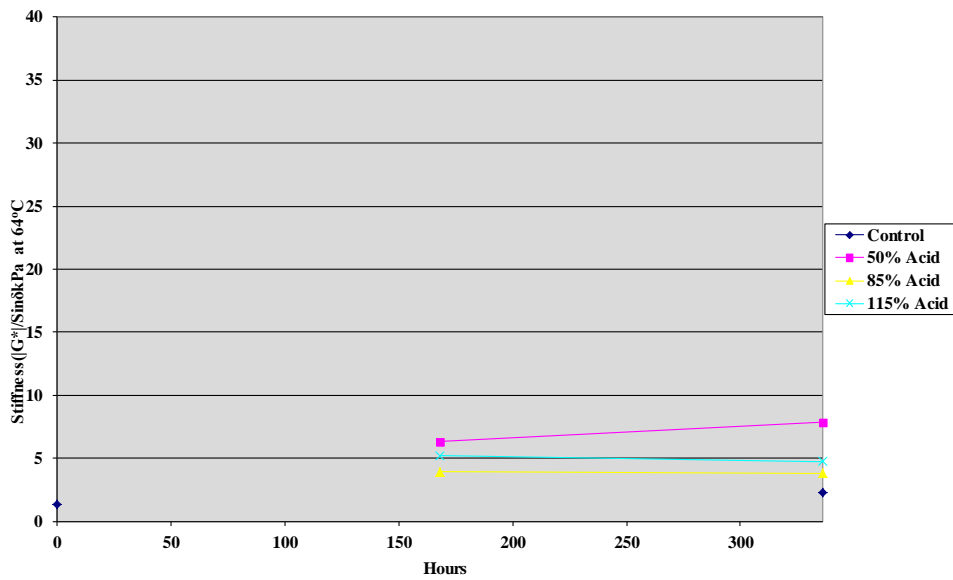
**Figure 32. Chart. PAV aging of asphalt ABM-1 modified with 1-percent phosphoric acid at 100 °C under air.**



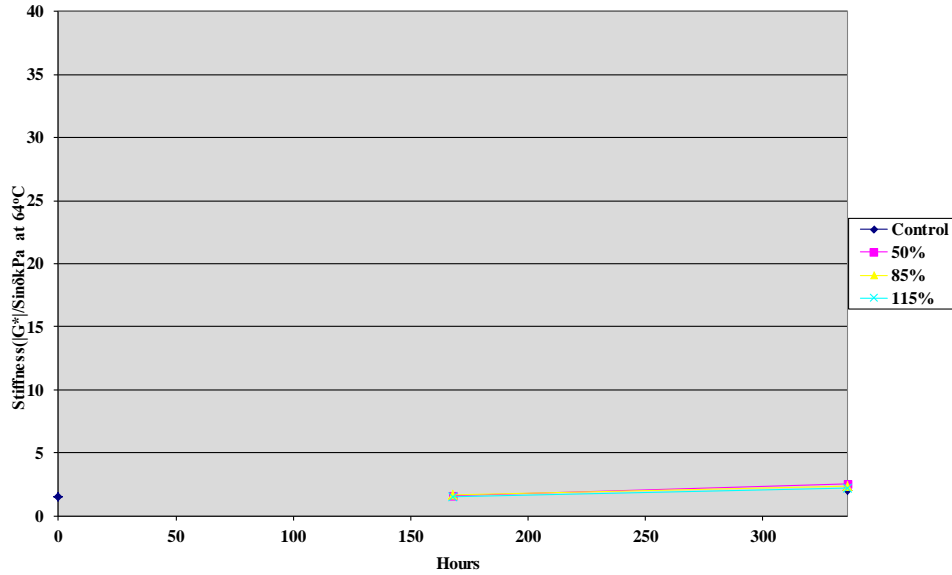
**Figure 33. Chart. PAV aging of asphalt AAD-1 modified with 1-percent phosphoric acid at 100 °C under nitrogen.**



**Figure 34. Chart. PAV aging of asphalt AAK-1 modified with 1-percent phosphoric acid at 100 °C under nitrogen.**



**Figure 35. Chart. PAV aging of asphalt AAM-1 modified with 1-percent phosphoric acid at 100 °C under nitrogen.**



**Figure 36. Chart. PAV aging of asphalt ABM-1 modified with 1-percent phosphoric acid, at 100 °C under nitrogen.**

## CONCLUSIONS

- Except for binder AAK-1, the phosphoric acid modified binders aged less than the unmodified controls.
- With the exception of AAK-1, phosphorus pentoxide did not cause increased stiffness compared to acids.
- The increase in stiffness of the samples aged under nitrogen was much less than those aged under air pressure. This suggests that any increase in stiffness is due to asphalt oxidation rather than chemical reaction of the binders with phosphoric acid.

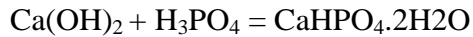


## CHAPTER 5. LIME AND LIMESTONE AGGREGATES

### LIME

When lime (calcium hydroxide) is used as an antistrip additive in asphalt binders, it is common to use 1 percent of lime based on the weight of aggregate. Concerns have been expressed that any phosphoric acid in the binder would react with the lime so that it would no longer be effective as an antistrip additive.

The chemistry of this reaction is given in the following equation:



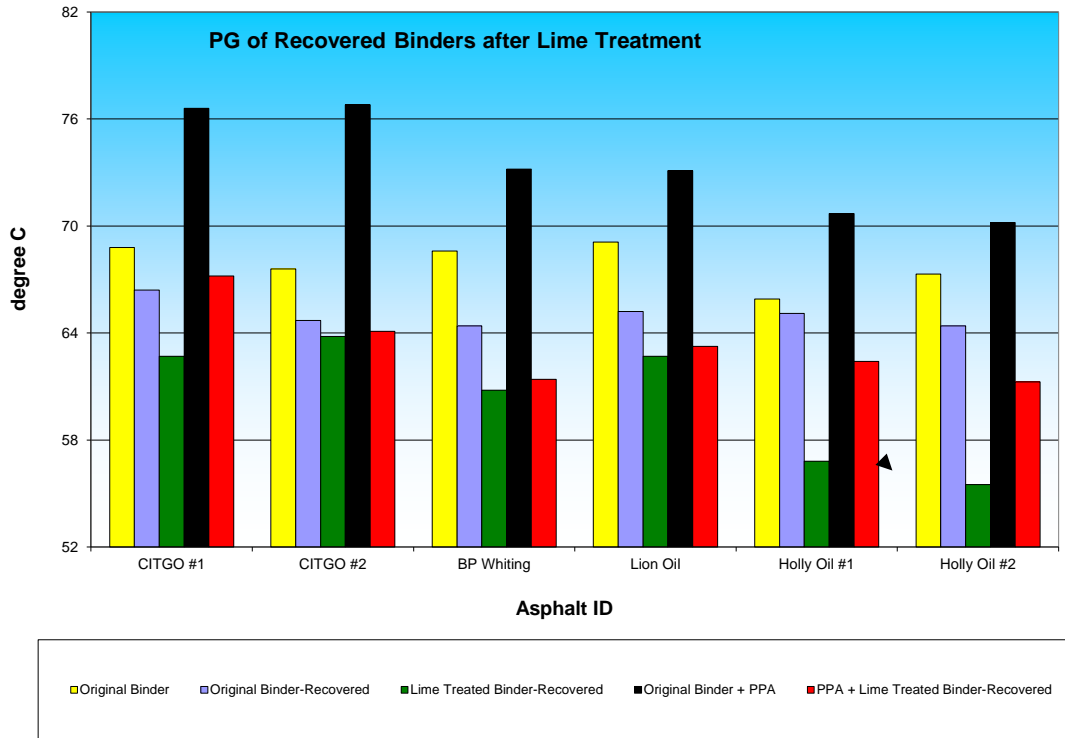
Stoichiometrically, 74 lb of lime would react with 98 lb of phosphoric acid yielding 172 lb of calcium phosphate. If the mix contains 1 percent of lime based on the aggregate and 1 percent of phosphoric acid based on the binder content, then there is a large excess of lime, about 25 times.

To determine whether or not the phosphoric acid in the binder would react with lime (calcium hydroxide), six different phosphoric acid Modified PG 64 binders were used; two from Citgo®, two from HollyFrontier®, one from Lion Oil, and one from BP Whiting. The binders were modified with 1-percent phosphoric acid and then mixed with 20-percent lime by weight of the asphalt at 165 °C using a propeller stirrer to blend the lime into the hot asphalt. To account for any possible reactions of lime with the binders themselves, samples of the unmodified binders were also treated with 20-percent lime.

The lime was removed by solvent extraction, the lime was filtered out, and the binder recovered by evaporation of the solvent. All the binders, both modified and unmodified, were put through the same extraction and recovery process.

The results given in figure 37 show the following:

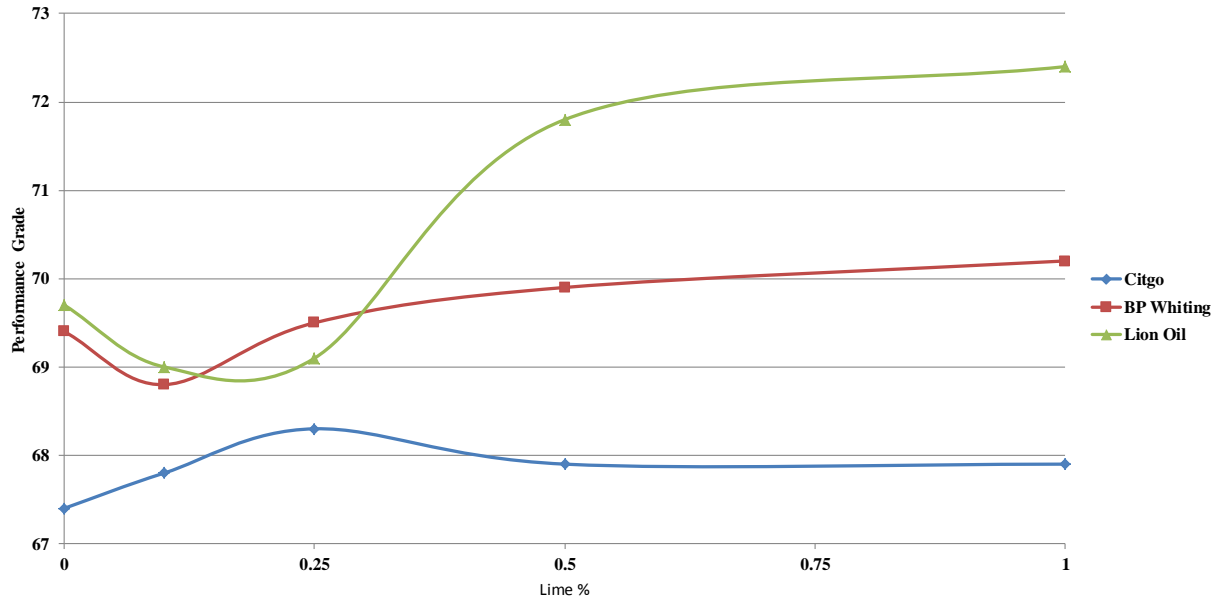
- The PG of phosphoric acid-modified binders (black bars) was different for each binder and considerably higher than that of the unmodified binders.
- The PG of the recovered unmodified binders (purple bars) was slightly lower than the original.
- The PG of the recovered binders treated with lime alone (green bars) was lower than the original, particularly so with the binders from HollyFrontier®.
- The PG of the phosphoric acid treated binders after lime treatment and recovery to remove the lime (red bars) was lower than the phosphoric acid-modified binders and was close to the PG of the original binders.



**Figure 37. Chart. Performance grades of binders after treatment with lime.**

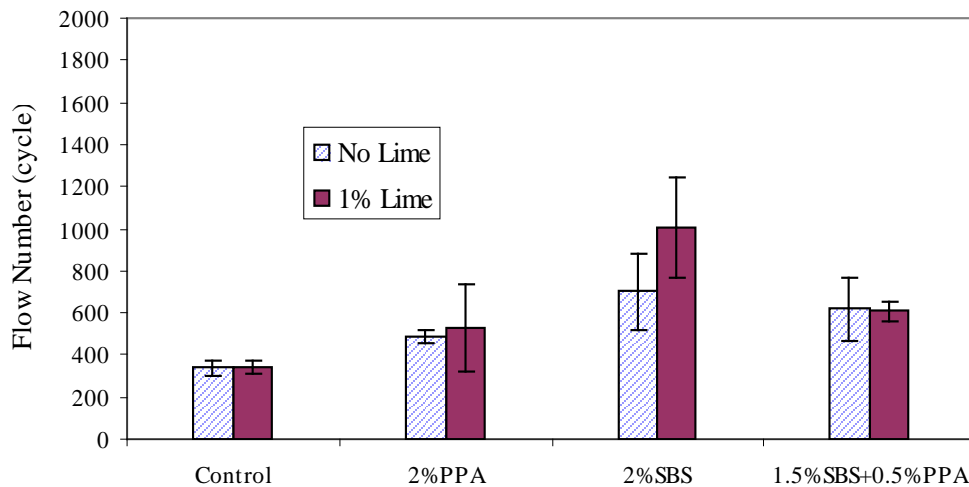
This study clearly shows that lime reacts with the phosphoric acid in a phosphoric acid-modified binder. To what extent this would occur in a mix is unknown. The stiffening effect of the acid is clearly lost after treatment with lime if the lime is removed during the binder recovery process. It is a complex issue because as figure 38 shows, the addition of an alkali like lime sometimes causes an increase in binder stiffness (PG). One might argue that if the mix is already treated with lime, then the addition of phosphoric acid to the binder might be superfluous.



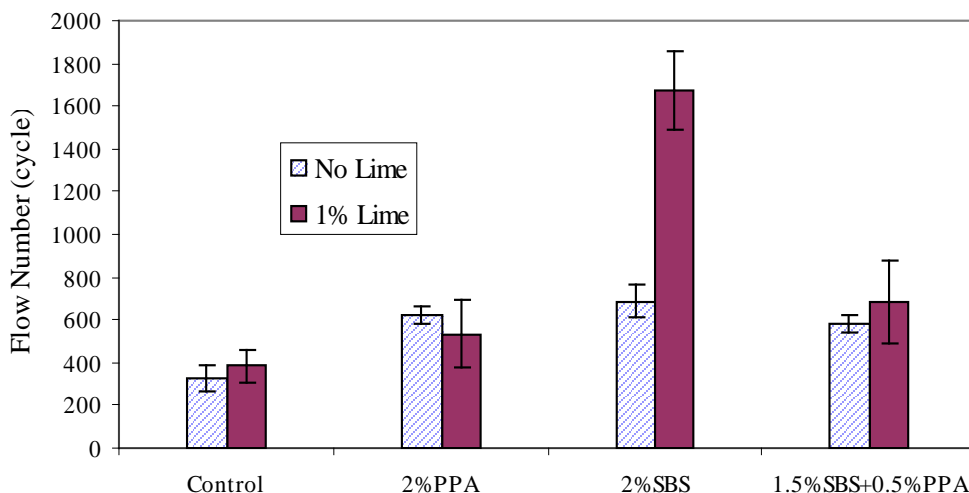


**Figure 38. Chart. Effect of lime content on asphalt stiffness.**

As part of another research effort, the flow numbers of gyratory specimens containing lime, phosphoric acid, and SBS polymer were measured using AASHTO test method TP-79 “Standard Method of Test for Determining the Dynamic Modulus and Flow Number for Asphalt Mixtures using the Asphalt Mixture Performance Tester (AMPT).” The aggregate in these specimens was diabase, and the asphalts were grade PG 64 from Lion Oil (binder B) and HollyFrontier® (binder C). The results are given in figure 39 and figure 40.



**Figure 39. Chart. Flow number for the mixture modified with binder from Lion Oil.**



**Figure 40. Chart. Flow number for the mixture modified with binder from HollyFrontier® asphalt.**

Lime addition to the HollyFrontier® asphalt samples showed no increase in flow number for the control, and the Lion Oil showed a modest increase. The addition of 2-percent phosphoric acid (a very high level of modification not generally used in practice) to the lime-treated samples showed a slight increase for the HollyFrontier® asphalt sample and a slight decrease for the Lion Oil binder. Modification with 2-percent SBS polymer showed a significant increase in flow number as would be expected. The addition of lime to the SBS modified samples appears to have a synergistic effect, with a substantial increase in flow number especially in the case of the HollyFrontier® asphalt binder. This synergy appeared to be almost totally absent when the binder was modified with 1.5-percent SBS and 0.5-percent phosphoric acid.

## LIMESTONE

This experiment was designed to determine whether phosphoric acid in the binder would react with basic aggregates, e.g., limestone (primarily calcium carbonate). Several HMA samples were made with different limestone aggregates. The asphalt was recovered, tested for the high temperature PG, and the phosphorus content determined. The asphalt type and limestone aggregate sources were varied to see the effect.

Three asphalts from different sources were used: Citgo® (B6362), BP Whiting (B6364), and Lion Oil (B6367). Three aggregates were used: Maryland limestone (designated as MD) and two limestone samples from New York State Department of Transportation (NYSDOT) (designated NY3 and NY4).

The initial high temperature performance grade was 64 °C for all three asphalts. The asphalts were modified with 1-percent phosphoric acid by weight of the binder and DSR measurements of the original and RTFOT samples were made. The resulting high temperature PG of the phosphoric acid modified asphalts was 70 °C.

Loose mix was made with both the control and the phosphoric acid-modified asphalt for each aggregate. This resulted in 18 loose mix samples. All of the loose mix samples were short-term

oven aged at 135 °C for 4 h. The job mix formula for NY3 and NY4 aggregate was provided by NYSDOT and is summarized in table 7.

**Table 7. Limestone mix designs.**

Aggregate	MD	NY3	NY4
	Percent	Percent	Percent
Fine	56	50	37
Middle	—	—	31
Coarse	44	50	32
Asphalt	5.5	6.5	5.4

— Indicates not applicable.

The loose mix was extracted using AASHTO: T164 “Quantitative Extraction of Asphalt Binder from Hot-Mix Asphalt (HMA)” and recovered using AASHTO: T170 “Recovery of Asphalt from Solution by Absorb Method.” The extraction solvent was trichloroethylene (TCE). Every attempt was made to minimize the amount of aging that took place during the procedures by following the times and temperatures specified in the methods. The recovered binders were analyzed by Fourier transform infrared spectroscopy to ensure that no residual TCE solvent was present. DSR measurements were made, and the high temperature and continuous high temperature PG (using the RTFOT criteria of 2.2 kPa) was calculated. All of the recovered binder samples were analyzed for the presence of phosphoric acid with XRF as described earlier in this report.

The results summarized in table 8, show that all the recovered phosphoric acid-modified binders contained phosphorus.

**Table 8. Phosphorus in recovered asphalt binders.**

		Phosphorus Present?			
		Binder Only	Recovered		
			NY4	NY3	MD
CITGO®	Unmodified	no	no	no	no
(B-6362)	1% phosphoric acid	yes	yes	yes	yes
BP Whiting	Unmodified	no	no	no	no
(B-6364)	1% phosphoric acid	yes	yes	yes	yes
Lion Oil	Unmodified	no	no	no	no
(B-6367)	1% phosphoric acid	yes	yes	yes	yes

While there was a slight increase in the continuous grade temperature in some of the modified binders recovered from the limestone mixes, this was less than 6 °C, indicating no change in the PG. The binder grade did not decrease in any of the samples in contrast to the case with lime.

Figure 41 shows a plot of the data grouped by aggregate type; the DSR results are in table 9.

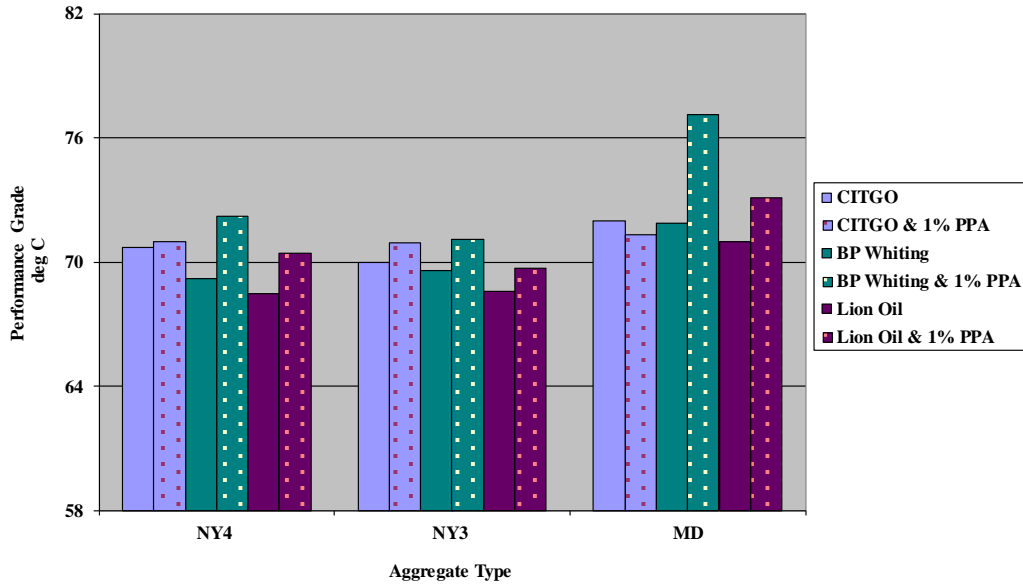


Figure 41. Chart. PGs of phosphoric acid-modified binders recovered from limestone mixes.

Table 9. High temperature PGs of phosphoric acid-modified binders recovered from limestone mixes.

		RTFOT Binder PG	Recovered Binder		
			Aggregate type		
			NY4	NY3	MD
CITGO®	PG	64	70	70	70
	Continuous PG	66.2	70.7	70.0	72.0
CITGO® and 1-percent PPA	PG	70	70	70	70
	Continuous PG	74.8	71.0	70.9	71.3
BP Whiting	PG	64	64	64	70
	Continuous PG	66.0	69.2	69.6	71.9
BP Whiting and 1-percent phosphoric acid	PG	70	70	70	76
	Continuous PG	73.0	72.2	71.1	77.1
Lion Oil	PG	64	64	64	70
	Continuous PG	66.9	68.5	68.6	71
Lion Oil and 1-percent phosphoric acid	PG	70	70	70	70
	Continuous PG	70.8	70.4	69.7	73.1

## CONCLUSIONS

- Lime (calcium hydroxide) in HMA can react with the phosphoric acid in phosphoric acid-modified binders.
- Limestone aggregates in HMA do not readily react with the phosphoric acid in phosphoric acid-modified binders.



## CHAPTER 6. MOISTURE

### EFFECT OF WATER ON ASPHALT MASTICS WITH AND WITHOUT PHOSPHORIC ACID

Phosphoric acid is a very hydrophilic material. Some concerns were expressed that its use may negatively affect the moisture resistance of asphalt mixes. Tests were performed that involved immersing samples of mastics and binders in water for extended periods of time. This condition is rarely found in practice, and therefore represents an extreme case and should not be interpreted as an indication of what would happen on a real highway.

To measure the moisture resistance, mastics containing 50-percent aggregate fines (sand, diabase, gravel, and montmorillonite) were cast into silicone rubber molds in the shape of either direct tension dog bones or Bending Beam Rhometer (BBR) samples. (These were the only silicon rubber molds available.) Montmorillonite was used because it is water-sensitive expansive clay. The presence of such materials can have a deleterious effect on asphalt pavements. The asphalt binder used (B6317) was supplied by Citgo® and was a blend of 60-percent Bachaquero and 40-percent Menemota 21.

The mastic samples were weighed and then immersed in a water bath at 7 °C. At intervals over the next 105 days, the dog bones were dried with a paper towel, weighed, and the amount of water absorbed calculated. The results are shown in the figure 42 through figure 45. The effect on the stiffness of soaked specimens of Citgo® asphalt are shown in figure 46.

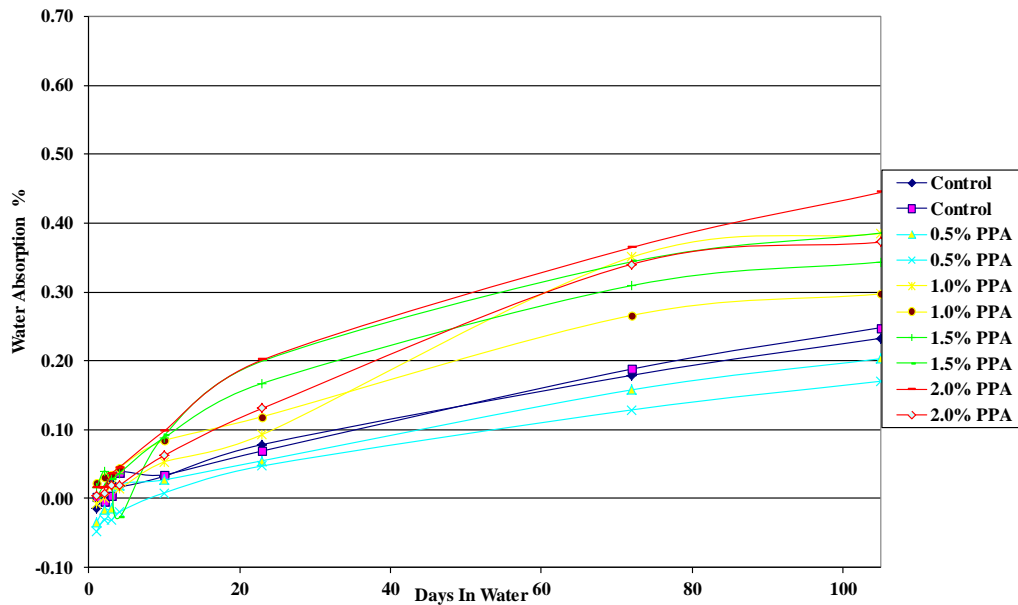
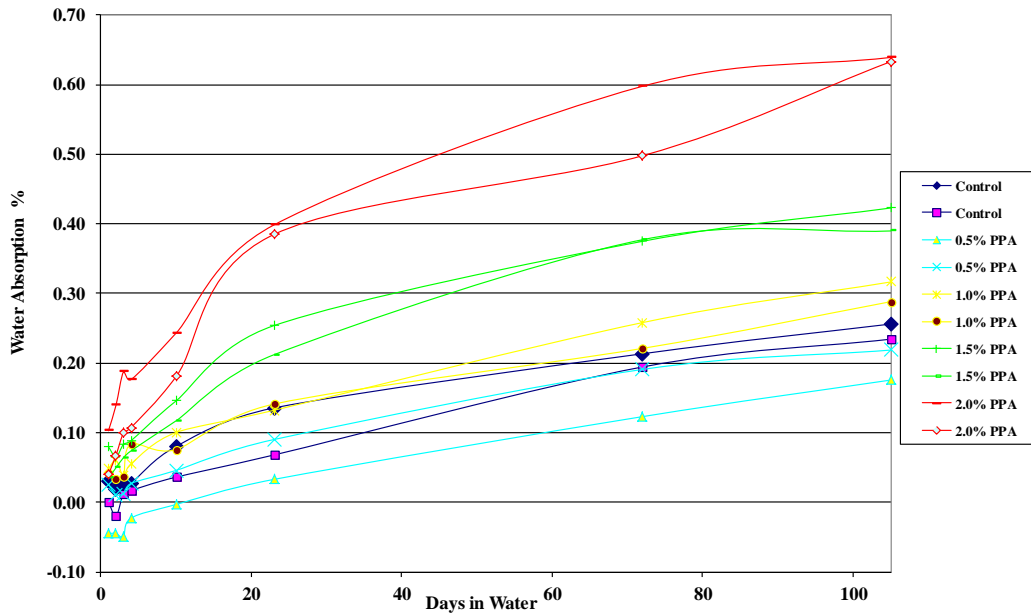
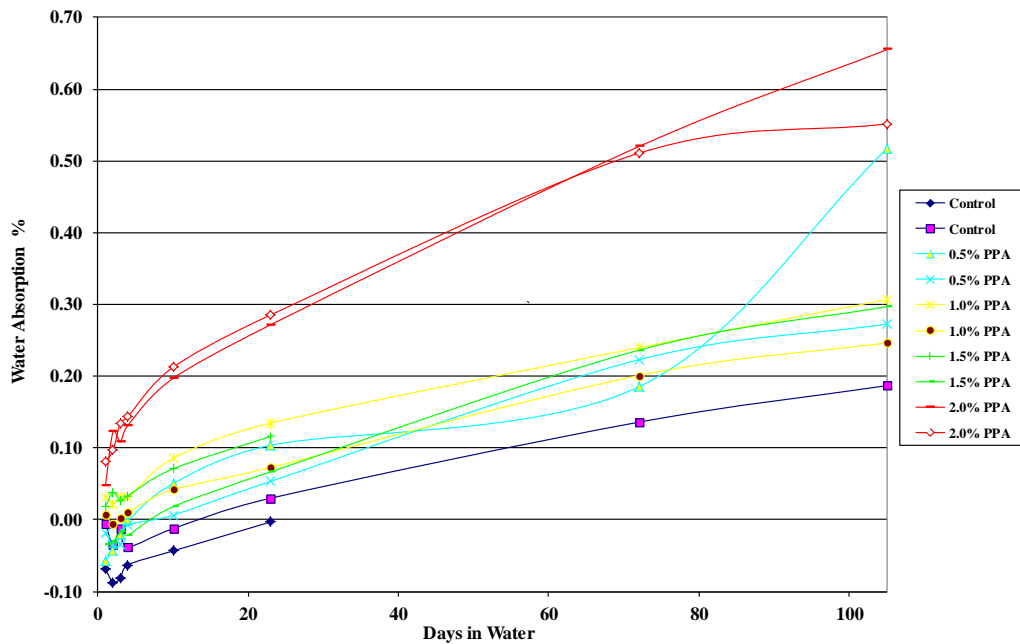


Figure 42. Chart. Plot of moisture absorption of Citgo® 50-percent asphalt/sand mastic modified with 115-percent phosphoric acid.

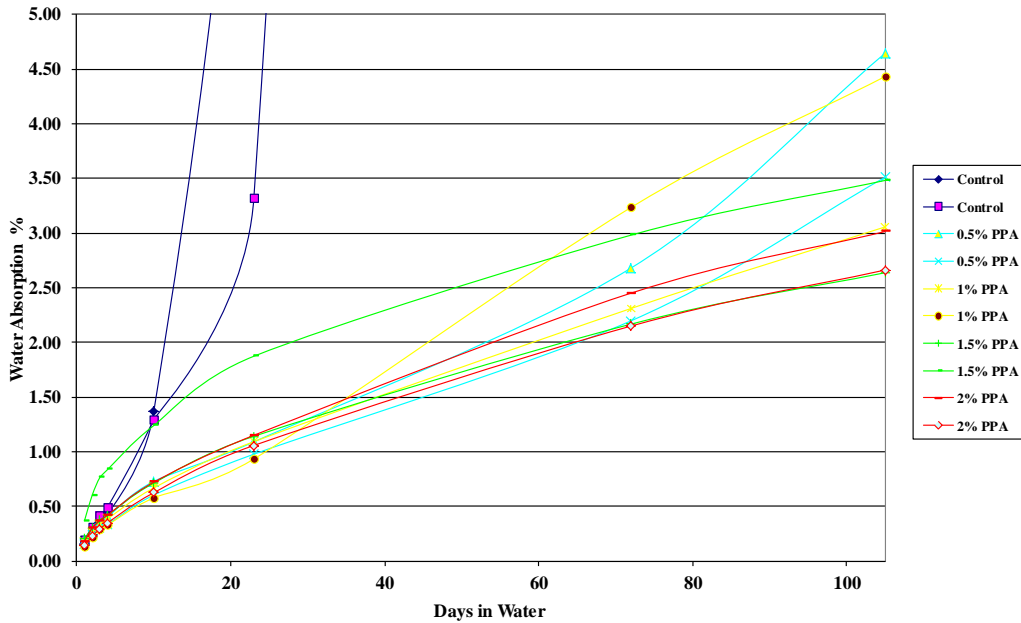


**Figure 43. Chart. Plot of moisture absorption of Citgo® 50-percent asphalt/diabase mastic modified with 115-percent phosphoric acid.**



**Figure 44. Chart. Moisture absorption of Venezuelan 50-percent asphalt/gravel mastic modified with 115-percent phosphoric acid.**

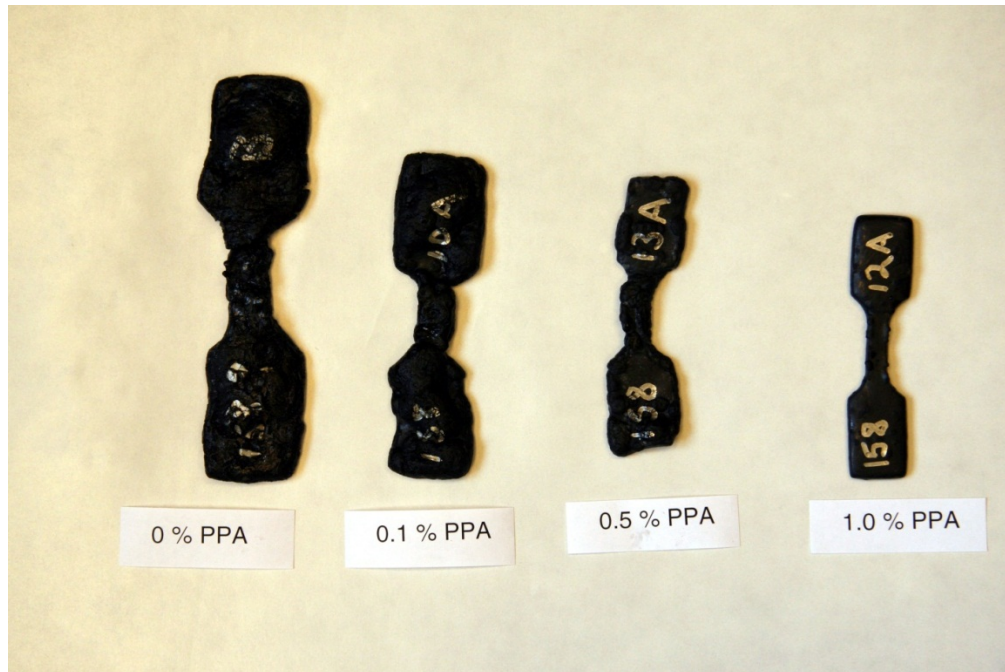




**Figure 45. Chart. Moisture absorption of Citgo® 50-percent asphalt/montmorillonite mastic modified with 115-percent phosphoric acid.**

### Conclusions

- The amount of water absorbed by the control samples after 105 days was independent of the aggregate. Most of the mastics absorbed 0.2 to 0.3 percent. The exception was montmorillonite, which was expected to be water sensitive. It absorbed 105 percent water.
- The water absorption of the mastics tended to increase with increasing acid levels although the differences are rather small. Again the exception was montmorillonite, which showed the opposite effect; moisture absorption decreased with increasing acid levels.
- The most significant effect of phosphoric acid modification was with the mastics containing montmorillonite clay, which is well known for its water absorption properties. The unmodified control samples absorbed 105 percent water over the 105-day test period whereas the samples containing phosphoric acid absorbed only 3 to 4 percent water. This is clearly demonstrated in figure 46 with asphalt from the BP Whiting Refinery.



**Figure 46. Chart. Fifty-percent montmorillonite asphalt binder mastic after water immersion for 105 days.**

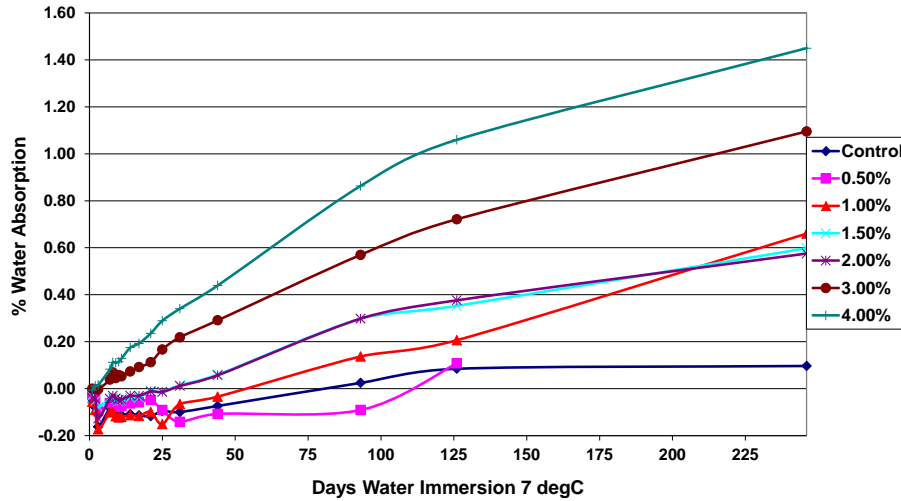
#### **EFFECT OF WATER ON NEAT ASPHALT BINDERS**

Similar tests to those described above were carried out using BBR beams of neat Venezuelan asphalt (B6317) modified with 115-percent phosphoric acid at levels up to 4 percent. The results are shown in figure 47 indicate the following:

Most samples, including the unmodified control, lost 0.1- to 0.25-percent weight almost immediately. These samples subsequently gained weight and ultimately had an overall weight gains. This suggests the possibility that water-soluble materials are initially being extracted from the asphalt itself; however, no attempt was made to identify the nature of this material.

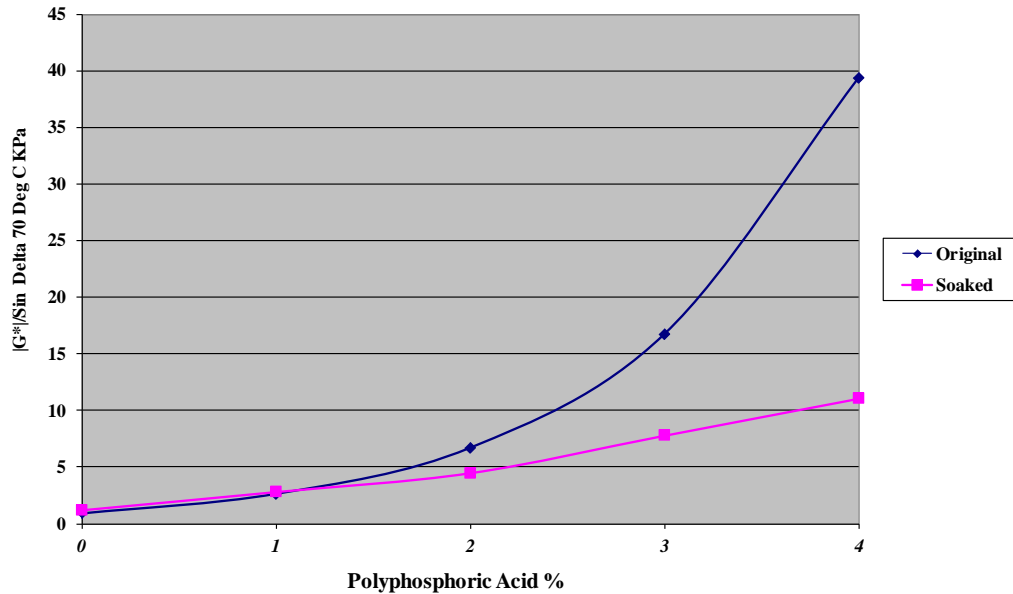
The control, 0.5- and 1-percent modified samples all showed approximately the same level of increase in weight after 126 days of immersion in water. This weight gain was between 0 and 0.1 percent.

Long immersions and increasing phosphoric acid levels resulted in higher levels of water absorption.



**Figure 47. Chart. Plot of water absorption of Venezuelan asphalt beams modified with 115-percent phosphoric acid.**

The effect of this water absorption on the stiffness of the Citgo® asphalt was examined; the results are shown in figure 48.



**Figure 48. Chart. Plot of stiffness of phosphoric acid modified Citgo® asphalt after 245 days of water immersion.**

As mentioned earlier, phosphoric acid is a very hydrophilic material; it is very water soluble. To determine whether there is a risk of rain leaching phosphoric acid from a pavement, a number of soaking tests were devised. Because there is no standard test to determine leachates from HMA pavements, a test protocol was established for comparison purposes. The amount of phosphoric acid extracted from a pavement on a daily basis is likely to be below the limits of detection. To

determine whether this could become an issue over a period of time, the following procedure was used to test the likelihood of this event.

The test consisted of immersing gyratory specimens in distilled water contained in clean high density polyethylene (HDPE) buckets. Periodically, the phosphate content of the water over 245 days was measured. This is an extreme case—the specimens were completely immersed in water whereas pavements rarely are.

Gyratory specimens 6 by 4.5 inches were made using the standard TFHRC Accelerated Loading Facility dense coarse graded 12.5-mm nominal maximum aggregate size Superpave mix with a 5-percent binder content. The aggregate was a diabase. Each core contained approximately 4,885 g of aggregate and 258 g of binder (Citgo® binder referenced earlier). The binder was modified with levels of PPA from 0 to 4 percent. The cores were placed in new clean HDPE buckets to which 2.5 L of distilled water were added; this amount was sufficient to cover the specimens. The phosphoric acid content of the water was measured over a period of 245 days using ion exchange chromatography (Dionex™ ICS-2000). The calculations were made assuming the phosphate was present in the water as orthophosphoric acid.

To determine whether there was any asphalt or aggregate dependency, a second suite of samples was tested. In this case, two asphalt binders were used with two different aggregates, namely a Lion Oil (B6367) and BP Whiting (B6364) binder and diabase and Georgia granite aggregates. To gain some insight on the effect of air void content, the samples were tested as both gyratory specimens and uncompacted loose mix. Six levels of PPA modification were chosen; 0, 0.5, 0.75, 1.0, 1.5, and 3 percent.

The results are presented graphically in figure 49 through figure 52, and the percent of the added phosphoric acid extracted is given in table 10, which shows that only a very small percent of the phosphoric acid is extracted after 245 days in water.

The amount of phosphate leached from the gyratory specimens made with diabase or granite aggregates was the same for both the Lion Oil and BP Whiting binders although extraction levels for the granite specimens was significantly higher, some being leached even at a phosphoric acid modification level as low as 0.5 percent. As would be expected, more phosphate was leached from the loose mixes compared with the compacted gyratory specimens. Slightly more phosphate was leached from the loose mix made with the Lion Oil binder. The results for the loose mixes are presented in figure 53 and figure 54.

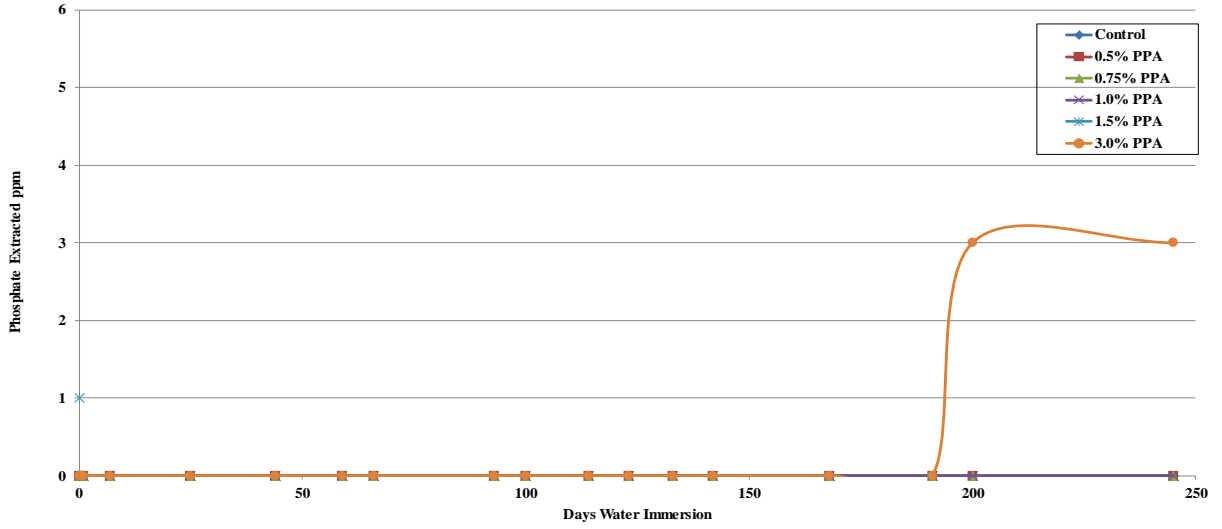


Figure 49. Chart. Plot of phosphate extracted from Lion Oil binder diabase aggregate gyrotory specimen.

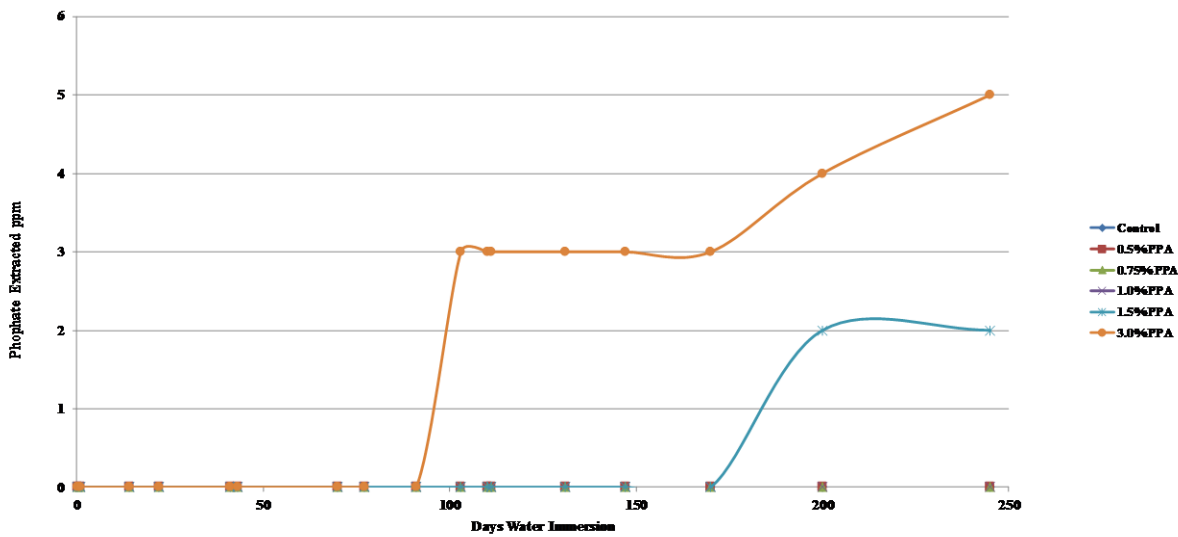
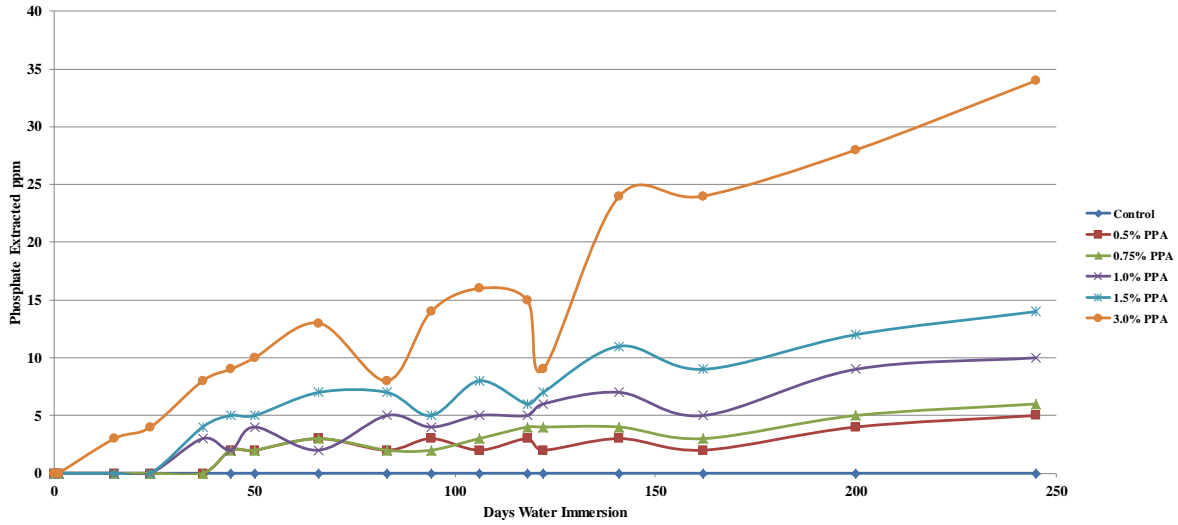
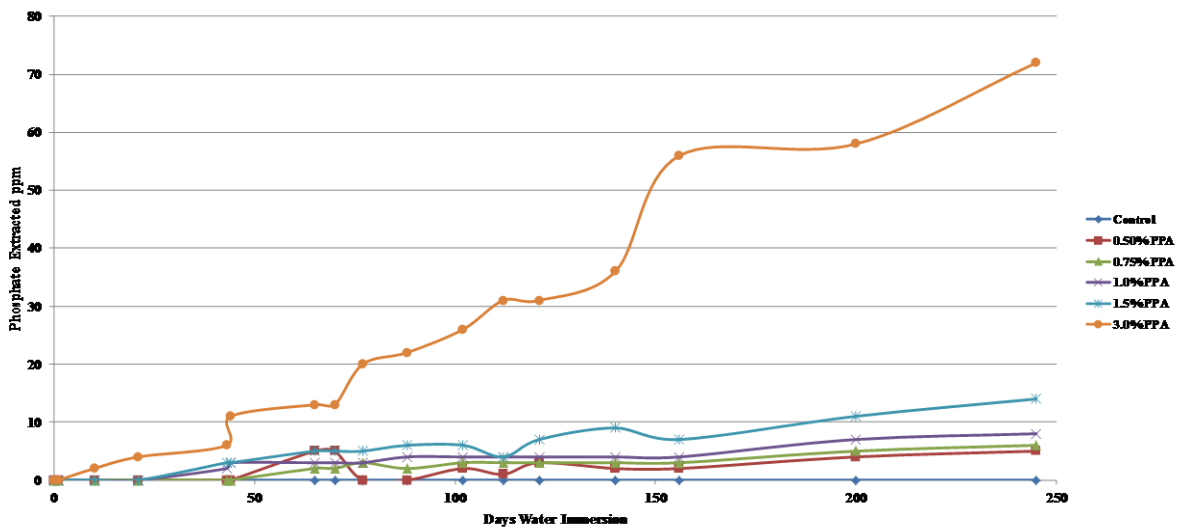


Figure 50. Chart. Plot of phosphate extracted from BP Whiting binder diabase aggregate gyrotory specimen.



**Figure 51. Chart. Plot of phosphate extracted from Lion Oil binder granite aggregate gyrotory specimen.**

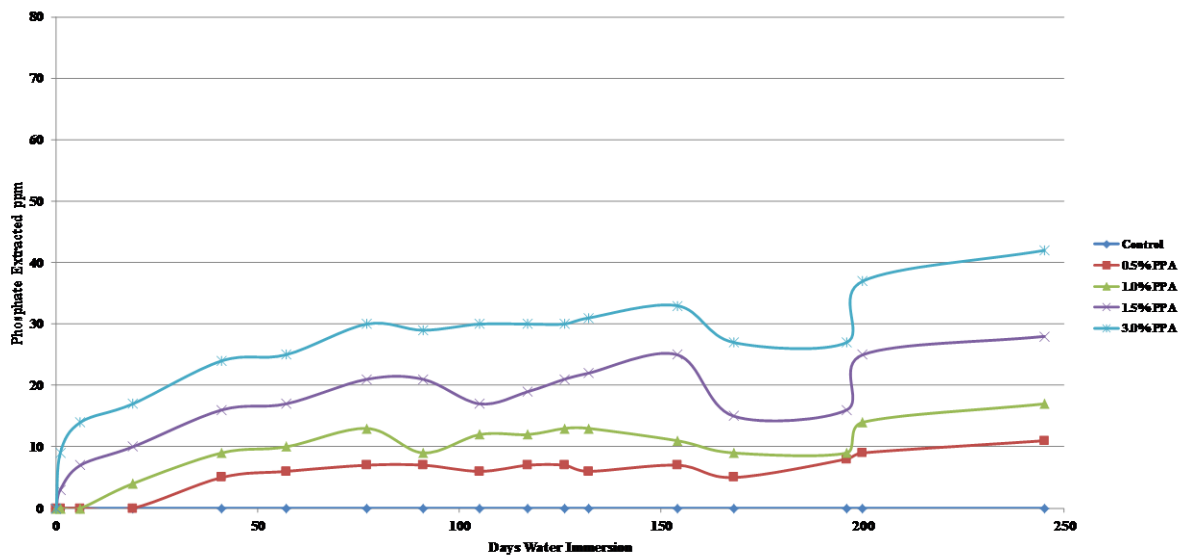


**Figure 52. Chart. Plot of phosphate extracted from BP Whiting binder granite aggregate gyrotory specimen.**

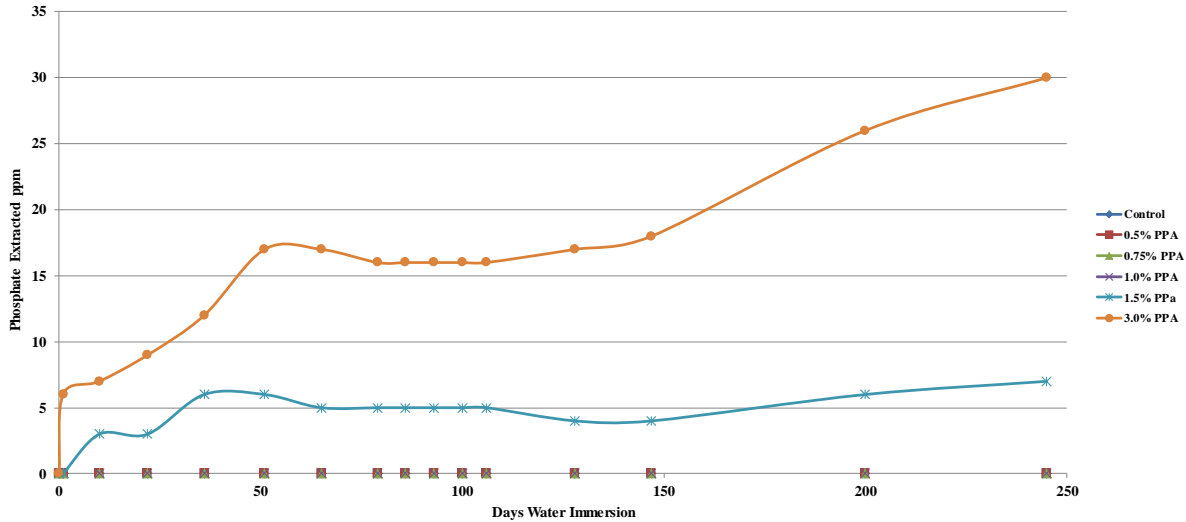
**Table 10. Percentage of the added phosphoric acid extracted after 245 days of immersion in water.**

PPA Percent	B6317/ Diabase	Lion Oil/ Diabase	BP/ Diabase	Lion Oil/ Granite	BP Granite	Lion Oil/ Diabase	BP/ Diabase
	Gyratory	Gyratory	Gyratory	Gyratory	Gyratory	Loose Mix	Loose Mix
0	0	0	0	0	0	0	0
0.5	0	0	0	0.39	0.39	0.85	0
0.75	0	0	0	0.31	0.31	—	0
1.0	0.14	0	0	0.39	0.31	0.66	0
1.5	0.14	0	0.05	0.36	0.36	0.72	0.18
2.0	0.28	0	—	—	—	—	—
3.0	0.78	0.04	0.06	0.44	0.93	0.54	0.39
4.0	1.63	—	—	—	—	—	—

— Indicates not measured



**Figure 53. Chart. Plot of phosphate extracted from Lion Oil binder diabase aggregate loose mix.**



**Figure 54. Chart. Plot of phosphate extracted from BP Whiting binder diabase aggregate loose mix.**

### Conclusions

- Mastics binders and mixes modified with phosphoric acid soaked in water absorbed more moisture than the unmodified controls except for the mastics containing montmorillonite.
- The absorption increased with increasing phosphoric acid levels.
- Some limited sensitivity in the gyratory specimens to aggregate type was found but the evidence suggests that the extraction rate is independent of the binder type.
- The effect of water soaking on asphalt binder moisture content (figure 47) and stiffness (figure 48) as well as the data for mastics (figure 42 through figure 45) suggest that phosphoric acid modification levels above 0.5 to 0.75 percent or so might negatively influence the moisture resistance of the pavement.
- The amount of phosphoric acid leached from compacted gyratory specimens even after the extreme case of 245 days soaking in water was very small.
- The increased leaching from uncompacted mixes suggests some consideration might be given to the leaching that might occur if a phosphoric acid modified binder were used in a porous mix such as an open graded friction course for example.

### EFFECT OF PHOSPHORIC ACID MODIFICATION IN THE USE OF ANTISTRIP ADDITIVES

One of the preconceived notions on the use of phosphoric acid as an asphalt binder was that it could not be used with liquid amine antistrip additives because it is an acid and would react with the basic components in the additives. It was also proposed that nonamine liquid antistrip additives, for example 2-ethylhexyl phosphate, could be used because they would not react chemically with the phosphoric acid.



To confirm that phosphoric acid reacts chemically with liquid amine antistripping additives, samples were dissolved in ethanol (they are not soluble in water) and titrated with phosphoric acid using a standard acid/base indicator. One g of AD-HERE® LOF 65-00 was found to be equivalent to 0.49 g PPA and AD-HERE® LA-2 to 0.57 g PPA. If the binder contains 0.5 percent of antistripping additive and 1 percent of PPA, then the PPA is in excess, with about 25 percent being neutralized by the amine.

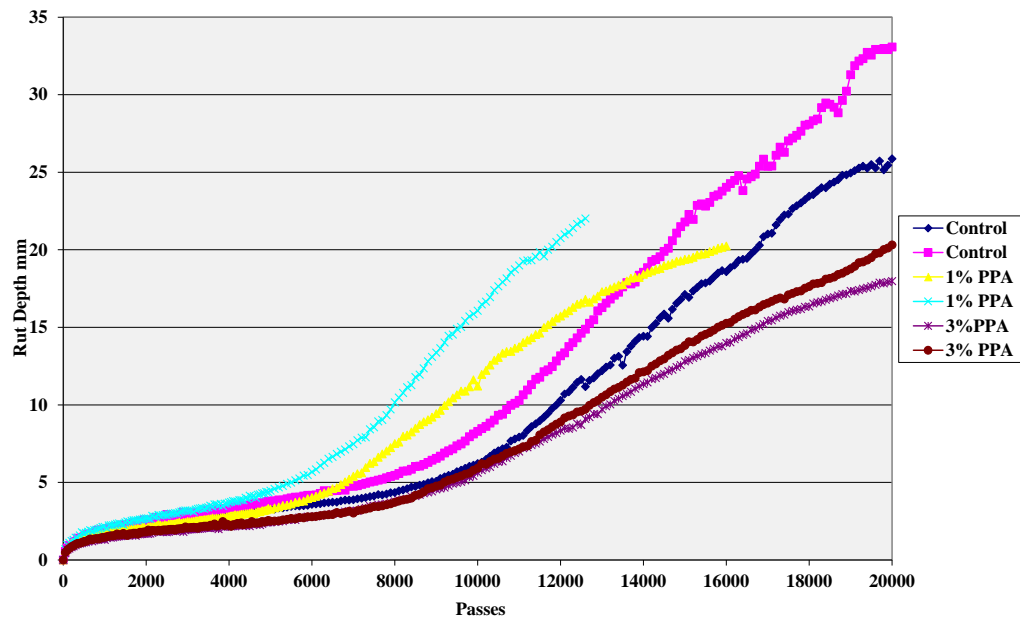
In this study, a number of commercially available liquid amine antistripping additives were evaluated with several different aggregates and binders to test the validity of these concerns and the effect that phosphoric acid modification would have on moisture resistance of HMA pavements.

The antistripping additives were the following:

- ArrMaz®, AD-HERE® LOF65-00 AD-HERE® LA2.
- Innophos: Innovalt®-W (2-ethyl-hexyl phosphate).
- Chemical Lime Company: Lime.

The aggregates used were sandstone (Keystone Aggregates, MD), limestone (H.B. Mellot, MD), and granite from Georgia (unknown origin). The binder was supplied by Citgo®.

The stripping tests were carried out using the Hamburg wheel tracker. The water temperature was 50 °C and the pass/fail criterion 20,000 cycles with a maximum rut depth of 12.5 mm. Results are shown in figure 55 through figure 69.



**Figure 55. Chart. Hamburg rut test of Citgo® asphalt sandstone aggregate.**

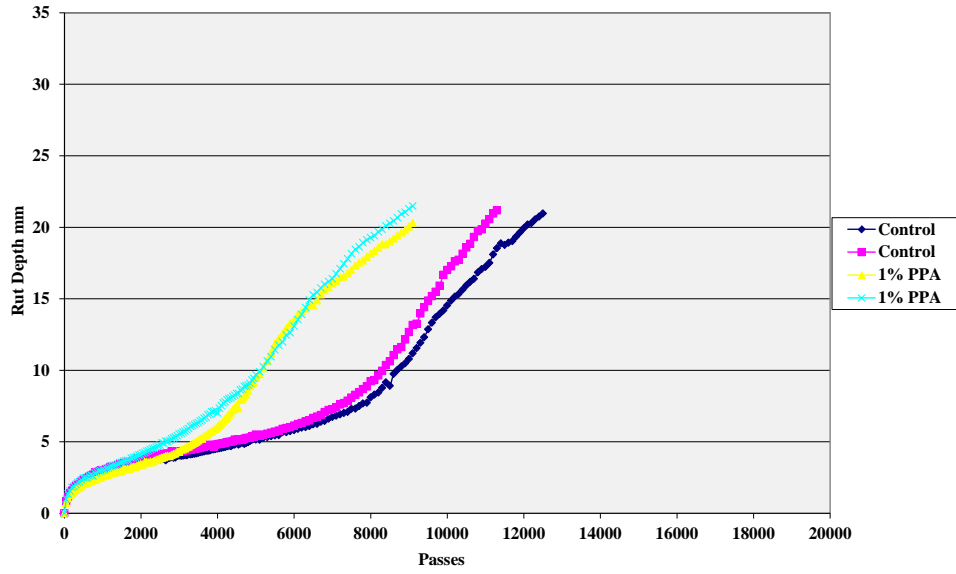


Figure 56. Chart. Hamburg rut test of Citgo® asphalt limestone aggregate.

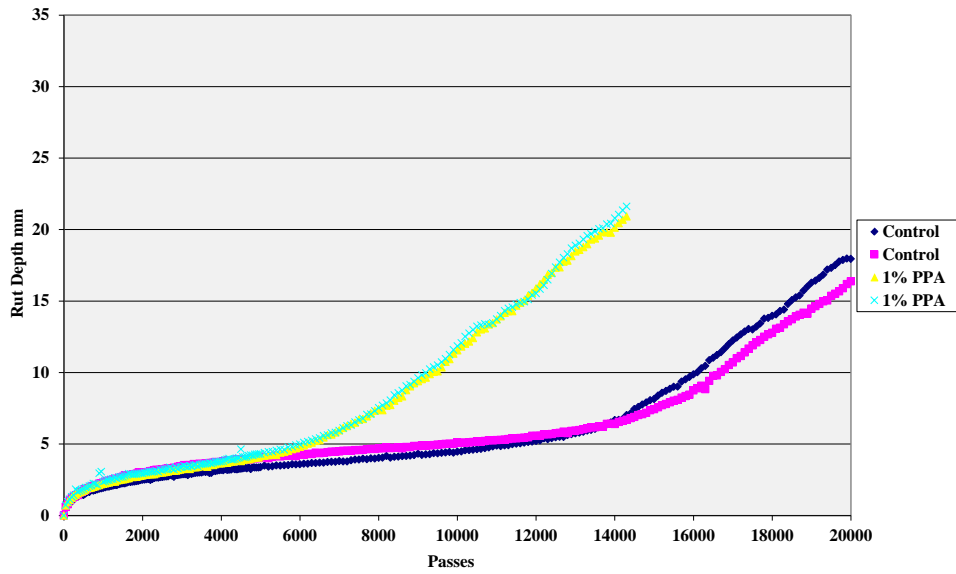


Figure 57. Chart. Hamburg rut test of Citgo® asphalt granite aggregate.

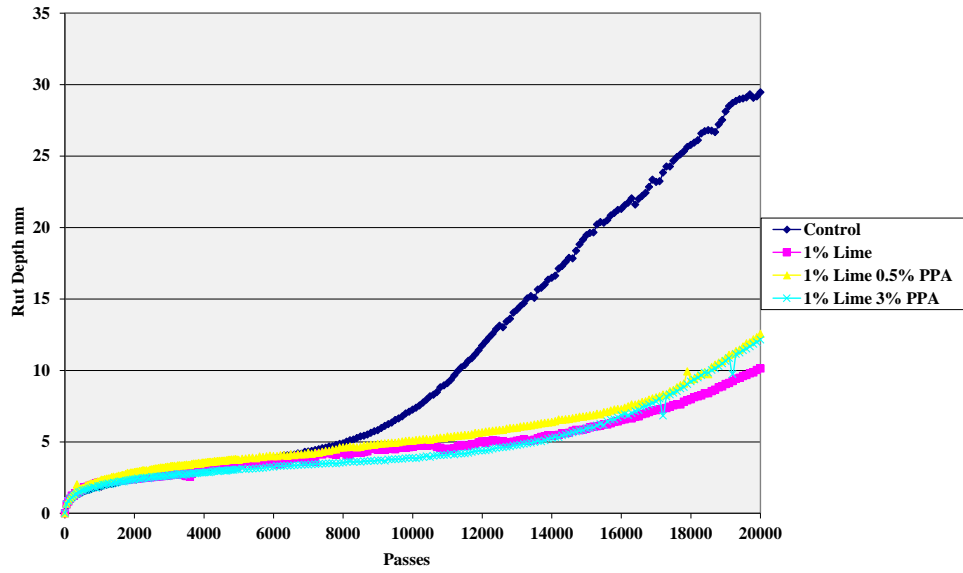


Figure 58. Chart. Hamburg rut test of Citgo® asphalt lime-treated sandstone aggregate.

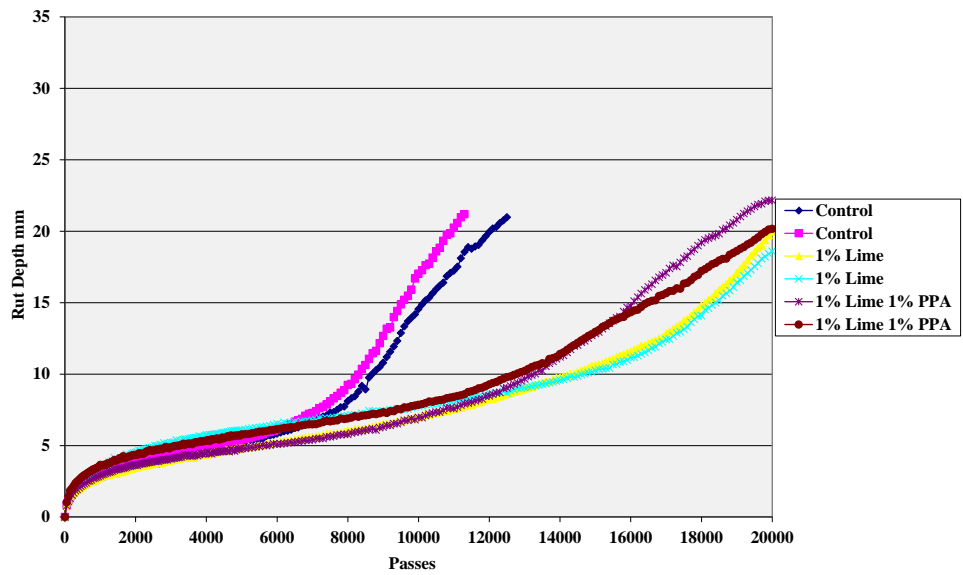


Figure 59. Chart. Hamburg rut test of Citgo® asphalt lime-treated limestone aggregate.

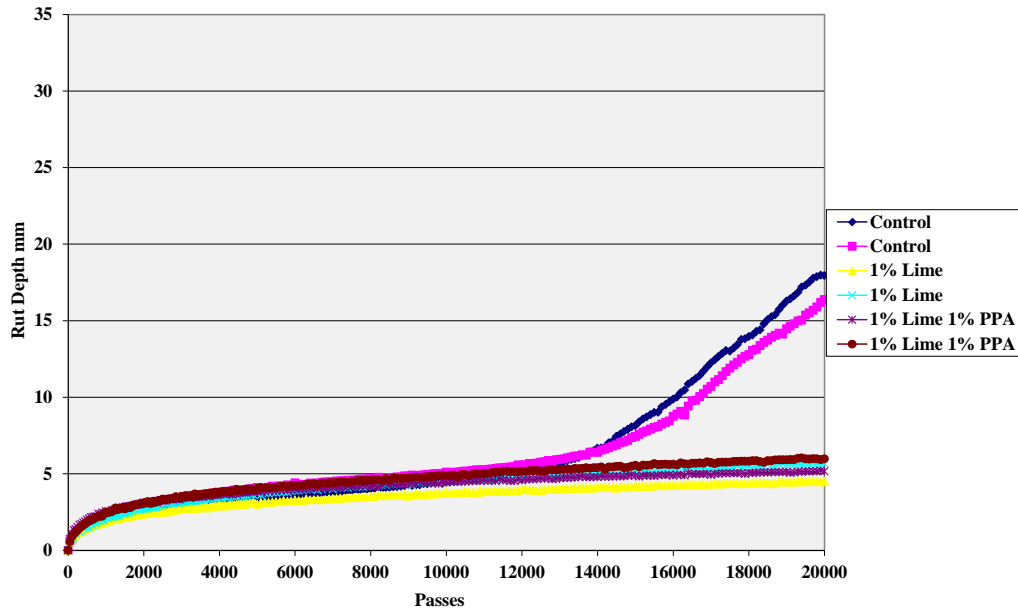


Figure 60. Chart. Hamburg rut test of Citgo® asphalt lime-treated granite aggregate.

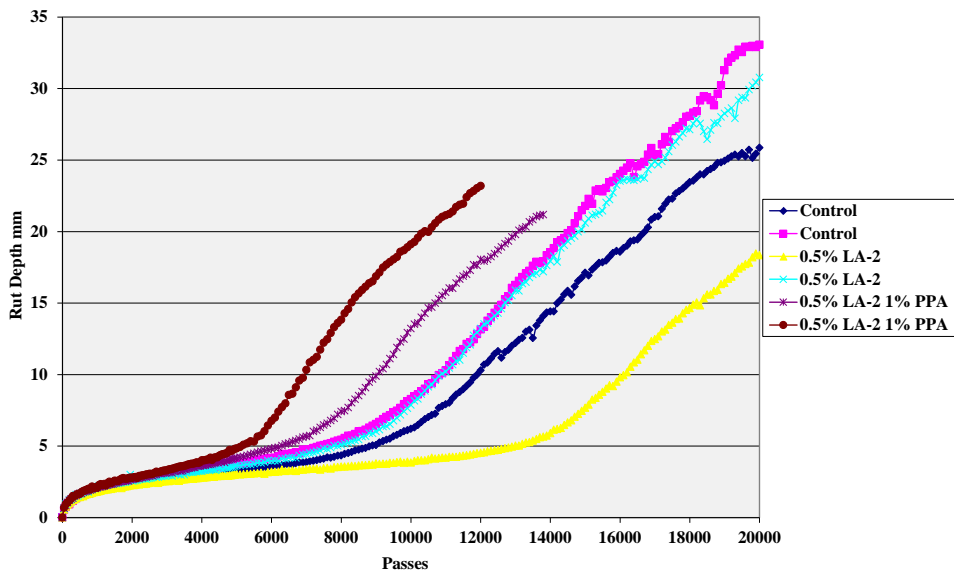


Figure 61. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LA-2 antistrip-treated sandstone aggregate.

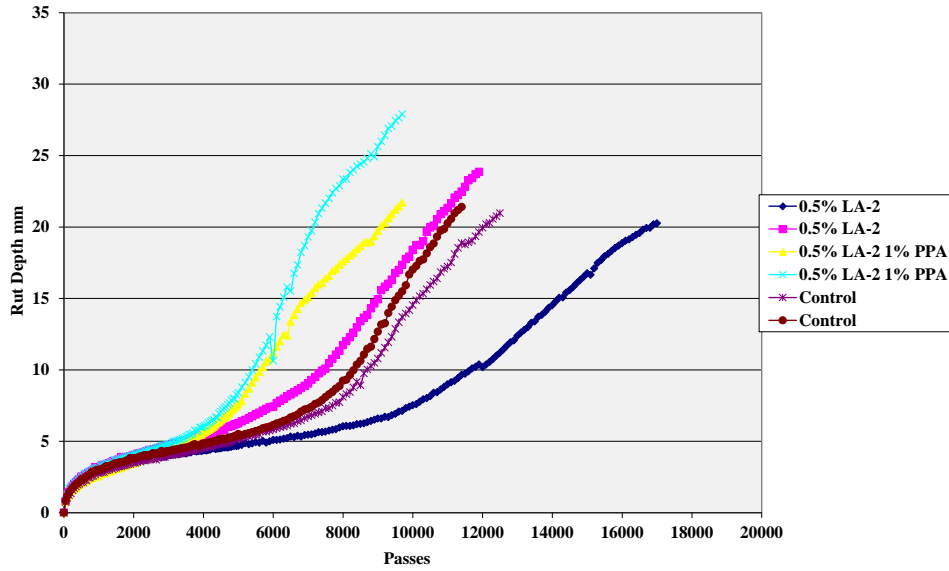


Figure 62. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LA-2 antistrip-treated limestone aggregate.

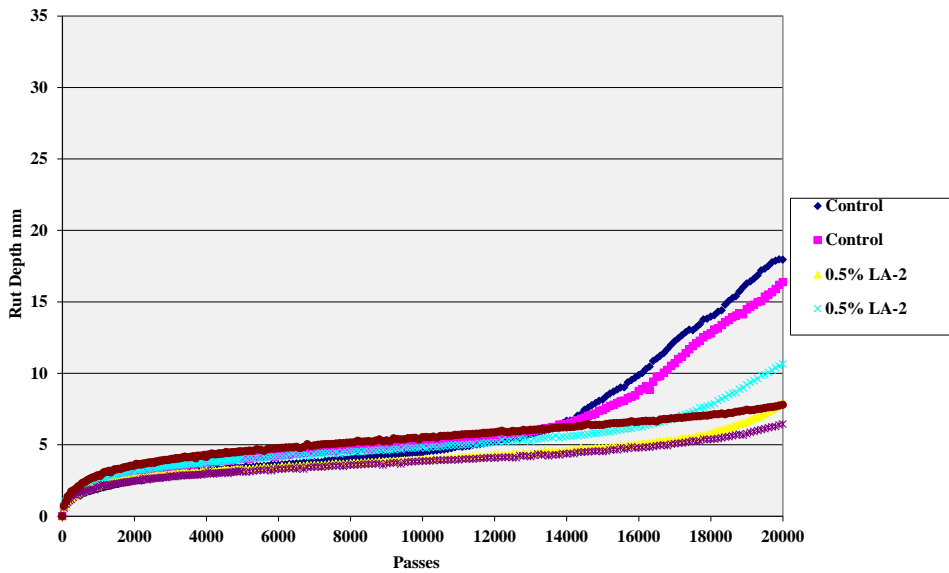
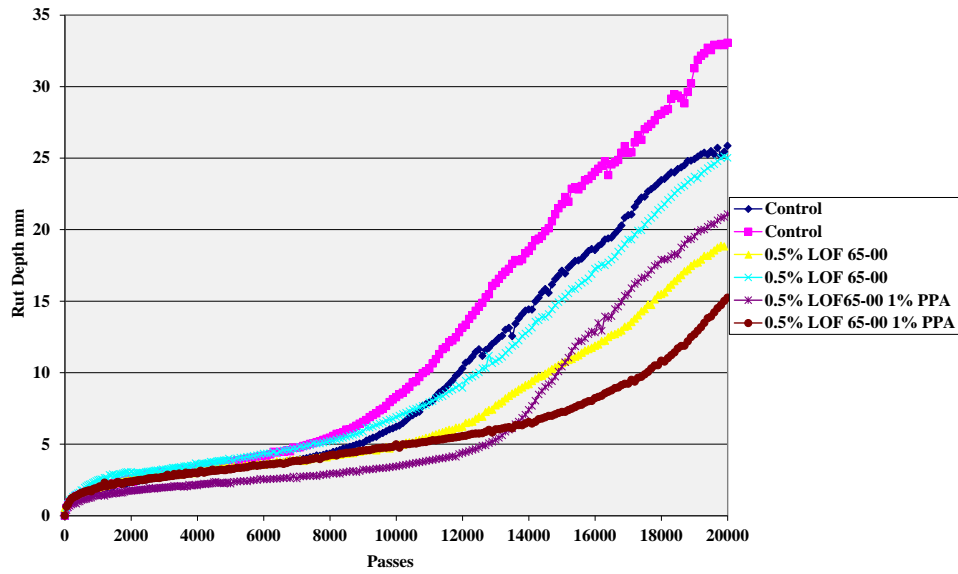
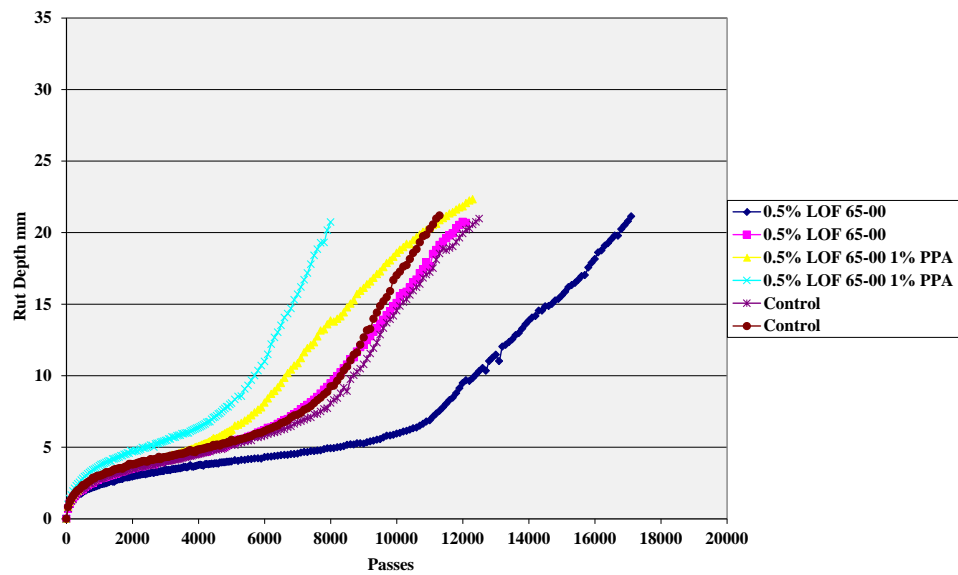


Figure 63. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LA-2 antistrip-treated granite aggregate.



**Figure 64. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LOF 65-00 antistrip-treated sandstone aggregate.**



**Figure 65. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LOF 65-00 antistrip-treated limestone aggregate.**

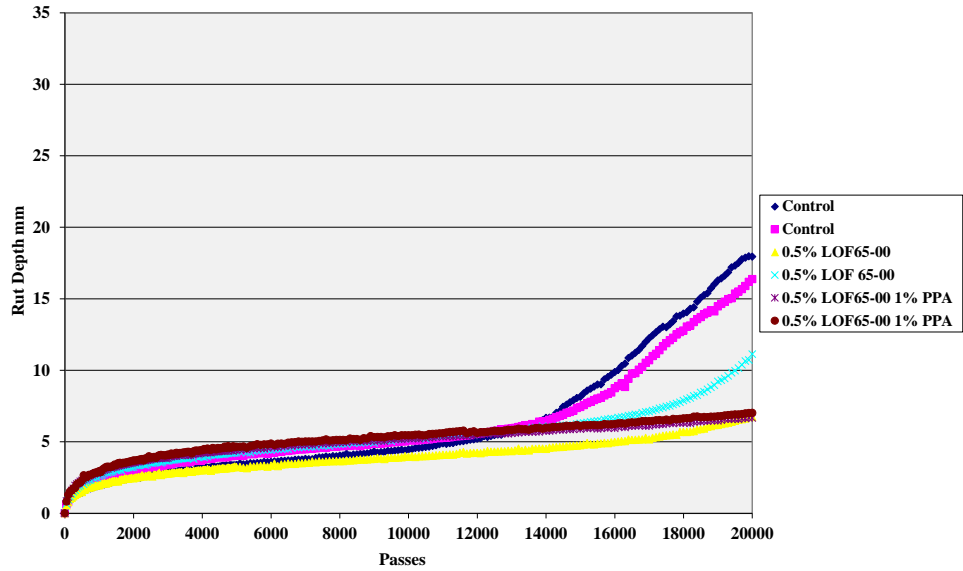


Figure 66. Chart. Hamburg rut test of Citgo® asphalt AD-HERE® LOF 65-00 antistripped granite aggregate.

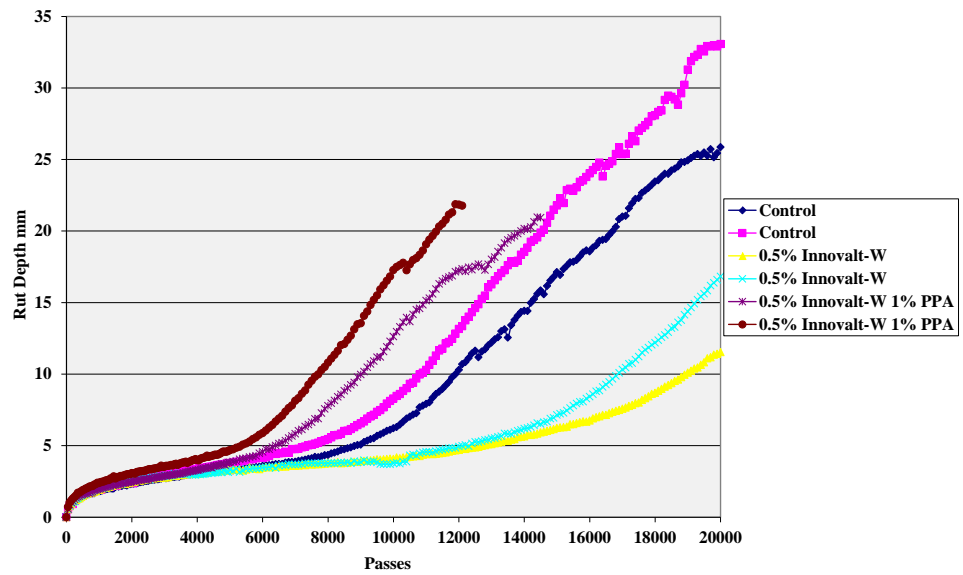
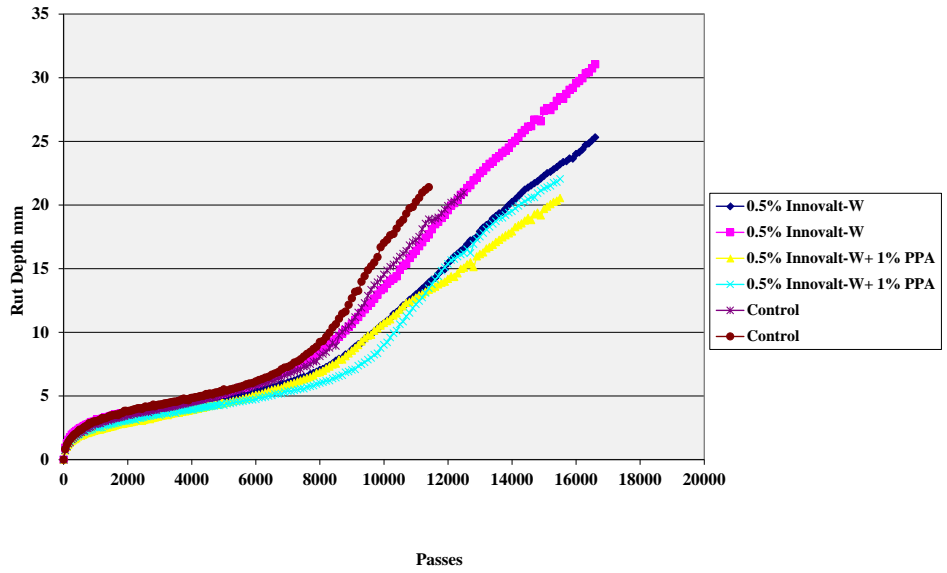
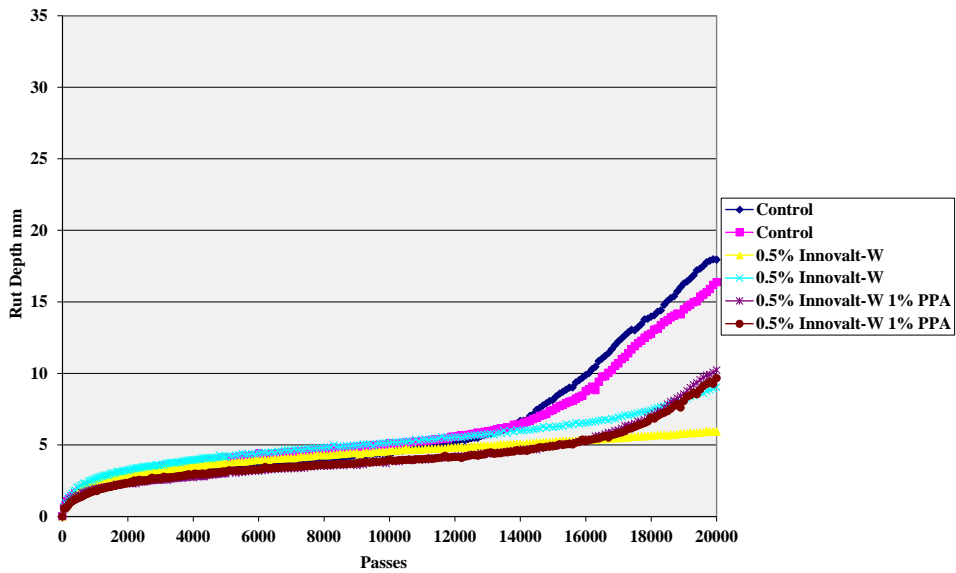


Figure 67. Chart. Hamburg rut test of Citgo® asphalt Innovalt®-W antistripped sandstone aggregate.



**Figure 68. Chart. Hamburg rut test of Citgo® asphalt Innovalt®-W antistripped limestone aggregate.**



**Figure 69. Chart. Hamburg rut test of Citgo® asphalt Innovalt®-W antistripped granite aggregate.**

The data are summarized table 11. The results are compared with the control for each aggregate. The results are the average of the duplicate specimens that were tested. Bold indicates the samples performed better than the control; those in *italic* were worse than the control.



**Table 11. Summary of Hamburg rut testing results with antistrip additives.**

Aggregate	Additive	Cycles to 12.5 mm	Failure Cycles	Depth at 20,000 Cycles mm
Sandstone	Control	12,500	—	29
	1 Percent Phosphoric Acid	<i>9,500</i>	<i>14,300</i>	—
	3 Percent Phosphoric Acid	<b>14,550</b>	—	<b>19</b>
	AD-HERE® LA-2	<b>14,350</b>	—	24
	AD-HERE® LA-2 + 1 Percent Phosphoric Acid	<i>8,700</i>	<i>13,000</i>	—
	AD-HERE® LOF 65-00	<b>15,150</b>	—	<b>22</b>
	AD-HERE® LOF 65-00 + 1 Percent Phosphoric Acid	<b>17,300</b>	—	<b>18</b>
	1 Percent Lime	—	—	<b>10</b>
	1Percent Lime+0.5 percent Phosphoric Acid	—	—	<b>12</b>
	1 percent Lime+3 percent Phosphoric Acid	—	—	<b>12</b>
	Innovalt®-W	<b>18,200</b>	—	<b>14</b>
	Innovalt®-W+1 Percent Phosphoric Acid	<i>9,300</i>	<i>13,200</i>	—
Limestone	Control	9,200	11,800	—
	1 Percent PPA	<i>5,800</i>	<i>9,050</i>	—
	AD-HERE® LA-2	<b>10,600</b>	<b>14,400</b>	—
	AD-HERE® LA-2+1% Phosphoric Acid	<i>6,100</i>	<i>9,700</i>	—
	AD-HERE® LOF 65-00	<b>11,250</b>	<b>14,650</b>	—
	AD-HERE® LOF 65-00 + 1 percent Phosphoric Acid	<i>6,900</i>	<i>10,100</i>	—
	1 percent Lime	<b>17,000</b>	—	<b>19</b>
	1 percent Lime+0.5 percent Phosphoric Acid	<b>14,700</b>	—	<b>21</b>
	Innovalt®-W	<b>10,350</b>	<b>16,550</b>	—
	Innovalt®-W+1% Phosphoric Acid	<b>11,150</b>	<b>15,450</b>	—
Granite	Control	17,450	—	17
	1 Percent Phosphoric Acid	<i>10,250</i>	<i>14,250</i>	—
	AD-HERE® LA-2	—	—	<b>9</b>
	AD-HERE® LA-2 + 1Percent Phosphoric Acid	—	—	<b>7</b>
	AD-HERE® LOF 65-00	—	—	<b>9</b>
	AD-HERE® LOF 65-00 + 1 Percent Phosphoric Acid	—	—	<b>7</b>
	1 Percent Lime	—	—	<b>5</b>
	1 Percent Lime + 0.5 Percent Phosphoric Acid	—	—	<b>6</b>
	Innovalt®-W	—	—	<b>8</b>
Innovalt®-W+1 Percent Phosphoric Acid	—	—	<b>10</b>	

Bold indicates sample performed better than the control sample  
 Italic indicates sample performed worse than the control sample  
 — Indicates not applicable

### Conclusions

- The moisture resistance was worse with PPA modification for all three aggregates, with the exception of the 3-percent case with sandstone. This was likely the result of the high level of modification stiffening the asphalt.
- The enhanced performance of antistrip additive AD-HERE® LA-2 was worse with phosphoric acid for sandstone and limestone but was not affected with the granite aggregate.

- The enhanced performance of antistrip additive AD-HERE® LOF 65-00 with phosphoric acid was not affected in the case of limestone (where it actually showed some improvement) and granite but was worse in the limestone samples.
- Lime performed well with all three aggregates and was not affected by phosphoric acid modification.
- The enhanced performance of Innovalt®-W, the nonamine phosphate ester antistrip additive, was worse with phosphoric acid modification for sandstone but was unaffected in the limestone and granite samples.
- All the antistrip additives performed very well with granite aggregate, and none were affected by phosphoric acid modification.

## CHAPTER 7. SUMMARY OF CONCLUSIONS

The following summarizes the conclusions of this study:

- The phosphoric acid content of binders can be readily measured using XRF, and from the phosphorus content, a presumed level of phosphoric acid can be calculated.
- The addition of phosphoric acid to asphalt binders causes an increase in the heptane insoluble fraction, which is not necessarily accompanied by a corresponding increase in binder stiffness. The phosphorus from the acid all ends up in the heptane insoluble phase.
- The stiffening effect of phosphoric acid is asphalt dependent.
- Any grade of phosphoric acid can be used.
- Phosphoric acid does not appear to cause increased binder aging except in the binder AAK-1 used in the study.
- Phosphoric acid in asphalt binders reacts with lime (calcium hydroxide).
- Phosphoric acid in asphalt binders does not readily react with limestone aggregates.
- Phosphoric acid is not readily leached from HMA mixes although some consideration might be given to the possible environmental impact of very high levels of modification.
- According to the Hamburg test results, phosphoric acid can negatively affect the stripping of asphalt mixes. It may also negate the effect of some liquid amine antistrip additives. It works very well with lime-treated aggregates.



## APPENDIX

### IATROSCAN® TEST METHOD FOR SARA ANALYSIS OF ASPHALT BINDERS

The heavy metals (typically vanadium and nickel) present in the asphaltene portion of asphalt binders have a tendency to contaminate the silica coating on the chromatographic rods. For this reason, the asphaltenes are first separated by extracting the binder with n-heptane and removing the insoluble asphaltenes by filtration. The n-heptane soluble portion is then absorbed on 5-micron silica-gel coated glass rods (Chromarods®) and fractionated by upward elution using specific solvent types, development methods, and duration. The three separated fractions are then burned from the rods using flame ionized detection (FID). As the materials burn the ionic combustion products can be detected by a FID system. The FID system provides specific response to organic compounds; therefore, three chromatographic fractions are separated and identified as resins, cyclics, and saturates. These, together with asphaltenes, comprise the four generic fractions found in asphalt. The FID system provides specific response to compounds containing nitrogen and or halogens.

#### Apparatus

The following apparatus is used to conduct the test:

- Iatroscan® TH-10 hydrocarbon analyzer.
- Utilities—110-volt AC, compressed air (dry), compressed hydrogen, drying oven.
- Flasks—250-mL Erlenmeyer with ground-glass joint
- Condensers—400-mm type with ground-glass joint
- Filtering Apparatus—47 mm, Millipore all glass.
- Squeeze Bottle—pint size.
- Forceps—fine to medium pointed.
- Analytical Balance.
- Filter Disc—Whatman® GF/C microfiber 47 mm.
- Magnetic-Stirrer.
- Hot Plate—equipped with regulator.
- Reagent Bottles—8-oz amber glass with ground-glass stopper.
- Whatman® Chromatographic Paper ICHR (cat no 3001917) 46 cm by 570 cm.
- Glass Solvent Tanks, 1.5 by 7 inches.
- Reagents.
  - n-Heptane—99.0 min. mol% (pure grade).
  - n-Pentane—HPLC grade.
  - Toluene—HPLC grade.
  - Chloroform—HPLC grade.

#### Asphaltene/Material Separation

- Asphaltenes—The asphaltene fraction is obtained in accordance with ASTM D3279 Standard Test Method for the n-Heptane Insoluble Fraction.

- Maltenes—The maltene fraction (resins, cyclics, saturates) is contained in the n-heptane filtrate after asphaltene extraction.

## **Iatroscan® TH-10 Procedure**

### ***Sample Preparation***

During the asphaltene oven drying period, obtain the volume of filtrate by pouring it into a graduated cylinder. Note this volume because it will be needed to calculate the maltene concentration. Pour n-heptane filtrate into an amber glass bottle and place in a cool, dark area for  $2 \pm 0.10$  h.

During this period, asphaltenes analysis may be completed. After obtaining the asphaltene weight, calculate the maltene concentration as follows:

$$\text{Maltene Concentration} = (\text{Sample Wt.} - \text{Asphaltene Wt.}) / \text{Volume n-Heptane Filtrate}$$

### **Figure 70. Equation. Calculation of maltene concentration**

Report this concentration in micrograms per milliliter ( $\mu\text{g mL}^{-1}$ ).

Approximately 20  $\mu\text{g}$  of maltenes are needed on each Chromarod® for analysis. Therefore, the quantity of n-heptane filtrate in  $\mu\text{L}$  (microliters) may be calculated as follows:

$$\text{Quantity } (\mu\text{g}) = \text{Quantity Required } (\mu\text{g}) / \text{Concentration } (\mu\text{g mL}^{-1}) \times (1000)$$

### **Figure 71. Equation. Calculation of n-heptane filtrate**

Report the value in microliters ( $\mu\text{L}$ ) and round up to the nearest whole unit. This is the volume to be injected on each Chromarod®.

### ***Solvent Preparation***

Use two solvent tanks (1.5 by 7 inches) as solvent baths. Place clean filter paper on the inside of the back of the tank to enhance vapor transmission in the tank. Fill the first solvent tank with n-pentane (chromatographic grade) to a point just below the spotting point on the rack (approximately 1 inch). The next tank should be filled to the same level as the pentane tank with a 90/10 volume percent ratio toluene/chloroform (chromatographic grade) solvent mixture.

### ***Spotting Chromarods®***

To spot the sample on the Chromarods®, use a syringe capable of delivering 0.2  $\mu\text{L}$ . Using SIII Chromarods®, spot the calculated quantity in applications of 0.2  $\mu\text{L}$ , rotating the rod to cover the circumference of the rod to yield five even spots around the circumference of the rod.

### ***Component Separation***

After spotting the rods, allow 2 min in the desiccator at room temperature and  $50 \pm 5\%$  relative humidity (RH) for drying. Place the rods in the n-pentane tank for 20 minutes allowing the solvents to migrate upwards to the 10 cm mark on the rod rack. This migration will elute the saturates portion of the maltene fraction to the 10 cm on the rod rack. When the solvent reaches

the 10 cm mark, remove the rods from the tank and allow 10 min at room temperature and  $50 \pm 5\%$  RH for drying. After drying, place the rods in the 90/10 toluene/chloroform tank for 7 min, allowing the solvents to migrate upward to the 5 cm mark on the rod rack. This migration will elute the resins and cyclics portion of the maltene, where cyclics are moved by the blend of toluene and chloroform, and the resins remain on the rod slightly above the original spot. Remove the rod rack from the development tank and dry in a forced air oven at  $90\text{ }^\circ\text{C}$  for 15 min. Cool in desiccator for 10 min.

Place the rods in the Iatroscan® hydrocarbon analyzer and burn them with the hydrogen flame. The results are collected by the Iatroscan® software.

Iatroscan Settings used: Hydrogen Flow,  $160\ \mu\text{L}/\text{min.}$ , Air Flow,  $2.0\ \text{L}/\text{min.}$  Scanning Speed: 30 s for each rod. The heptane solution contained 0.25 g of maltene in 25 mL, which required a  $4.0\ \mu\text{L}$  spot to be placed on the rods with the syringe.

## Report

Report the asphalt composition in percents of each component as follows:

- Asphaltenes = A%.
- Resins = R%.
- Cyclics = C%.
- Saturates = S%.

Initial stiffness of acid-modified binders and after oven aging for 24 h at  $165\text{ }^\circ\text{C}$  are reported in table 12 through table 15.

**Table 12. Change in stiffness of asphalt AAD-1 with phosphoric acid modification immediately after mixing and after 24 h at  $165\text{ }^\circ\text{C}$ .**

Acid Strength (percent)	G* /Sin $\delta$ at $64\text{ }^\circ\text{C}$			
115	0.89	1.25(1.38)	1.77(1.83)	4.23(4.47)
105	0.89	1.07(1.57)	1.44(2.20)	2.87(3.74)
85	0.89	1.45(1.57)	2.04(2.49)	3.89(3.90)
75	0.89	1.51(1.91)	2.04(2.38)	3.43(3.69)
50	0.89	1.68	2.71	5.6
Addition Level (percent)	0	0.25	0.5	1.0

**Table 13. Change in stiffness of asphalt AAM-1 with phosphoric acid modification immediately after mixing and after 24 h at  $165\text{ }^\circ\text{C}$ .**

Acid Strength (percent)	G* /Sin $\delta$ at $64\text{ }^\circ\text{C}$			
115	1.69	1.98(2.09)	2.89(2.80)	6.14 (4.48)
105	1.69	1.98(2.08)	2.59(2.58)	4.23(3.65)
85	1.69	2.07(2.19)	2.70(2.95)	3.98(4.50)
75	1.69	2.18(2.25)	2.63(3.40)	4.67(4.68)
50	1.69	2.30	3.48	6.34
Addition Level (percent)	0	0.25	0.5	1.0

**Table 14. Change in stiffness of asphalt AAK-1 with phosphoric acid modification immediately after mixing and after 24 h at 165 °C.**

Acid Strength (percent)	G* /Sinδ at 64 °C			
	115	2.43	3.60(3.17)	3.85(4.65)
105	2.43	3.24(4.09)	4.58(4.67)	8.49(9.69)
85	2.43	3.74(4.18)	4.46(4.91)	8.52(8.79)
75	2.43	3.86(3.76)	4.47(5.75)	8.04(7.69)
50	2.43	3.79	6.17	10.17
Addition Level (percent)	0	0.25	0.5	1.0

**Table 15. Change in stiffness of asphalt ABM-1 with phosphoric acid modification immediately after mixing and after 24 hours at 165 °C.**

Acid Strength (percent)	G* /Sinδ at 64 °C			
	115	1.65	1.25(1.34)	1.25(1.25)
105	1.65	1.28(1.34)	1.23(1.33)	1.13(1.28)
85	1.65	1.41(1.59)	1.36(1.40)	2.47(1.49)
75	1.65	1.20(1.36)	1.26(1.51)	1.22
50	1.65	1.28	1.48	1.83
Addition Level (Percent)	0	0.25	0.5	1.0

**EFFECT OF OVEN AGING 12 DAYS AT 165 °C ON ASPHALT STIFFNESS**

**Table 16. Oven aging at 165 °C asphalt AAD-1 modified with 115-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
	0	0.89	1.25	1.77
24	—	1.38	1.83	4.47
48	—	1.69	1.92	4.89
72	—	2.39	2.77	6.62
96	—	3.03	3.18	9.88
120	1.13	4.5	4.61	12.41
288	5.92	5.02	7.53	27.95
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 17. Oven aging at 165 °C asphalt AAD-1 modified with 105-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
	0	0.89	1.07	1.44
24	—	1.57	2.2	3.74
48	—	1.95	1.9	3.37
72	—	2.99	2.84	4.34
96	—	4.43	3.58	5.62
120	1.13	4.85	4.26	6.44
288	5.92	7.21	7.54	9.52
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured



**Table 18. Oven aging at 165 °C asphalt AAD-1 modified with 85-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	0.89	1.45	2.04	3.89
24	—	1.57	2.49	3.9
120	1.13	1.58	2.88	—
288	5.92	3.9	5.15	9.04
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 19. Oven aging at 165 °C asphalt AAD-1 modified with 75-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	0.89	1.51	2.04	3.43
24	—	1.91	2.38	3.69
120	1.13	2.61	3.36	4.49
288	5.92	4.66	5.46	6.67
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 20. Oven aging at 165 °C asphalt AAD-1 modified with 50-percent “green” phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	0.89	1.68	2.71	5.6
120	1.13	—	—	—
168	—	2.46	3.45	7.54
288	5.92	—	—	—
336	—	3.65	4.7	10.53
Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 21. Oven aging at 165 °C asphalt AAK-1 modified with 115-percent phosphoric acid .**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	2.43	3.6	3.85	9.13
24	2.8	3.17	4.65	9.07
48	—	4.34	6.28	12.7
72	—	6.33	7.95	17.37
96	—	8.09	12.04	22.39
120	10.5	10.53	17.11	33.2
288	12.9	19.24	24.98	39.96
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 22. Oven aging at 165 °C asphalt AAK-1 modified with 105-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	2.43	3.24	4.58	8.49
24	2.8	4.09	4.67	9.69
48	—	5.06	5.68	13.62
120	10.5	8.49	8.94	17.77
288	12.9	17.85	19.97	43.05
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 23. Oven aging at 165 °C asphalt AAK-1 modified with 85-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	2.43	3.74	4.46	8.52
24	2.8	4.18	4.91	8.79
120	10.5	7.88	7.97	15.42
288	12.9	14.72	16.8	30.46
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 24. Oven aging at 165 °C asphalt AAK-1 modified with 75-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	2.43	3.86	4.47	8.04
24	2.8	3.76	5.75	7.69
48	—	5.37	7.85	11.82
120	10.5	16.69	22.25	23.79
288	12.9	33.38	33.02	45.31
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 25. Oven aging at 165 °C asphalt AAK-1 modified with 50-percent “green” phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	2.43	3.79	6.17	10.17
24	2.8	—	—	—
120	10.5	—	—	—
168	—	6.03	6.65	17.01
288	12.9	—	—	—
336	—	10.6	11.62	22.94
Acid Addition Level (percent)	0—	0.25	0.5	1

— Indicates not measured

**Table 26. Oven aging at 165 °C asphalt AAM-1 modified with 115-percent phosphoric acid**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.69	1.98	2.89	6.14
24	—	2.09	2.8	4.48
48	—	2.81	3.5	6.93
72	—	4.06	4.49	7.26
120	1.96	5.8	7.5	8.04
288	11.68	11.48	14.9	13.11
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 27. Oven aging at 165 °C asphalt AAM-1 modified with 105-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.69	1.98	2.59	4.23
24	—	2.08	2.58	3.65
48	—	2.61	3.44	4.1
72	—	3.59	4.07	4.41
120	1.96	5.26	5.27	3.36
288	11.68	9.15	8.74	7.11
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 28. Oven aging at 165 °C asphalt AAM-1 modified with 85-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.69	2.07	2.7	3.98
24	—	2.19	2.95	4.5
120	1.96	5.51	7.92	5.49
288	11.68	12.73	12.77	8.83
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 29. Oven aging at 165 °C asphalt AAM-1 modified with 75-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.69	2.18	2.68	4.67
24	—	2.25	3.4	4.68
120	1.96	2.32	10.17	6.49
288	11.7	12.11	14.52	13.37
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 30. Oven aging at 165 °C asphalt AAM-1 modified with 50-percent “green” phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.69	2.3	3.48	6.34
120	1.96	—	—	—
168		7.92	8.75	7.47
288	11.68	—	—	—
336	—	15.66	15.11	9.84
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 31. Oven aging at 165 °C asphalt ABM-1 modified with 115-percent phosphoric acid**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.65	1.25	1.25	1.43
24	—	1.34	1.25	1.58
48	—	1.53	1.37	1.62
72	—	1.72	1.69	2.01
120	1.52	3.12	2.11	4.23
288	1.81	8.86	2.34	18.79
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 32. Oven aging at 165 °C asphalt ABM-1 modified with 105-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.65	1.28	1.23	1.13
24	—	1.34	1.33	1.28
48	—	1.43	1.58	—
120	1.52	1	1.85	1.37
288	1.81	1.72	2.68	3.36
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 33. Oven aging at 165 °C asphalt ABM-1 modified with 85-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.65	1.41	1.36	2.47
24	—	1.59	1.4	1.49
120	1.52	1.46	2.39	2.75
288	1.81	3.54	5.49	10.47
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 34. Oven aging at 165 °C asphalt ABM-1 modified with 75-percent phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.65	1.2	1.26	1.22
24	—	1.36	1.51	—
120	1.52	1.83	3.09	2.96
288	1.81	5.09	7.97	8.89
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**Table 35. Oven aging at 165 °C asphalt ABM-1 modified with 50-percent “green” phosphoric acid.**

Hours at 165 °C	Stiffness  G* /Sinδ at 65 °C			
0	1.65	1.28	1.48	1.83
120	1.52	—	—	—
168		4.14	6.28	6.98
288	1.81	—	—	—
336		21.45	30.37	45.27
Acid Addition Level (percent)	0	0.25	0.5	1

— Indicates not measured

**DOES PHOSPHORIC ACID CAUSE OXIDATION IN ASPHALT BINDERS?****Table 36. PAV aging asphalt ABM-1 under air pressure at 100 °C.**

Hours	Control	105 percent	115 percent	P <sub>2</sub> O <sub>5</sub>
0	1.37	1.12	1.3	1.46
24	1.68	1.12	1.19	1.41
168	5.09	2.83	2.62	2.87
336	9.13	5.88	6.08	5.66

**Table 37. PAV aging asphalt AAD-1 under air pressure at 100 °C.**

Hours	Control	105 percent	115 percent	P <sub>2</sub> O <sub>5</sub>
0	1.03	4.05	4.75	1.38
24	1.21	4.07	3.95	1.73
168	14.35	10.83	12.26	12.4
336	36.83	21.17	20.31	37.82

**Table 38. PAV aging asphalt AAK-1 under air pressure at 100 °C.**

Hours	Control	105 percent	115 percent	P <sub>2</sub> O <sub>5</sub>
0	2.27	8.65	7.99	2.65
24	3.23	9.36	7.47	2.93
168	9.84	19.04	17.5	13.85
336	20.67	28.30	29.87	31.61

**Table 39. PAV aging asphalt AAM-1 under air pressure at 100 °C.**

Hours	Control	105 percent	115 percent	P <sub>2</sub> O <sub>5</sub>
0	1.65	3.85	6.50	1.95
24	2.16	3.80	5.02	2.11
168	10.94	8.03	8.52	9.17
336	30.1	11.68	9.32	19.21

**Table 40. PAV aging asphalt ABM-1 under nitrogen pressure at 100 °C.**

Hours	Control	50 percent	85 percent	115 percent
0	0.73			
24				
168		7.35	4.18	3.67
336	1.17	9.37	5.3	4.41

— Indicates not measured

**Table 41. PAV aging asphalt AAD-1 under nitrogen pressure at 100 °C.**

Hours	Control	50 percent	85 percent	115 percent
0	0.73			
24				
168		7.35	4.16	3.67
336	1.17	9.37	5.3	4.41

— Indicates not measured

**Table 42. PAV aging asphalt AAK-1 under nitrogen pressure at 100 °C.**

Hours	Control	50 percent	85 percent	115 percent
0	2.35			
24				
168		15.21	8.02	9.21
336	4.37	16.38	9.64	9.53

— Indicates not measured

**Table 43. PAV aging asphalt AAM-1 under nitrogen pressure at 100 °C.**

<b>Hours</b>	<b>Control</b>	<b>50 percent</b>	<b>85 percent</b>	<b>115 percent</b>
0	1.38			
24				
168		6.34	3.95	5.22
336	2.31	7.87	3.8	4.73

— Indicates not measured

## REFERENCES

1. Engberger, S.L. and Reinke, G.H. U.S. Patent 6,117,926 Acid-reacted polymer-modified asphalt compositions and preparation thereof. September 12.
2. Engberger, S.L. and Reinke, G.H. U.S. Patent 6,399,680 Acid-reacted polymer-modified asphalt compositions and preparation thereof. June 4, 2002.
3. Puzic, O. et al., "Percentage of 115% Polyphosphoric Acid in Modified Asphalt," ExxonMobil AmTS Procedure: R 122206, Revision No. 2, December 22, 2006.
4. Reinke, G.H. et al., Mathy Technology and Engineering Services Inc. (Private communication 4/18/2007).
5. SHRP Materials Reference Library: Asphalt Cements: A Concise Data Compilation, SHRP-A-645, 1993.





## ADDITIONAL READING

Li, X. et al., “Laboratory Evaluation of Asphalt Binders and Mixtures Containing Polyphosphoric Acid,” *Journal of the Transportation Research Board*, No. 2210, Asphalt Binders and Mixtures, 4, pp. 47–56, 2011.

Baumgardner, G.L. et al., “Polyphosphoric Acid Modified Asphalt: Proposed Mechanisms,” *Association of Asphalt Paving Technologists*, 74, pp. 283–305, 2005.

Orange, G. et al., “Chemical Modification of Bitumen Through Polyphosphoric Acid: Properties-Microstructure Relationship,” in *Proceedings of the Third Eurasphalt and Eurobitume Congress, Vienna, 1*, pp.733–745, May 2004.

Bishara, S.W. et al., “Modification of Binder with Acid—Advantages and Disadvantages,” Kansas Department of Transportation Report FHWA-KS-02-2, February 2003.

De Filippis, P. et al., “Sulphur Extended Asphalt: Reaction Kinetics of H<sub>2</sub>S Evolution,” *Fuel*, 77, No 5, pp. 459–463, 1998.

Bonemazzi, F. and Giavarini, C., “Shifting the Bitumen Structure from Sol to Gel,” *Journal of Petroleum Science and Engineering*, 22, Issues 1–3, pp. 17–24, 1999.

Giavarini, C. et al., U.S. Patent 5,565,510, “Mixtures of Bitumen and Polymer Composition,” October 15, 1996.

De Filippis, P. et al., “Stabilization and Partial Deasphalting of Thermal Residues by Chemical Treatment,” *Energy and Fuels*, 8, pp. 141–146, 1994.

Alexander, S. U.S. Patent 3,751,278, “Method of Treating Asphalt,” August 1973.

Hoiberg, A.J., U.S. Patent 3,028,249, “Asphaltic Compositions,” April 3, 1962.

Hoiberg, A.J. et al., U.S. Patent 2,890,967, “Asphalt Coating,” June 16, 1959.

Hoiberg, A.J., U.S. Patent 2,450,756, “Air Blown Asphalt and Catalytic Preparation Thereof,” October 5, 1948.

Hoiberg, A.J., U.S. Patent 2,421,421, “Process of Treating High Molecular Weight Hydrocarbons,” June 3, 1947.



