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**Polyphosphoric
Acid Modification of
Asphalt Binders**

A Workshop

April 7–8, 2009
Minneapolis, Minnesota

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OF THE NATIONAL ACADEMIES

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Preface

The modification of asphalt binder to improve performance properties has grown significantly since the implementation of the SHRP binder specifications. There has been increased use of polymers, crumb rubber modifier, and polyphosphoric acid (PPA). This has caused concern by many highway agencies about the performance characteristics of PPA modification and possible negative interactions with other mix components, such as lime and liquid antistrips. There have been anecdotal stories about both failures and successes. To address these concerns, TRB's General Concerns on Asphalt Technology Committee and Characteristics of Asphalt Materials Committee, with the FHWA, and Minnesota Department of Transportation, sponsored a workshop on PPA modification. This workshop was an attempt to pull together the real facts about PPA-modified asphalt and its performance. Researchers and practitioners with real knowledge and experience presented the latest information on the PPA modification and performance characteristics. The workshop agenda was developed to promote interactive discussion between presenters and participants. This published proceeding in the form of a TRB E-Circular is intended to document the research and presentations made at the workshop. In addition, copies of all the PowerPoint presentations (in PDF format) and recordings of most of the actual presentations are available on the North Central Superpave Center website at <https://engineering.purdue.edu/NCSC/PPA%20Workshop/2009/index.html>.

This document contains several papers and summaries of presentations on the evaluation of the performance characteristics of PPA-modified asphalt. Several state highway agencies, the Ontario Ministry of Transport, and industry representatives provided presentations on the status of evaluation of the use of PPA as a modifier for asphalt binder. No language should be construed as consensus findings or recommendations on the part of the workshop participants, the sponsoring committees, or TRB.

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Workshop Summary

JOHN A. D'ANGELO

Federal Highway Administration

The modification of asphalt binder to improve performance properties has grown significantly since the implementation of the SHRP binder specifications. There has been increased use of polymers, crumb rubber modifier, and polyphosphoric acid (PPA). Several highway agencies have been concerned about the performance characteristics of PPA modification and possible negative interactions with other mix components such as lime and liquid antistrips. There have been anecdotal stories about both failures and successes. A Workshop on Polyphosphoric Acid Modification of Asphalt Binders was held in April 2009 in an attempt to pull together the facts about PPA-modified asphalt and performance. Researchers and practitioners with real knowledge and experience presented the latest information on PPA modification and performance characteristics. The workshop agenda was developed to promote interactive discussion between presenters and participants.

To establish a reference point in time, Dean Maurer of the Pennsylvania Department of Transportation (DOT) conducted a survey of state DOTs in the winter of 2008–2009 to determine their current specification requirements with respect to the use of PPA. The survey had 37 responses from state DOTs. The Ontario Ministry of Transport (MTO) had also conducted a survey in 2007 on the use of PPA to modify asphalt binder. Pennsylvania combined the data from the two surveys to achieve a combination of 48 responses.

Following are several of the key questions in the survey:

1. Does your asphalt binder specification address or acknowledge the use of PPA modification?
2. If you allow the use of PPA, do you restrict the use in any way? Such as, only with (in conjunction with) polymer modification or specific binder grades or use applications.
3. What binder grades have you used that contain PPA?

At the specific point in time of the survey, 12 of the 48 Canadian provinces and U.S. states that responded had no restrictions on the use of PPA. Fifteen reported outright bans on the use of PPA. Restrictions had been placed on the use of PPA in 14 agency specifications. Since the survey was conducted the number of states restricting the use of PPA has decreased according to the state specifications reported by the Asphalt Institute (http://www.asphaltinstitute.org/public/engineering/State_Binder_Specs/State_Binder_Specs_Index.asp; accessed October 1, 2010).

These restrictions included only allowing the use of PPA as a comodifier with polymers or establishing limits on the amount of PPA that could be used to modify the binder. Seven agencies indicated that they were neutral on the use of PPA. In these agencies the only restriction was that the binder had to meet Superpave binder specifications. Of the agencies that either banned PPA or restricted its use, none reported actual poor performance in the field. However, several reasons for not using PPA were listed: preference for polymers; possible adverse reaction with other additives such as hydrated lime; unknown long term performance; and negative reports by others.

The survey responses overall provided a snapshot in time on the use of PPA and the general policies of the highway agencies on its use, including the following:

- There is a wide spectrum in the use of PPA from outright bans to unrestricted use.
- No specific documentation of poor performance was brought forward.
- A potential exists to significantly expand the currently limited performance database and available documentation on PPA as a binder modifier.
 - Due to fluctuating binder/modifier supply, agencies will need to be more flexible and knowledgeable concerning modifiers.
 - The workshop agenda should go a long way toward filling critical gaps in knowledge on PPA modification.

The background on PPA chemistry, patents, and PPA binder modification was covered in two presentations made by Mark Buncher of the Asphalt Institute and Gaylon Baumgardner of Paragon Technical Services. These presentations laid the foundation for why PPA is used as an asphalt modifier and its history of use.

Polysphosphoric acid ($H_{n+2}P_nO_{3n+1}$) is a polymer of orthophosphoric acid (H_3PO_4). PPA can be manufactured in one of two ways. The first method is derived from orthophosphoric acid by the abstraction of water and a condensation process. A second manufacturing procedure is by the direct burning of elemental phosphorus with introduction of the vapor to a hydrator which uses acidic sprays. The same water-free polymerized acid is obtained by either method. PPA, as opposed to orthophosphoric acid, has no free water. This eliminates issues of foaming and corrosion at the refinery or terminal. PPA's major applications are surfactant production, water treatment, pharmaceutical synthesis, pigment production, flame proofing, metal finishing, and asphalt modification. This circular will specifically discuss the use of PPA in asphalt modification.

There have been several patents on the use of PPA with asphalt. One of the first patents for binder modification was in 1973. This patent involved adding PPA to the asphalt binder to increase viscosity without increasing the penetration. Subsequent patents typically involved the use of PPA with polymer modification. Past experience has shown PPA increases the high temperature stiffness of an asphalt binder with only minor effects on the intermediate and low temperature properties.

The Superpave Performance Grade (PG) binder specification is used predominantly in the United States. In the PG system the high and low temperature performance range is specified, e.g., PG 64-22. The 64 represents the expected high temperature range of the binder and the -22 represents the expected low temperature range. The difference between the high and low temperature range of the binder is called the useful temperature interval (UTI). A PG 64-22 would have a UTI of 86°C or $64 - (-22) = 86^\circ\text{C}$. All asphalt binders refined from crude oil have a specific UTI. Changes in the refining process can shift the UTI up or down, but in general they cannot change the UTI. Specific crude may be refined to make a PG 64-22 or a 70-16, but it cannot be refined into a 70-22. To change the UTI of an asphalt binder, it would have to be blended with an asphalt binder which has a different UTI or modified with some type of additive.

The use of the Superpave binder specifications have encouraged agencies to specify stretch grades, which go beyond the UTI of most neat asphalts. A PG 76-22 would require a UTI of 98°C , well beyond most normally refined asphalts. To meet the requirements for these grades some type of modification is needed. In many cases this would be a polymer. Polymers do quite

well in increasing the high-temperature properties of a binder. However, polymer modification can also affect the low and intermediate temperature properties of the binder. In many cases adding a polymer alone to a PG 64-22 will not change it to a PG 76-22. The polymer will have a tendency to raise the low and intermediate stiffness of the binder so the grade may come out to be a PG 76-16. The use of PPA in combination with the polymer will minimize the increase in stiffness of the low and intermediate stiffness and allow for the production of the PG 76-22. The amount of PPA needed will vary based on the crude source and polymer being used. This is what makes PPA such a useful tool to the formulator to achieve the required properties for the stretch PG grades.

The next section of the workshop covered binders. Three presentations were made covering the interaction of PPA and asphalt binders, changes in binder properties, and testing for PPA in an asphalt binder. These presentations were made by John D'Angelo, Terry Arnold, and Gerry Reinke,

It was clearly demonstrated that the increase in binder stiffness from the addition of PPA was crude source dependent. Higher asphaltene content/more polar asphalts had greater increases in stiffness for a specific loading of PPA. This clearly demonstrated that there is no one application rate that will work for all asphalts. A low level of stiffening was achieved with California Valley asphalt which indicated very little reaction to even high dosage rates of PPA. The most responsive binders are those with high asphaltene content such as Boscan.

PPA is a hydrophilic material and easily absorbs water. Using a binder produced from a Venezuelan crude it was demonstrated that modification with higher percentages of PPA, above 1%, had a tendency to absorb water and lose strength. Beam samples of binders and mastics were prepared and placed in a water bath at 7.2°C for up to a year. This binder with 1% or less PPA did not indicate any increased absorption of water or loss of strength above the control. This was true for both neat binders and mastics. This specific Venezuelan asphalt is one that is very reactive with PPA, requiring only 0.5% to bump a grade.

The interaction of PPA and polymer modification was evaluated using the multistress creep and recovery test. The testing demonstrated that there is an interaction between PPA and styrene-butadiene-styrene (SBS) polymers. The data indicated that the improved high temperature stiffness of the SBS+PPA combination was greater than just the addition of the stiffening effects of the two materials. This was also true of the delayed elastic response of the SBS+PPA combination. The percent recovery from the SBS+PPA combination was always greater than just the SBS alone even though the PPA, when tested by itself, provides no increase in the percent recovery. In addition to the additional stiffening effect of the PPA, it also acts as a cross-linker improving the polymer network. This was demonstrated by the evaluation of fluorescent micrographs of the binder samples along with the improved percent recovery.

Once highway agencies realized that PPA may be used as an asphalt modifier their first question was can it be measured in the asphalt binder? Gerry Reinke, MTE Services Inc., presented an X-ray fluorescence approach to measure the amount of phosphorus in an asphalt binder. He demonstrated that phosphorus is the element that is determined in the sample, not the acid content. Acid content is calculated based on assumptions that all the phosphorus came from PPA and using an assumed concentration of PPA. It was shown that it is virtually impossible to remove all of the phosphorus from aggregates in bituminous mixtures. If the amount of PPA used in the binder to produce the mix is unknown, there will be no way, via simple binder extraction, to accurately identify the amount of PPA used in the binder.

The acid functionality of the PPA is the cause of the binder stiffening and not the phosphorus. Inability to quantitatively recover the phosphorus from a mixture does not mean that the aggregate or other mix components have neutralized the acid reaction with the binder. The acid functionality and the amount of phosphorus recovered are not interdependent when it comes to mixture performance. PPA does not phase-separate from binders. This was shown through lack of marked change in dynamic shear rheometer (DSR) stiffness properties and lack of marked differences in phosphorus content between top and bottom portions in the separation tube conditioning study.

Extraction of PPA-modified binders from mixtures can be impacted by stabilizing chemicals in the extraction solvent. Care must be taken to be sure that acid scavengers are not present in the extraction solvents used with PPA containing mixtures. If acid scavenging chemicals are present, the stiffening impact of the PPA can be partially destroyed.

A study was done by Rutgers University to evaluate SBS-modified binder against binder modified with a combination of SBS+PPA and neat binder. The neat binder was a PG 64-22 and the SBS and SBS+PPA modified binders were both PG 76-22. Dynamic modulus, beam fatigue, and flow number testing were conducted on a 12.5-mm Superpave mix at N_{design} of 100 gyrations. From the study the following conclusions were made:

1. SBS+PPA-modified asphalt binders can provide fatigue and durability resistance as well as asphalt binders solely modified with SBS.
2. Flexural beam fatigue test results on short-term and long-term oven-aged samples were statistically equal at a 95% confidence level.
3. Results from the tensile strength ratio (TSR) tests concluded that the SBS+PPA-modified asphalt achieved a slightly higher TSR value than the SBS-modified samples.

Dynamic modulus testing conducted on SBS+PPA- and SBS-modified asphalts that were laboratory aged under short-term and long-term oven-aging (LTOA) conditions as specified in the AASHTO document AASHTO R30, showed that both modified asphalts provided very similar modulus values after undergoing LTOA. The SBS+PPA-modified asphalt achieved slightly higher modulus values at higher test temperatures at the short-term oven-aged (STOA) condition. When evaluating the ratio between LTOA and STOA modulus, the SBS+PPA asphalt achieved slightly lower ratios than the SBS-modified asphalt. This may indicate that the SBS-modified asphalt underwent a greater extent of age hardening when compared to the SBS+PPA-modified asphalt.

Repeated load permanent deformation testing conducted on hot-mix asphalt (HMA) samples showed that both the SBS and SBS+PPA asphalts achieved almost identical resistances to permanent deformation when tested in uniaxial compression.

The question of increased moisture damage has been a concern when a PPA-modified binder is used. Two of the presentations in the workshop covered extensive work done to evaluate the potential for increased moisture damage with the use of PPA. Arnold evaluated one binder using three different aggregates with and without lime and liquid antistrips and Reinke evaluated both neat and polymer-modified binders with and without PPA on three different binders.

Both of the moisture damage studies had similar results. Aggregates that are already prone to moisture damage may show an increased propensity to strip when a PPA-modified binder is used. In all cases the use of hydrated lime could easily overcome the potential for

moisture damage even in the presence of PPA. Liquid antistripping additives also worked in mitigating moisture damage problems, but they had a tendency to be aggregate binder combination specific. However, this has always been the case with liquid antistripping. Overall, the data indicates PPA may or may not increase the potential for moisture damage depending on the asphalt–aggregate combination, but this is overcome by using an antistripping additive either lime or liquid. In all cases, the prudent thing to do whether PPA is used or not is to perform moisture damage testing and take appropriate measures to mitigate any potential that may be present.

The workshop included five case studies by agencies that have or are evaluating PPA. These studies included field trials, test track sections, laboratory studies, and a detailed evaluation plan. The results from the actual field sections and test track sections provided positive results for the performance of PPA-modified binders. The laboratory study indicated that there was a potential for performance issues and the evaluation plan was based on anecdotal information about the field failures with the use of PPA.

The Arkansas DOT undertook a major reconstruction plan of their Interstate system in 1999. Under the program 380 mi of Interstate would be reconstructed over 5 years, with 340 mi reconstructed with HMA. The program included 7.4 million tons of mix produced with modified asphalt binder. Most of the binder included PPA. In 1999, 37% of the system had a poor international roughness index (IRI) greater than 170 in/mi and 33% had a moderate IRI rating of 120 to 170 in/mi. As of 2006, after completion on the rehabilitation program, over 73% of the Arkansas interstate system is in good condition with an IRI less than 95 in/mi. There have been only very minor distresses on individual projects not related to the binder.

The National Center for Asphalt Technology (NCAT) operates a test track in Auburn, Alabama. The track is used to evaluate various mixtures and pavement sections for performance. In 2000, 18 SBS-modified sections were placed to evaluate SBS-modified asphalt binders against neat binders. All of the SBS-modified binder also contained PPA at 0.25% with lime or a liquid antistripping. These sections received 10 million equivalent single-axle loads (ESALs) during the first loading cycle with no indications of poor performance. All rutting for the sections was less than 6 mm. There was no evidence of moisture damage. In 2003, a second cycle of the track was constructed where nine of the existing SBS+PPA sections were left in place and nine new SBS+PPA sections were constructed. Again after 10 million ESALs, 20 million for the original sections, rutting was less than 9 mm on all the sections and there was no fatigue cracking that was attributed to the mixture. After 6 years with over 40 in. of rain per year, no moisture damage could be identified on the track sections.

MnROAD is the pavement test track operated by the Minnesota DOT. In 2007, they placed five test sections with PG 58-34 binder produced with PPA as the sole modifier or in combination with polymers. Hydrated lime and a phosphate ester antistripping were added to each mix. After 18 months there was less than 3 mm of rutting in each of the sections and no signs of moisture damage. Only one transverse crack had appeared in one section, which was attributed to a construction issue at the road sensor. Performance will continue to be monitored for 5 years.

The Utah DOT has done some lab evaluation of PPA-modified binders. In mix testing with lower levels of PPA (0.85% maximum), they have identified a potential increase in moisture damage in some mixes. Utah has elected to address this with mixture test requirements as opposed to a ban on PPA. Utah requires Hamburg wheel tracking tests for all mixes and believes this will catch any stripping problem. They also require elastic recovery for the binder which they believe will guarantee the presence of polymers.

MTO had significant concerns after hearing anecdotal information about the poor performance of PPA-modified binder. To investigate the issue, they conducted a survey in 2007 of U.S. and Canadian highway agencies to determine the existing policies and experiences of those agencies. At that time there had been many small laboratory studies but few major studies or field trials had been completed. Ontario established a task group that included agency and industry people to establish a policy that would allow development of new technology to continue, but reduce risk to the agency. Based on recommendations of the task group limitations were placed on the use of PPA as opposed to banning it. Binders that are for heavy duty pavements that require polymer modification could have up to 0.5% PPA added. On lower-volume roads binders could be bumped one grade by using up to 1% PPA. This was done by supplier certification. As more information becomes available the ministry will reevaluate its policy.

The PPA producers provided an industry best practices document on the use of PPA for binder modification. In their document they covered the addition of PPA to the base asphalt binder and discussed that different binders react differently to the PPA addition level. General PPA addition levels of 0.25% to 1.5% were noted with reference to higher levels for certain specific usages. Recommendations were made on several antistripping additives that are compatible with PPA and tests must be conducted to verify the mix performance. The use of PPA as a comodifier with SBS or other polymer modifiers and overall improvements to the binder properties were presented.

The final session of the workshop was a panel discussion led by three state highway agencies: Arizona, Louisiana, and Wisconsin. Each of these states has elected to not restrict PPA, but instead have used either asphalt mixture requirements or SHRP plus binder tests to provide what they want. Arizona from the desert southwest, Louisiana from the Gulf Coast, and Wisconsin from the upper Midwest, all have very different climates. Each agency reported using PPA successfully by addressing performance properties as opposed to placing restrictive formulation specifications on the suppliers.

SUMMARY OF WORKSHOP DISCUSSIONS

The PPA workshop covered extensive laboratory and field evaluations on the use of PPA as a modifier for asphalt binder. The following points were made by various workshop participants during the discussions.

- The stiffening effect of PPA on the binder is crude source dependent with anywhere from 0.5% to more than 3% needed to increase the binder grade.
- PPA works as a stiffener and cross-linker when used with polymers such as SBS and ethylene terpolymers (e.g., Elvaloy).
- PPA can significantly improve the delayed elastic response of the polymer-modified binder.
- There is some indication that hydrated lime can somewhat reduce the stiffening effect of PPA but the increased stiffening from the lime outweighs any loss.
- Limestone aggregate could not reverse or reduce the stiffening effect of PPA on the binder.

Several laboratory studies evaluated the moisture damage potential of mixes produced with PPA-modified binders.

- Mix testing indicated that PPA-modified binder could increase the moisture damage potential at applications rates of 1.5% or greater for particular asphalt–aggregate combinations.
- Below the level of 1.5%, there did not appear to be any increase in moisture damage potential. The lab testing indicated that PPA can work with amine, hydrated lime, and phosphate ester antistrips to mitigate moisture damage potential. This was seen in both the Hamburg wheel tracking test and the AASHTO T-283 TSR test.
- Typical mix moisture sensitivity testing will identify if any issue exists with binder aggregate combinations.

Extensive field testing has shown no negative performance related to PPA.

- More than 27 test sections were placed on the NCAT test track with SBS+ PPA combinations; all performed well with little rutting or cracking and no indication of moisture damage.
- The MnROAD test track has four sections with up to 0.75% PPA modification that have all performed well with minimal rutting and no cracking.

Several states that have used PPA extensively indicated that there have been no instances of negative performance issues that can be attributed to the PPA. All field studies covered in the workshop had between 0.25% to 1.2% PPA.

- Sections have been in place for over 10 years with good performance.
- Sections have been placed in hot desert climates, hot wet climates, and cold wet climates.
- These states have used mix verification to determine the potential for moisture damage using their typical moisture tests.
- Negative interactions with aggregate types such as limestone have not been identified in any of the field projects.

Typical mix design and verification testing provided is included moisture damage evaluations is adequate for PPA dosage rates up to 1.5%. PPA dosage rates greater than 1.5% may be used, however, testing above typical mix design and verification will be needed. Performance testing to evaluate rutting and fatigue should be conducted on mixes with PPA dosage rates above 1.5% to assure no negative interactions are taking place between the binder and aggregate or any other additives in the mix.

Department of Transportation Perspective *A Survey on Polyphosphoric Acid Use and Issues*

DEAN MAURER

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JOHN A. D'ANGELO

Federal Highway Administration

To establish a reference point in time, Dean Maurer of the Pennsylvania Department of Transportation (DOT) conducted a survey of the state DOTs to determine their current specification requirements with respect to the use of polyphosphoric acid (PPA). This survey was conducted in the winter of 2008–2009. The survey had 37 responses from the state DOTs. The Ontario Ministry of Transport (MTO) had also conducted a survey in 2007 on the use of PPA to modify asphalt binder. Pennsylvania combined the data from the two surveys to achieve a combination of 48 responses. The survey contained the nine questions listed below:

1. Does your asphalt binder specification address or acknowledge the use of PPA modification?
2. If you allow the use of PPA, do you restrict the use in any way? Such as only with (in conjunction with) polymer modification or specific binder grades or use applications.
3. What binder grades have you used that contain PPA?
4. Have you documented or tracked performance of pavements using PPA as a modifier relative to other pavements with the same grade binder, except produced in a different way or with another modifier? If yes, do you have any reports available?
5. If you currently do not permit the use of PPA, is there a specific reason such as poor past performance or experience, or concerns and problems expressed or reported by others? If you have had poor past performances with the use of PPA do you have forensic data that can be shared?
6. Were you aware that Turner–Fairbank Highway Research Center has been conducting an extensive laboratory study to address the risks and benefits associated with the use of PPA as an asphalt binder modifier?
7. Were you aware that the FHWA is conducting a study that includes the use of PPA as a comodifier with styrene-butadiene-styrene?
8. Would you be interested in participating in a national workshop on the use of PPA as an asphalt binder modifier, planned to be conducted in Minneapolis, Minnesota, on April 7 and 8, 2009?

Data on the DOT's specifications in relation to the use of PPA, Questions 1 and 2, was compiled based on the response to the survey questions. The DOT responses were broken down into five categories: allow, don't allow, restrict, neutral and no response. The DOT responses, except the no responses, were almost evenly distributed over the five categories. The specification data is shown in [Figure 1](#) and [Table 1](#).

The state highway agencies that do not allow PPA did so either through a direct ban on PPA or through plus specifications. The plus specifications included items such as elastic

recovery or phase angle. Agencies that restricted use would typically set restrictions on PPA. New York State does not allow the use of PPA with limestone aggregate. Pennsylvania only allows the use of PPA on an experimental basis. Other agencies, such as Wyoming, only allow a maximum dosage rate of 0.5%. Another typical restriction is that the PPA can only be used in conjunction with polymer modification. Several highway agencies are neutral on the use of PPA, which indirectly allows it use. These agencies typically have no additional requirements on PG binder specifications and only require that the binder meet the PG spec as is.

Question 3 of the survey was on the types of binder have been used with PPA as an additive. Only about a third of the states provided an answer to Question 3 and these answers were very limited. From the 17 agencies that replied to Question 3, seven different binder grades were listed. These grades cover almost the full spectrum of grades which would be expected to be modified. With only 17 agencies responding though, it is likely that many are not aware of which grades they have used that may have been modified with PPA. The grades and agencies that responded are listed in [Table 2](#).

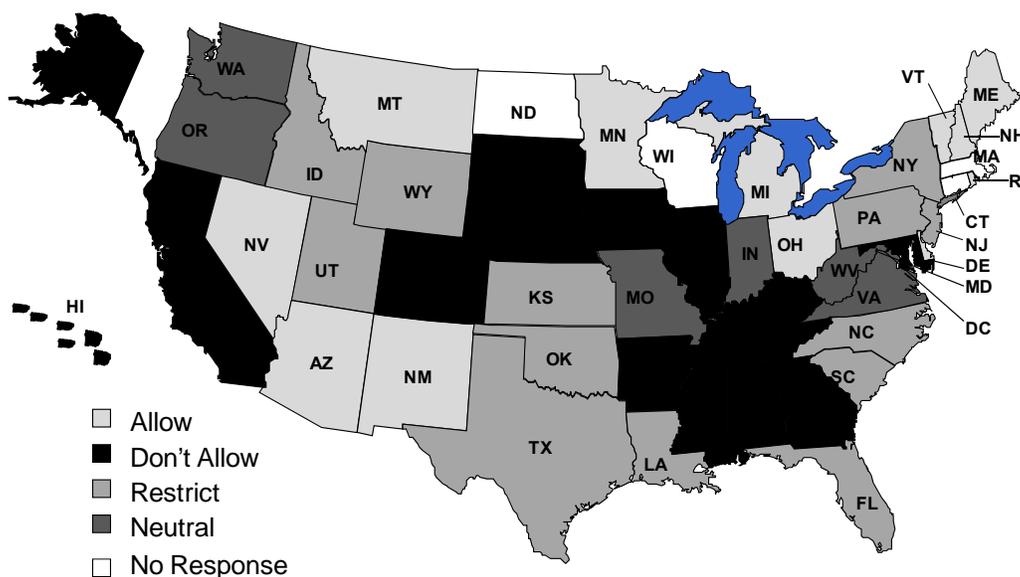


FIGURE 1 Map showing responses of state DOTs to their use of PPA as a modifier for asphalt binder.

TABLE 1 State DOT Responses to the Use of PPA as Modifier for Asphalt Binder, by State and Category

Allow	Unrestricted	AZ, CT, ME, MI, MN, MT, NH, NM, NV, OH, RI, VT
Don't Allow	Directly or Indirectly	AK, AL, AR, CA, CO, GA, HI, IL, IA, KY, MD, MS, NE, SD, TN
Restrict		FL, ID, KS, LA, NC, NJ, OK, TX, UT, NY, PA, SC, WY, MO
Neutral	Indirectly Allow	DE, IN, MO, OR, VA, WA, WV
No Response		MA, ND, WI

TABLE 2 Agency Responses: Binder Grades That Have Been Modified with PPA

PG Grade	Agency Reporting
PG 64-22	LA *
PG 76-22	NJ *, NC *
PG 64-28	CT, ME, MT, NH, NY, OH, PA, WY
PG 70-22	NY, NC, SC
PG 70-28	MT, UT, WY, MTO
PG 58-34	MN
PG 64-34	MN, UT

* Possible or suspected but not documented

Question 4, “Have you documented or tracked performance of pavements using PPA as a modifier relative to other pavements with the same grade binder, except produced in a different way or with another modifier?”, was answered negatively by most of the states. Several, however, were attempting to track use and performance.

- Connecticut has had general observations with no reports yet.
- Maine is monitoring test sections with a PG 64-28 PPA binder and PG 58-28 no PPA.
- Minnesota has built several sections at MnROAD to evaluate PPA.
- Montana has established a lab study of PPA to be evaluated with the Hamburg loaded wheel tester.
- Nevada has one project with PPA compared to a neat asphalt control.
- Pennsylvania is monitoring two projects using a PG 64-28 produced with PPA. More projects are planned for the future.
- Utah has lab study underway using the multistress creep and recovery to evaluate PPA with polymer modification.
- MTO is just starting to place field sections for evaluation.

Question 5 was “Are reports available on PPA performance?” None of the agencies reported that they have existing reports addressing performance, but as reported in Question 4, those agencies indicated they will have reports when their field trials are completed. Many agencies have had presentations the use of PPA.

Question 6 asked “If you currently don’t permit the use of PPA, is there a specific reason(s), such as, poor past performance or experience, or concerns or problems expressed or reported by others? If you have had poor past performances with the use of PPA do you have forensic data that can be shared?” No agencies reported actual poor performance in the field. However several reasons for not using PPA were listed: preference for polymers, possible adverse reaction with other additives such a hydrated lime, unknown long-term performance, negative reports by others, and possible issues with the recovery of the binder.

Questions 7 and 8 explored whether the states were aware of ongoing FHWA research regarding PPA. None of the agencies responded that they were actually following the progress and most indicated that they were not aware of any studies.

Question 9 asked if the agencies would like to participate in the workshop on PPA. Of the agencies responding, 31 said they would attend, but many listed concerns about travel restrictions.

The survey overall provided a snapshot in time on the use of PPA and the general policies of the highway agencies on its use. The general conclusions from the survey were the following:

- There is a wide spectrum in the use of PPA from outright bans to unrestricted use.
- No specific documentation of poor performance was brought forward.
- A potential exists to significantly expand the currently limited performance database and available documentation on PPA as a binder modifier.
 - Due to fluctuating binder–modifier supply, agencies will need to be more flexible and knowledgeable concerning modifiers.
 - The workshop agenda should go a long way toward filling critical gaps in knowledge on PPA modification.

**Establishing a Baseline of Knowledge Through 2005
by Reviewing AI IS-220
*Polyphosphoric Acid Modification of Asphalt***

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The purpose of this presentation was to clarify issues regarding polyphosphoric acid (PPA) modification of asphalt binders and to help highway agencies make informed decisions on its use. The presentation and the Asphalt Institute (AI) publication IS-220 was not to promote the use of PPA. It was intended to provide factual information on the use of PPA. The document was developed through AI's Technical Advisory Committee and Affiliate Committee by AI member representatives.

AI's position on binder modification and PPA is

- AI supports responsible modification of asphalt for improved performance and life cycle costs;
- AI does not endorse any specific or proprietary form of modification;
- PPA can improve physical properties of asphalt when used correctly and in appropriate amounts;
- Inappropriate use of PPA can result in problems;
- There is a need to continue developing performance-related specifications; and
- There is a need to test modified binder after all additions.

PPA is a liquid mineral polymer. It has a high viscosity at room temperature. It has no free water, allowing total miscibility with asphalt. No free water also significantly lowers corrosivity for steel compared to orthophosphoric acid. The major uses for PPA are surfactant production, water treatment, pharmaceutical synthesis, pigment production, flame proofing, metal finishing, and asphalt modification.

PPA can be an effective and economical tool for chemical modification, used alone or in conjunction with a polymer. It can improve the high-temperature performance grade (PG) and, with some asphalt sources, may slightly improve the low-temperature PG grade. PPA does not oxidize asphalt or lower the m-value.

When used with polymer, PPA provides flexibility in reaching specified dynamic shear rheometer (DSR) and elastic recovery criteria, while limiting the viscosity increase at 135°C (275°F). For acidic aggregates such as granite, PPA can enhance moisture resistance of a mix such that an antistripping may not be necessary. When an antistripping additive is used, a neutralization reaction may occur (depends on the nature of the asphalt, aggregate, and antistripping). If so, then a partial loss of binder stiffness will result without loss of adhesion properties.

PPA does not work equally well in all asphalts. Interactions are dependent on asphalt chemistry. PPA-modified asphalt is not the same as an oxidized asphalt. The relaxation

properties determined in the bending beam rheometer do not deteriorate. Under certain conditions, PPA may react with certain antistrips leading to a partial decrease of the high-temperature PG improvement from PPA modification. The antistrip function will not be inhibited, but correct formulation is necessary. There are antistrips that can be used with PPA-modified binder that will not inhibit gains from PPA. Phosphate esters do not react with PPA and are effective antistrips in both neat and PPA-modified binders. PPA does not cause premature aging or brittleness in the binder. No evidence of accelerated aging or worsened low temperature properties from modification with PPA have been found.

Asphalt manufacturers using PPA must do so responsibly. They need to use careful formulation to ensure appropriate dosage based on the type of asphalt. The formulator should ensure compatibility with any antistrip additives. The supplier must maintain good communication with contractors regarding potential use of amine-based antistrips.

Specifiers and agencies have helped ensure responsible use of PPA by using PG plus binder tests to ensure the presence of polymer when one is required. DSR testing has been used to check for compatibility of PPA with amine-based antistrips before and after the antistrip is added. Mix performance tests may be used to evaluate moisture susceptibility (T 283, wheel tracking under water, etc.) with all additives included in the mix.

Why and How of Polyphosphoric Acid Modification

An Industry Perspective

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Evolution of asphalt binder specifications continually challenges asphalt practitioners to seek tools allowing production of binders from most readily available materials. These tools must facilitate production of asphalt binders that not only meet existing specifications, but ensure long-term performance. Polyphosphoric acid (PPA) is just one such tool. PPA modification of asphalt is not a new concept as asphalt binders have been chemically modified with PPA to improve high-temperature rheological properties without adversely affecting low-temperature rheological properties since the early 1970s. More recently, PPA has been used in Superpave performance grade (PG) binders to extend the range between the high- and low-temperature performance. PPA use has increased, as it is being used not only to produce nonpolymer-modified binders but is used in polymer-modified binders as well. While use of PPA in nonpolymer-modified asphalt binders has a 30-plus year performance history, experienced asphalt practitioners have found that addition of small amounts of PPA to polymer-modified binders brings benefits in both handling and performance. Used in conjunction with polymers, PPA enables suppliers to achieve PG grades that can be handled, mixed, and compacted at reasonable temperatures. Both nonpolymer-modified and polymer plus PPA-modified binders have shown improved rutting resistance by the addition of PPA. Though successful PPA modification of asphalt binders has a long track record, its use is often debated, sometimes to the point where PPA-modified asphalt binders have been banned. Opinion has it that such actions result from misinformation as well as lack of understanding of the benefits of PPA as an available tool to improve the performance of asphalt binders. While PPA is banned in some states, others continue its use without issue. This paper discusses common asphalt binder specifications, the relationship of asphalt binder chemical composition to PG properties of asphalt binders, necessary use of PPA modification to meet specifications, the relationship of asphalt composition to PPA loadings necessary to achieve desired properties, expected PG enhancements of PPA-modified asphalt binders, and the effects of using PPA in nonpolymer- and polymer-modified asphalt binders to meet current PG specifications.

INTRODUCTION

PPA modification of paving asphalt was first reported in U.S. Patent No. 3,751,278, issued August 7, 1983 (1). The objective of the invention was to provide a method to alter the penetration–viscosity relationship of paving asphalt binders. More specifically, the objective was to substantially increase the viscosity of asphalt without significantly decreasing the penetration. Yet another objective was to provide a paving asphalt binder with unique temperature susceptibility characteristics. Prior to this, most use of phosphorous compounds in asphalt dealt with use of ortho-phosphoric acid (H_3PO_4) and phosphorous pentoxide (P_2O_5) as a catalyst in production of air blown asphalt for industrial purposes (2–4).

Prior to 1970, paving asphalt binders were typically graded and specified worldwide by penetration, which is defined by the ASTM as the distance in tenths of a millimetre that a standard needle vertically penetrates a sample of asphalt under known conditions of loading, time, and temperature (5). PGs for paving asphalt binders were classified by AASHTO as a range in penetration measured by application of a 100 g weight for 5 s at 25°C (77°F); specified grades were 40 to 50, 60 to 70, 85 to 100, 120 to 150, and 200 to 300 (6,7).

Beginning in 1970, the United States began to specify paving asphalt binders according to absolute viscosity, or the viscosity of an asphalt binder determined by vacuum capillary viscometers measured at 60°C (140°F) (8). Viscosity grades based on unaged or original asphalt binders were classified by AASHTO M 226 Table 1 as either AC-2.5, AC-5, AC-10, AC-20, or AC-40 where AC is designated as asphalt cement and the number designation represented the absolute viscosity in poises, with the specification range being the number designation multiplied by 100 plus or minus 20% (9). Later AASHTO added Table 2 to M 226 which included an intermediate AC-30 grading based on original binder. Some states specified original binder viscosity grades, in particular AC-40, in accordance with the then current AASHTO guidelines, with additional requirements for minimum 25°C (77°F) penetration values. These binders were desired to obtain binders that would resist rutting while providing good performance against thermal cracking. However, these binders proved difficult to produce from conventional refining methods, therefore, PPA was employed as described in U.S. Patent 3,751,278 (1) to increase the viscosity of a standard AC-30 to that of an AC-40 while minimally affecting the binder penetration. In addition to Tables 1 and 2, AASHTO M 226 contains Table 3, which viscosity grades asphalt binders based on residue from the rolling thin film oven test (RTFOT) and designates them as either AR-10, AR-20, AR-40, AR-80 or AR-160, where AR designates “asphalt residue” and the number designation represents the absolute viscosity in poises, with the specification range being the number designation multiplied by 100 plus or minus 25%.

In the 1990s (1995–1996) state departments of transportation began to specify paving asphalt binders according to PG as defined by the Superpave specification AASHTO M 320. According to AASHTO M 320, Superpave PG grading designations are related to the average 7-day maximum pavement temperature, and the minimum pavement design temperature. These grades are designated by a letter designation PG and the expected maximum 7-day average temperature of 46, 52, 58, 64, 70, 76, or 82, followed by the minimum pavement design temperature in 6°C increments from –10 to –46°C (10). The more common PGs specified are PG 58-28, PG 64-22, PG 64-28, PG 70-22, PG 76-22, and PG 82-22. In the Southeastern states an intermediate PG of PG 67-22 is typical due to previous experience with rutting of binders that meet the regional standard grade of PG 64-22. With the advent of Superpave and the application of PG grading, PPA has been used to improve the PG high-temperature parameter in unmodified (neat) asphalts or in combination with polymers. Specifically, this is because the PG specification made it necessary to use higher levels of polymers than previously required to produce polymer-modified asphalt binders to meet specifications based on absolute viscosity (as much as a 30% to 50% increase). This was generally due to lower-than-specified binder stiffness after the RTFOT and because such increases had a significant impact on rotational viscosity. Therefore, alternative formulations such as those based on PPA- and styrene-butadiene-styrene (SBS) –modified asphalt binders have seen increased use since implementation of the PG binder specification. In effect, the PG binder specification spawned the increased practice of combining PPA with polymers to modify asphalt binders. This is illustrated in several patents issued since the mid- to late 1990s (11–15).

Though asphalt specifications have been upgraded through time, and the United States predominantly uses PG specifications currently, all previous grading systems are subject to use.

USEFUL TEMPERATURE INTERVAL AND PG ASPHALT BINDERS: SUPERPAVE MADE SIMPLE

Superpave PG specifications for PG binders have been considered to define the grade range or performance range of asphalt binder which has been referred to as the useful temperature interval (UTI). Simply put, the UTI of asphalt is the differential, or spread in °C, between the high-temperature grading and the low-temperature grading. It is also known as the binder “true-grade range” or “continuous grade range.” For example, a standard grade of PG 64-22 would have a UTI of 86°C which is the differential between -22°C and 64°C; another example of an 86°C UTI would be a PG 58-28. [Figure 1](#) exhibits the UTIs of some common PG binders with respect to the high- and low-temperature grading parameters.

As a general rule, to achieve a UTI greater than 92°C the asphalt must be modified. Typically modification is accomplished by the addition of polymers, however, modification can also be accomplished by oxidation or chemical means such as with PPA. Depending on the crude from which a binder is derived, binders with narrower UTI’s such as 86°C or 89°C may also require modification. Before discussion of the specifics of PPA modification, it is necessary to discuss the relationship between crude source and refining processes and their influence on UTI and the grade of asphalts derived from crude oil.

CRUDE SOURCE, REFINING PROCESSES, AND THEIR EFFECT ON BINDER PERFORMANCE GRADE

The UTI of any binder is directly related to the crude or crudes from which it is derived, which can be attributed to the chemical composition of the resulting binder. A relationship of chemical composition of asphalt binder to UTI is shown in [Figure 2](#).

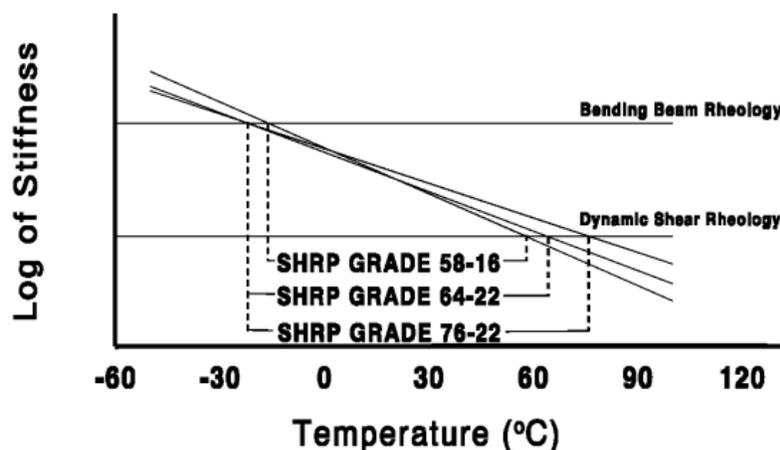


FIGURE 1 UTI of common PG binders.

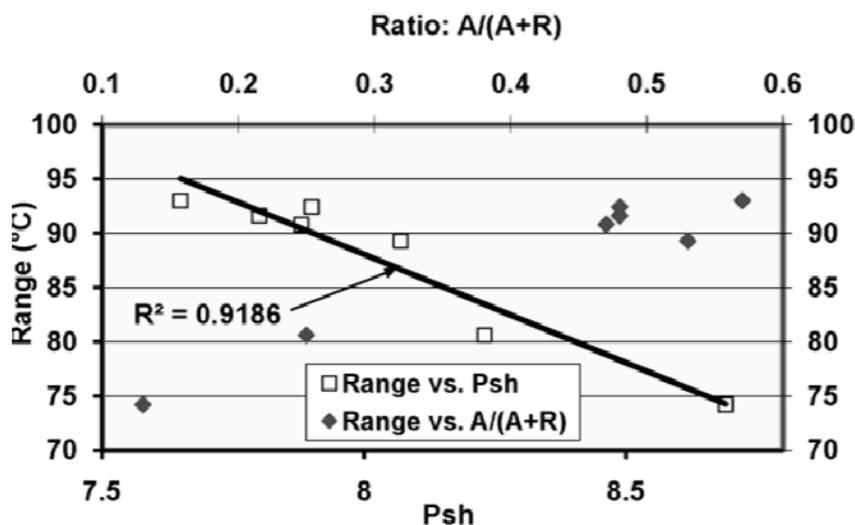


FIGURE 2 Relationship of asphalt composition to UTI.

Figure 2 presents results of compositional analysis of asphalt binders derived from seven different crude sources. Each binder was deasphalted according to ASTM Method D3279 “Standard Test Method for n-Heptane Insolubles” to yield asphaltenes (A), or the n-heptane insoluble fraction, and maltenes, which are the n-heptane soluble fraction. The n-heptane soluble fraction, maltenes, were further fractionated on an Iatroscan TH-10 Hydrocarbon Analyzer to yield the composition in saturates (S), cyclics (C), and resins (R). The method has been described in detail before (16, 17). n-Pentane was used to elute the saturates, and a 90/10 toluene–chloroform solutions was used to elute the cyclics. The resins were not eluted and remained at the origin. A solubility parameter (Psh) of the maltene fraction is represented by the sum of the factors of the known solubility parameter of the solvent which elutes the specific fraction and the percentage of that particular fraction. Psh is an indication of the solvency of the maltene fraction, and it can be determined from Figure 2 that asphalts with greater solvency tend to have narrow UTI while those with lesser solvency have greater UTI. A similar relationship can be observed between the asphaltene to resin ratio (Ar) represented by the asphaltene content divided by the sum of asphaltenes and resins fractions, where asphalts with higher Ar would have a narrow UTI and asphalt with lower Ar would have greater UTI.

The UTI of asphalt binders derived from crude refining is, for the most part, constant; meaning, regardless of the PG produced from a specific crude, the UTI temperature differential will be constant. Figure 3 presents an example of a crude that would yield soft asphalt with a PG 52-34 with a UTI of 86°C and a harder PG 64-22 through further refining that also has a UTI of 86°C.

Also from Figure 3, it can be seen that UTI determines the grades of asphalt yielded from a specific crude and determines the PG grade line for that crude. The PG grade line can be considered as the PG signature of that crude. Figure 4 shows the effect that varying process parameters, in this case vacuum distillation, has on the PG grade yielded from refining of a specific crude and the effect the PG grade line has on the grades yielded.

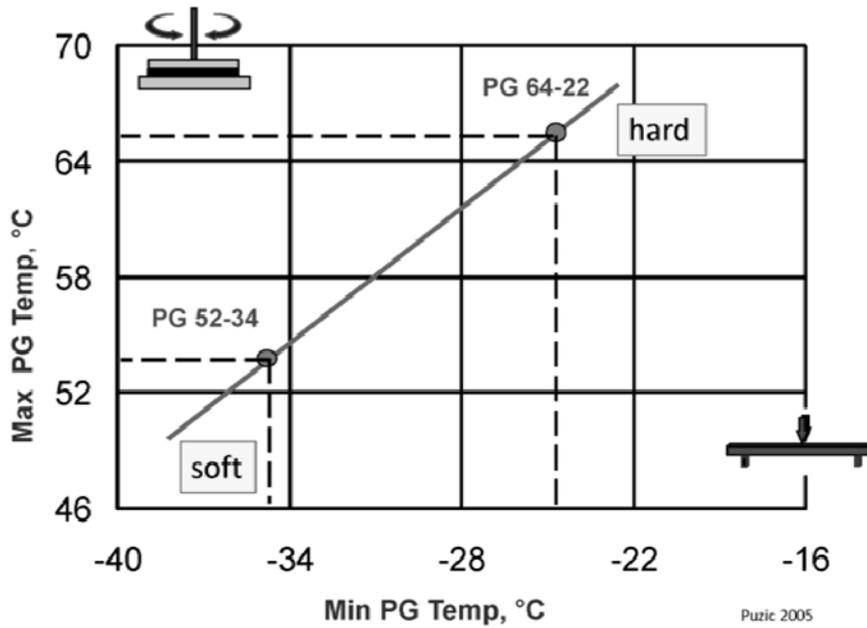


FIGURE 3 Superpave PG and the PG line.

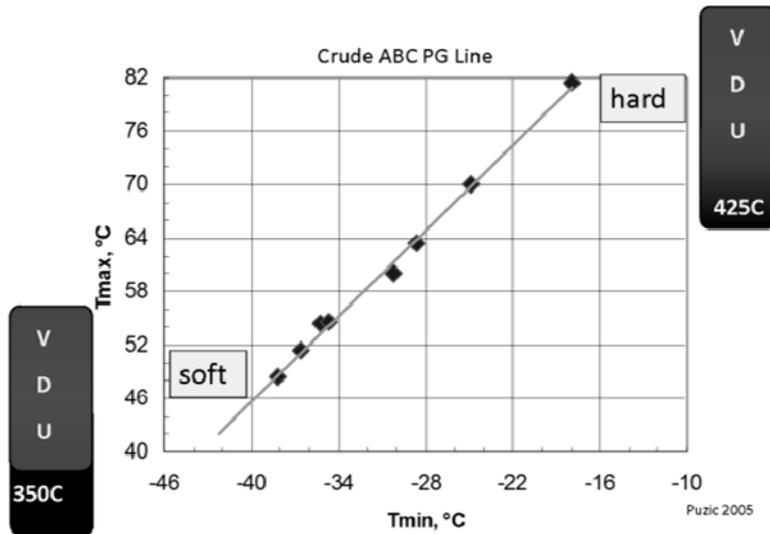


FIGURE 4 Effect of refining parameters on UTI and PG line.

Figure 5 presents a comparative example of the PG grade lines from three different crude sources. It can be seen that these crudes have distinctly different PG grade lines and that the grade line is the controlling factor on which PG grades can be produced from each crude. It can also be assumed that blending of these crudes or asphalt derived from these crudes will yield PG binders of intermediate grades between those yielded by the single crude or a single grade asphalt derived from those crudes.

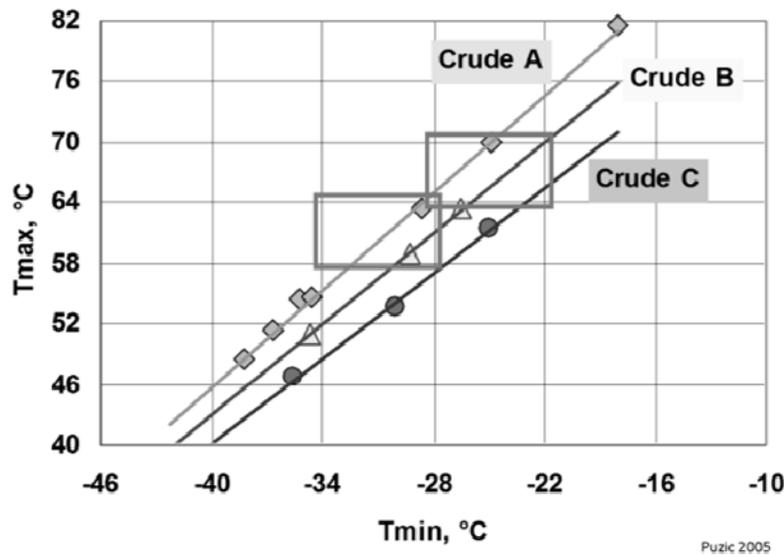


FIGURE 5 SuperPave PG line, the signature of a crude.

The desire of an asphalt producer, whether it be through crude oil refining or blending of various grades of asphalt available, is to get the widest UTI possible for the resulting finished asphalt produced. In cases where the crude or available asphalts will not produce the grades desired it is most always necessary to widen the UTI, requiring modification of the asphalt by some means. As previously stated, as a general rule to achieve UTIs greater than 92°C the asphalt must be modified and depending on the crude from which a binder is derived, binders with more narrow UTI such as 86°C or 89°C may also require modification. It is also common that modified binders with wider PG grades, those greater than 92°C, may require additional modification to achieve the PG grade desired and meet all specification requirements. Figure 6 presents two asphalts graded with the parameters defined by Superpave, one is a neat (nonmodified) PG 64-22 and the other PG 76-22 produced by modification with 4.75% SBS. While both of these binders seem to meet the PG specification for the grades indicated, with respect to the high and low temperature parameters, it is obvious that neither would meet the full PG specifications requirements due to failure to meet other PG specification requirements identified by the ovals.

In the case of the neat PG 64-22, this binder is failing the intermediate dynamic shear rheometer (DSR) maximum of 5,000 kPa at 25°C, with the intermediate stiffness reaching the 5,000 kPa maximum at just above 26°C. In addition to this, the PG grade range with respect to high and low temperature parameters presented are only those for a PG 64-22; should it be necessary to produce the higher grade of PG 67-22 required by most of the Southeastern states, it would not be possible from this crude as increasing the high-temperature stiffness would also increase the temperature at which this binder achieves the intermediate maximum 5,000 kPa. With respect to the PG 76-22 it was necessary to add sufficient SBS to achieve not only the original DSR requirements, but more specifically the RTFO DSR requirements which is the controlling factor in achieving the high-temperature grade for this particular binder. Again, this binder meets the high- and low-temperature requirements for PG 76-22, however, at 4.6 Pascal seconds, it is failing the PG specification requirement for rotational viscosity (RV) of a

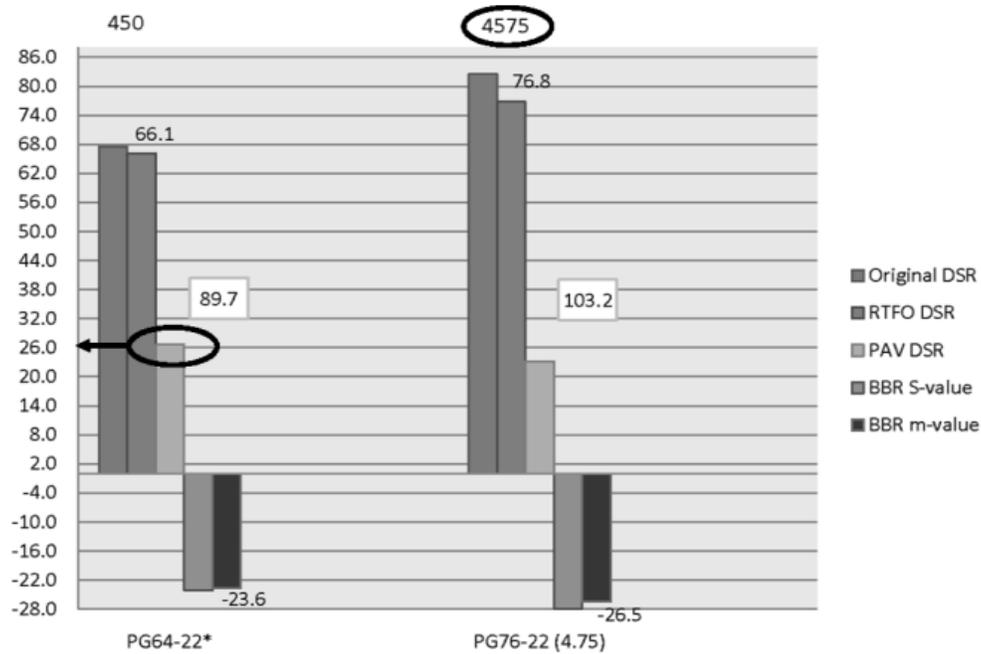


FIGURE 6 PG asphalt binders SuperPave specification requirements.

of a maximum 3.0 Pascal seconds at 135°C. In both cases if limited to only the crude which produces the neat asphalt or the base asphalt being modified in the SBS modified binder, the asphalt binder supplier is left with only two alternatives: simply not supply binder or turn to other forms of modification, in particular PPA.

PPA MODIFICATION OF ASPHALT BINDER

PPA, a medium strong acid (Hammet acidity function = 6, sulfuric acid H_2SO_4 = 12), is an inorganic polymer, more specifically an oligomer, obtained by condensation of monophosphoric acid or by hydration of phosphorous pentoxide (P_2O_5). PPA is typically a mixture of orthophosphoric acid with pyrophosphoric acid, triphosphoric acid, and higher acids, and contains no free water. PPA is produced and marketed on the basis of its calculated content of H_3PO_4 (orthophosphoric acid) or relative P_2O_5 (phosphorous pentoxide) content, for example 105% (super phosphoric acid). PPA is a viscous liquid at room temperature (25°C), from ~ 840 – 60,000 cP depending on the concentration; is highly soluble in organic compounds (such as asphalt); and is a nonoxidant compound. PPA reverts slowly to orthophosphoric acid on dilution with water.

Phosphoric acid and phosphorous pentoxide (P_2O_5) modification, used as early as 1948, are known methods of chemical modification of asphalt (19–21). More common PPA modification, increasingly used as a means of producing modified binders in North America since the early 1970s (1), provides the benefit of phosphoric acid and P_2O_5 modification without the risks associated with combining hot asphalt with water-containing orthophosphoric acid, more commonly referred to as 85% PPA or the handling risks associated with solid P_2O_5 . Similar to polymer modification, modification with PPA stiffens the asphalt at high temperature with

improved resistance to permanent deformation, and has no detrimental effects on low temperature properties. While some have compared PPA modification to oxidation or “air blowing” of asphalt, PPA modification is very different from air blowing as there is no asphalt oxidation, and PPA modified asphalt has very good low temperature properties compared to air blown asphalt. PPA actually exhibits antioxidative characteristics in asphalt binders modified with PPA (19, 20). PPA modification is a functional economic tool that can be used by binder suppliers to produce PG asphalt binders either with or without polymers depending on the specification and performance requirements.

The amount of PPA and effect of modification depends on asphalt chemical composition which, as previously discussed with respect to UTI, is related to the crude source from which the asphalt was derived. The PPA grade used—105%, 115%, etc.—typically has minimal effect on resulting properties, therefore, 105% PPA is more common due to lower viscosity and ease of handling. Figures 7 and 8 present comparative results of PPA modification of various asphalts derived from varied crude sources with two different grades of PPA, 105% and 115%. It is readily apparent that PPA modification provides improvement in both the high-temperature and low-temperature performance properties. PPA modification increases the asphalt UTI by improving performance characteristics at both upper and lower specification limits.

As seen in the two previous figures, the outcome of PPA modification varies depending on the asphalt binder composition, thus, some binders may require more PPA than others to achieve the same improvement in PG properties. Figure 9 illustrates typical amounts of PPA required to produce a one grade change in PG.

Some asphalt binders may not be suited for PPA modification if they require excessive amounts of PPA to achieve desired properties. More is not always better, and in this case other alternatives should be investigated. From Figure 9 it could be suggested that a maximum use level (~ 1.5% to 2.0%) be established.

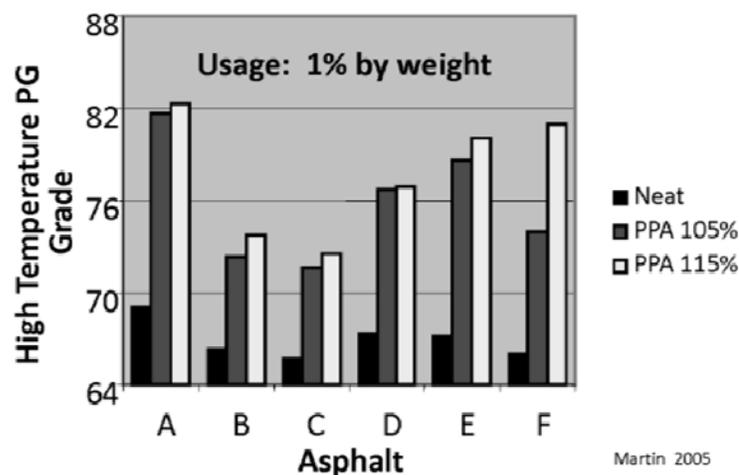


FIGURE 7 Effect of PPA modification on the high-temperature PG of various asphalts.

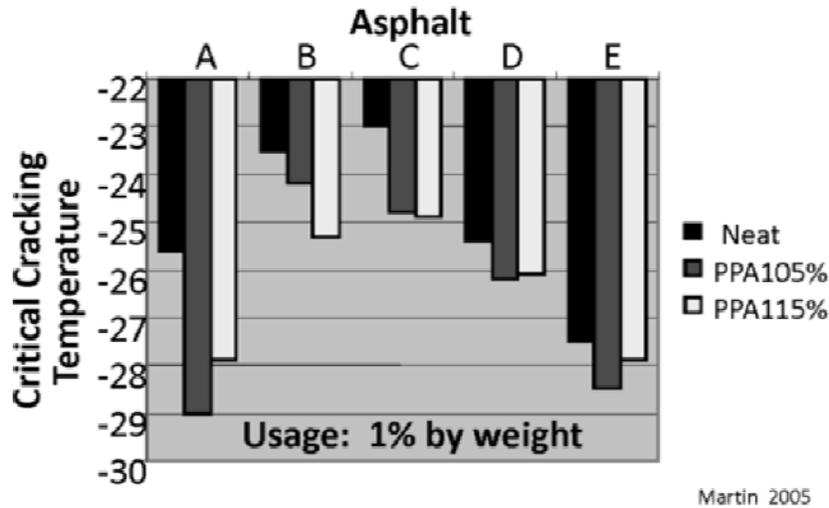


FIGURE 8 Effect of PPA modification on the low-temperature PG of various asphalts.

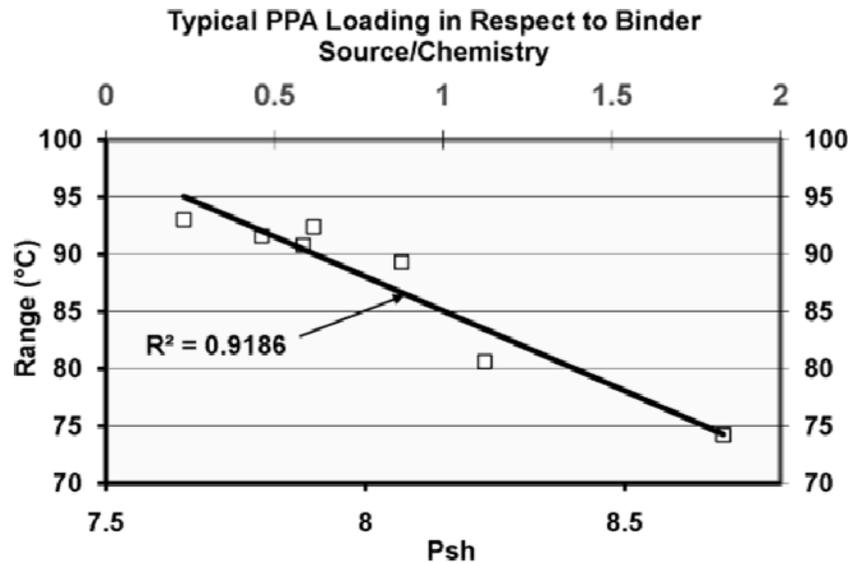


FIGURE 9 PPA loading with respect to asphalt composition.

SUMMARY

Earlier in this manuscript, Figure 6, two asphalts graded with the parameters defined by Superpave were presented. One neat (nonmodified) PG 64-22 and the other PG 76-22 produced by modification with 4.75% SBS, were presented as examples of how binders may seem to meet PG specification requirements with respect to high- and low-temperature parameters yet fail due to failure to meet other PG specification requirements. In the cases presented, those parameters were intermediate DSR for the nonmodified PG 64-22 and rotational viscosity, RV, of the PG 76-22 SBS-modified binder. These binders are presented again in Figure 10 with a comparison to binders produced using PPA modification to meet the

PG requirements. The new binders were produced from the same base asphalt binder as the previous two non-PPA-modified binders.

The neat PG 64-22 binder originally failed the intermediate DSR maximum of 5,000 kPa at 25°C, with the intermediate stiffness reaching the 5,000 kPa maximum at just above 26°C. After the addition of PPA, this binder now meets the higher grade of PG 67-22 required by most of the Southeastern states, which was actually the grade desired from this binder. The new binder comfortably meets PG 67-22 requirements with a 68.6°C high temperature grade and a -24.1°C low temperature grade. As stated and exhibited previously, PPA modification provided improvement in both high- and low-temperature PG requirements, but more importantly the intermediate temperature performance was also maintained now meeting not only the 26.5°C requirement for a PG 67-22, but also the 25.0°C requirement for a PG 64-22. This binder could actually be softened slightly and continue to meet all requirements for both PG 67-22 and PG 64-22. With respect to the PG 76-22, two things were accomplished. First, it was possible to reduce the polymer content to 3.4%, which is more comparable to the normal 3.0% SBS desired to meet PG 76-22. Second, this binder’s 2.2 Pascal seconds no longer exceeds the maximum 3.0 Pascal second maximum RV requirement at 135°C. This binder could be formulated to meet the economic and performance characteristics of a typical 3.0% SBS modified binder. The asphalt binder supplier is now able to use the available asphalt binder to produce neat and modified asphalt binders that not only meet the specification requirements, but also provide performance exceeding that observed from the non-PPA-modified binders.

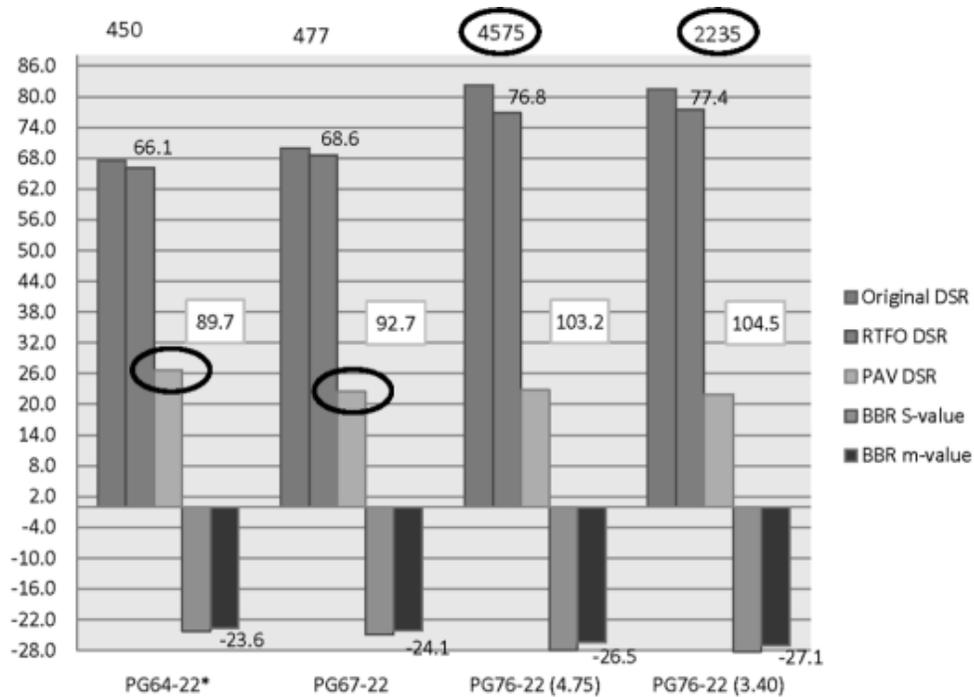


FIGURE 10 Improvement of PG asphalt binder properties with PPA modification.

CONCLUSION

It has been shown that the evolution of specifications has a major influence on asphalt binder supply and the steps necessary to produce binders that comply with specifications. An understanding of asphalt chemical composition and its relationship to binder performance reveals that performance of asphalt binder is directly related to the source of the crude from which the asphalt is derived. This is also the case for PPA modification as the results achieved are also directly related to asphalt binder chemical composition and the crude from which it is derived. PPA modification provides a widened asphalt service range, UTI, by improving both the high and low temperature performance characteristics. In addition, antioxidative characteristics of PPA provide improved aging of PPA modified binders.

PPA has been used to modify nonpolymer-modified asphalt in numerous locations from 1972 and in conjunction with polymers as early as 1997. It continues to be used in many locations at this time. While PPA has been used successfully for more than 30 years, somewhere around 2000–2002 the sky began to fall and PPA modification was believed to be the cause of every problem associated with asphalt binders, even those that did not contain PPA. It is important to understand that as asphalt binder supplies become more limited with respect to quality and quantity, PPA is a valuable tool to binder suppliers necessary to provide binders that meet current specifications and provide desired long-term performance.

The effect of PPA on asphalt binders and performance of PPA-modified asphalt binders in pavements with respect to pavement performance (permanent deformation, fatigue, low temperature cracking and long term aging) has been, and continues to be, extensively studied and documented (22–31). Use of PPA-modified binders is often debated, to the point that some agencies have banned the use of acid modified binders. Such actions result from a lack of understanding of the benefits of PPA as a tool to improve the performance of asphalt binders. Many are of the opinion that PPA is used solely to reduce the level of SBS modification in an attempt to “cheat” the PG specification; it fails to be that simple, and as presented, PPA serves more the purpose of providing a tool necessary to consistently comply with the requirements of Superpave than just reducing polymer levels.

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NOTE

This paper was also presented at the Association of Asphalt Paving Technologists Symposium on Polyphosphoric Acid Modification and is included in *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 79, 2010. AAPT gave permission to include it in this document.

Effect of Polyphosphoric Acid on Asphalt Binder Properties

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The use of modified asphalt binders has grown tremendously in the United States. This is due primarily to the increased stress on the highways from higher traffic volumes and heavier loads. Many different modifiers have been used to improve the binder properties to better meet specifications. These modifiers include both organic and inorganic material such as styrene butadiene (SB), styrene-butadiene-styrene (SBS), ethylene terpolymer, and polyphosphoric acid (PPA). Concerns have been raised by several highway agencies about the actual performance characteristics of the last polymer, PPA. These concerns include reversibility of the stiffening effect of PPA on asphalt binders and interactions with other additives in the mix such as hydrated lime.

This paper will evaluate the effect of PPA on several different binders from different crude sources. The evaluation also includes the use of PPA in combination with other modifiers such as SBS polymer and hydrated lime. Binder testing was done on the control neat binders and modified systems so that comparisons could be made between them.

TESTING PROCEDURES

SHRP developed a new specification for asphalt binders, which is now widely used in North America (1). This specification is designated as M320 by AASHTO (AASHTO M320) (2). The Superpave binder specification is based on the rheological properties of the asphalt binder measured over a wide range of temperatures and aging conditions. Various pieces of equipment are used to measure stress-strain relationships in the binder at the specified test temperatures. This equipment includes the dynamic shear rheometer (DSR), bending beam rheometer (BBR), and the direct tension tester. Measuring the binders' rheological properties over a wide range of temperatures, loading conditions, and aging conditions allows performance relationships to be established between the test results and the pavement.

The multistress creep and recovery (MSCR) test is currently being considered as a replacement for the Superpave high-temperature binder criteria $G^*/\sin\delta$. The MSCR test can distinguish between the rutting properties of both neat binders and polymer-modified binders. The MSCR test is a creep and recovery test that is conducted using a DSR and parallel plate geometry. The new test uses a 1-s creep loading with a 9-s recovery over the multiple stress levels 0.1 and 3.2 kPa at 10 cycles for each stress level. The test is started at the lower stress level and increased to the next stress level at the end of every 10 cycles with no time lags between cycles. The average nonrecovered strain for the 10 creep and recovery cycles is then divided by the applied stress for those cycles yielding the nonrecoverable compliance J_{nr} . The determination of the nonrecoverable compliance J_{nr} and the percent recovery are described in detail in the ASTM or AASHTO standards (2, 3). The determination of J_{nr} is shown in Figure 1. The MSCR test and related research have been previously described in detail elsewhere (4, 5).

$$J_{nr} = \text{avg. } \gamma_u / \tau$$

where

γ_u = unrecovered strain from the end of the 9-s recovery portion of the creep and recovery test
and

τ = shear stress applied during the 1-s creep portion of the creep and recovery test.

The MSCR test does a better job of identifying the rut resistance of both neat and polymer-modified binders, but some highway agencies still want to make sure polymer is in the binder for other purposes such as crack resistance and durability. Here the MSCR test provides great improvements over the existing tests like the elastic recovery and toughness and tenacity. Data from the exact same sample from the MSCR test that was used to do high-temperature grading provides information on the polymer modification as well. The one test provides the high-temperature grade and quality of polymer modification eliminating the need to run additional tests like elastic recovery on additional samples. The compliance value from the MSCR test, J_{nr} , provides the rut resistance, and the amount of recovered strain from the test identifies the presence of polymer and also the quality of the blending of the polymer in the binder as shown in [Figure 2](#).

Crude Source and PPA Effect

Commonly asked questions about PPA include how much PPA is required to change a binder one high-temperature performance grade (PG) and does PPA have the same effect on all asphalt binders. To evaluate this, 105% PPA was added to two very different binders from different crude sources. PPA at 0.5% by weight of binder was added to a PG 70-22 refined from Venezuelan crude and a PG 64-22 refined from Saudi crude. The high-temperature continuous grade for both the original and modified binders is shown in [Figure 3](#).

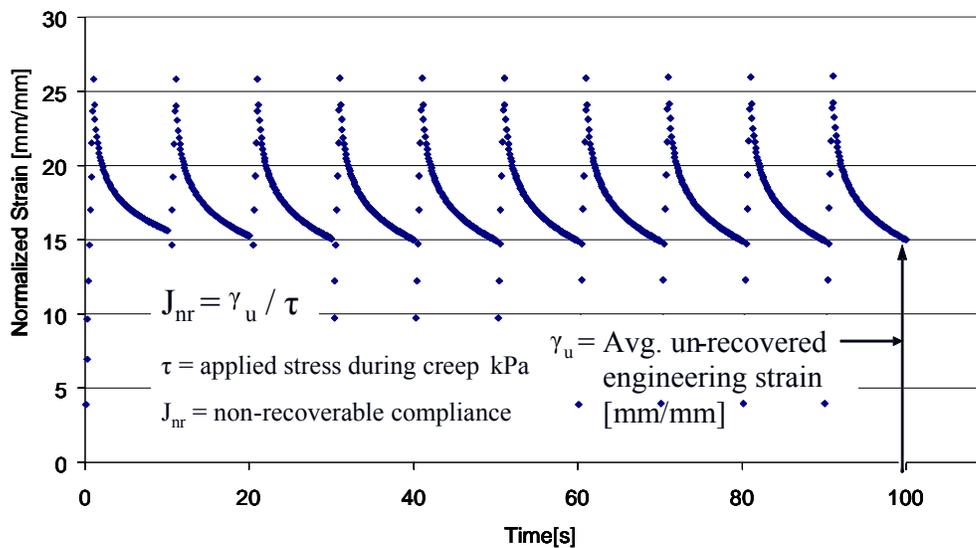


FIGURE 1 Plot showing determination of J_{nr} from the MSCR.

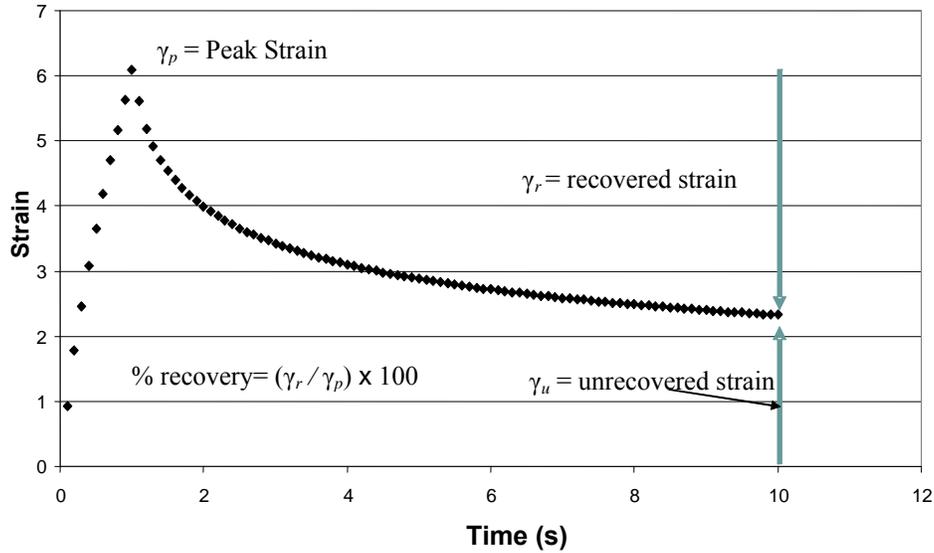


FIGURE 2 Plot showing determination percent recovered strain from the MSCR.

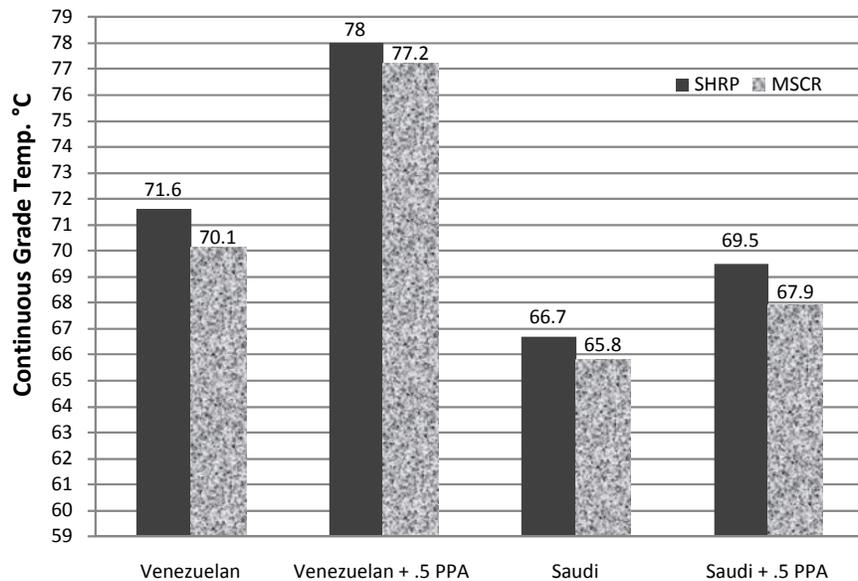


FIGURE 3 High-temperature continuous grades of binders from different crude sources and modified with 0.5% PPA.

The high-temperature binder properties were measured using two systems, the existing $G^*/\sin \delta$ and the MSCR J_{nr} . The addition of 0.5% PPA to the Venezuelan binder changed it one full high-temperature grade from 71.6°C to 78.0°C for $G^*/\sin \delta$ and from 70.1°C to 77.2°C for J_{nr} . The addition of 0.5% PPA to the Saudi binder only increased the high-temperature grade from 66.7°C to 69.5°C for $G^*/\sin \delta$ and 65.8°C to 67.9°C for J_{nr} . The 0.5% PPA only increased the high-temperature grade of the Saudi binder by less than 3°C for both the G^* and the MSCR grading.

Testing done by the FHWA's Turner-Fairbank Highway Research Center laboratory also indicated a large variation in the amount of stiffening that occurred with the addition of PPA to asphalt binders manufactured from different crude sources. The results of this testing are shown in Figure 4. A California Valley asphalt designated ABM-1 shows very little increase in stiffness with the addition of PPA even up to 3% by weight of binder. This is in sharp contrast to the Boscan asphalt AAK-1 which had a significant increase in stiffness with the addition of 3% PPA by weight of binder. Where binder ABM-1 only had an increase in its PG high-temperature grade of about 3°C with 3% PPA, the Boscan had a 47°C increase in its PG high-temperature grade. Both of these evaluations show how changes in the binder chemistry will vary the stiffening effect of PPA as a high-temperature binder modifier.

Interaction of PPA and Polymers

A PG 64-22, produced from a Saudi light crude oil by Lion Asphalt, was blended with one polymer content, but using different methods and slight variations in polymer type. The Lion asphalt is considered compatible asphalt in that the polymer mixes easily and will take significant time to separate from the base. The polymer used was a Kraton 1101 SBS linear polymer and a Kraton 1184 SBS radial polymer both added at 4% by weight to the base asphalt. The LC 4 formulation was created with the Kraton 1101 mixed directly with the Lion asphalt at 188°C using a high-speed Silverson mixer. The LC P4 was produced in the same manner except 0.5% PPA was also blended in. Mixing was continued for 2 h for each binder. The LOP 4 and LOP 4P binders were produced by diluting a concentrate of 15% Kraton 1184 polymer with the Lion asphalt to a final 4% by weight blend. In this case the concentrate was made by adding the

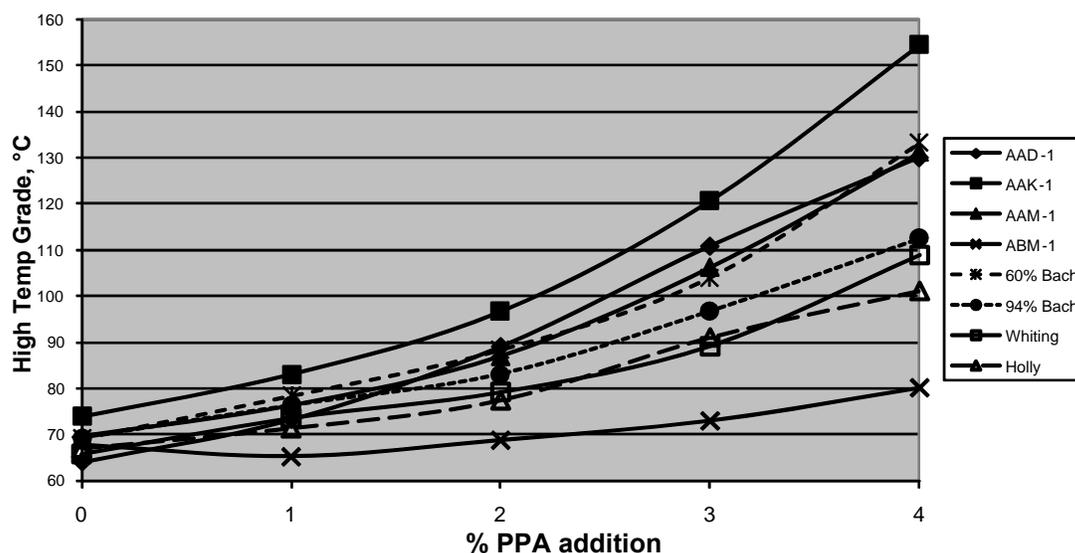


FIGURE 4 Change in the PG high-temperature continuous grade for various binders and PPA addition rates.

polymer into the Lion base at 200°C with a high-speed mixer. The LOP 4P had the additional 0.5% PPA added. [Table 1](#) provides the properties of the various blends.

Each one of the blends was produced from the same base asphalt and had 4% SBS polymer added, however, MSCR testing indicates that the binders are very different. The SHRP binder testing graded the LC 4 and the LOP 4 to have almost exactly the same high-temperature grade with only 0.9°C difference between their continuous grades. This was the same for the LC 4P and LOP 4P where the addition of PPA increased the high-temperature grade from 76°C to 81°C. The MSCR testing, however, graded the binders differently, indicating the differences associated with the blending, SBS type and PPA differences.

The MSCR J_{nr} value at 3.2 kPa indicates the LC 4 binder is the weakest. The LC 4P and LOP 4 binders are almost the same with the LOP 4P 37% less compliant than the other three. These results are very different than the SHRP binder grading where the LC 4 and the LOP 4 are equivalent and the LC 4P and the LOP 4P are equivalent. In addition to the differences identified by the J_{nr} results, very distinct differences of the polymer network in the binder can be seen by evaluating the percent recovery between the peak strain and the final unrecovered strain. These differences are shown clearly in [Figure 5](#).

The LC 4 and LC P4 binders, where the polymers was blended in at lower temperatures and with a less compatible polymer, have much lower percent recovery in the MSCR test than the LOP 4 and LOP 4P binders. The recovery for the LC 4 is only 19.2% but the addition of the 0.5% PPA to make the LC P4 increased it to 28.4% at 70°C. The improved processing with a more compatible polymer used to make the LOP 4 binder increased the recovery to 40.3%. The addition of the 0.5% PPA to produce the LOP 4P increased the percent recovery even higher to 52.1% indicating a superior polymer network in the binder. The elastic recovery (ER) testing using AASHTO T301 indicated the binders should have similar ranking to the SHRP binder testing. The ER test is used extensively to evaluate the presence of polymer in binders, but

TABLE 1 Data on Polymer-Modified Binders Indicating Differences Based on Blending Methods

Sample ID	Continuous Grade	Polymer	Acid	Temp °C	J_{nr} 3.2 kPa	% Recovery 3.2 kPa	Elastic Recovery
LC	66.7–24.1		0	64°C	3.1	0	5
LC 4	75.7–22.3	4% linear SBS	0	70°C	1.9	19.2	73.8
				76°C	4.6	6.0	
LC 4P	81.2–22.2	4% linear SBS	0.50%	70°C	1.1	28.4	93.8
				76°C	2.4	20.6	
LOP 4	76.6–25.2	4% radial SBS from concentrate	0	70°C	1.2	40.3	86
				76°C	2.4	37.0	
LOP 4P	81.6–24.5	4% radial SBS from concentrate	0.50%	70°C	0.7	52.1	91.6
				76°C	1.4	42.5	

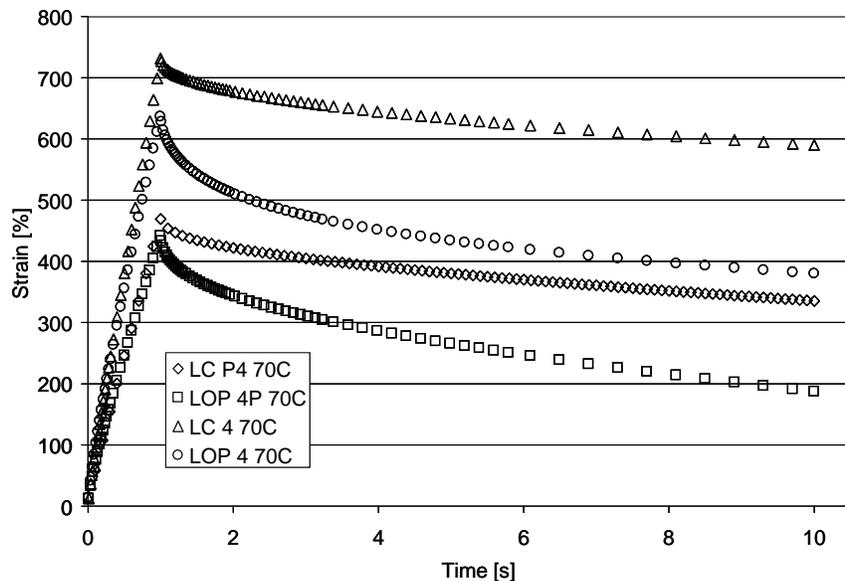


FIGURE 5 Plot of the creep and recovery cycle for 4% polymer blends of lion asphalt tested at 70°C.

does not seem to distinguish between polymer systems. The ER test ranks the LC 4 as the weakest binder with the LC 4P as the strongest.

The improved recovery results shown in the MSCR tests are attributed to the improved polymer network established in the binder by processing at higher temperatures and the addition of PPA. To verify that the MSCR percent recovery test results actually do reflect the extent of the polymer network in the binders, the morphology of the polymer network was evaluated. A Van Guard 1200 ECM microscope with an ultraviolet light source was used to create the fluorescence micrographs of the binders shown in Figure 6. A small sample of asphalt binder is placed on a glass plate and viewed through a microscope under ultraviolet light. The maltene fraction of the binder is absorbed into the SBS polymer and reflects the ultraviolet light indicating the polymer structure (6–8). The micrograph of LC 4 indicates that the polymer is simply floating in the asphalt. This is identified by the small glowing dots sometimes called the “night sky.” The LC 4P micrograph shows how the PPA has caused the polymer to start to cross-link as seen by the long polymer strands in the asphalt. The micrograph of the LOP 4 begins to show the complete networking of the polymer in the asphalt. The LOP 4 shows a continuous polymer network with some larger concentrations of polymer. The LOP 4P micrograph again shows a much more extensive polymer network with a leathery look, indicating extensive cross-linking and well-dispersed concentrations of polymer. This verifies results from the percent recovery measured in the MSCR test.

The AASHTO T301 elastic recovery test, the typical test used by many highway agencies to verify the presence of polymer in the asphalt binder, did not identify the nature of the polymer

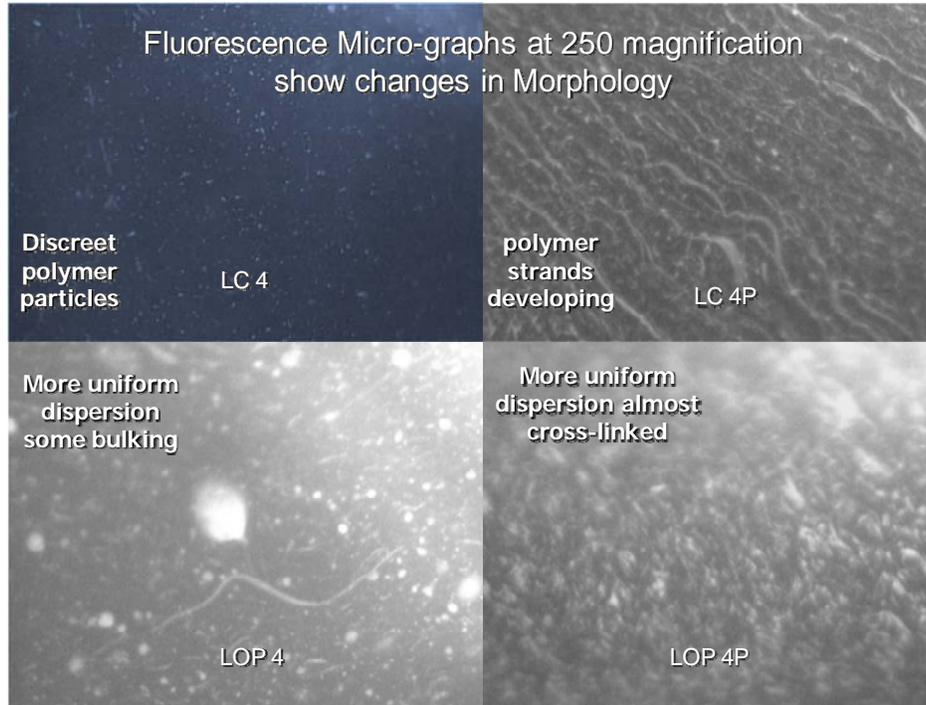


FIGURE 6 Fluorescence micrographs of the lion asphalt with different polymer process.

structure. The AASHTO test T 301 cannot identify the nature of the polymer network because the test is performed at 25°C a temperature where the base binder is significantly stiff enough to provide support for the polymer thus masking the nature and extent of the polymer network. All four binders had high ER test results well above typical highway agencies requirements. The ER test indicates the LC 4 and LOP 4 should be similar and the LC 4P and LOP 4P should be similar. The MSCR test percent recovery (percent recovery) at 76°C indicates the LC 4 and LC 4P are reacting like a neat asphalt where the polymer is only a filler which has stiffened the asphalt to a 76 grade. The percent recovery for the LC 4 and LC4P was only 6% and 20.6%, respectively, while the LOP4 and LOP 4P had 37% and 42.5% recovery at the higher temperature. These higher recoveries indicate the improved nature of the polymer network in the binder, which is not shown by the ER test.

The evaluation of the effect of PPA on polymer-modified binders was continued by looking at a PG 58-28 binder refined from Venezuelan crude. Several combinations of SBS polymer with elemental sulfur and PPA were evaluated. The original binder was modified with 3% by weight linear SBS polymer and used as the control. This was compared to the control with sulfur cross-linker, control with PPA, and the control with sulfur and PPA. The blends and test results are shown in [Table 2](#).

The PG 58-28 with 3% SBS would be classified as a PG 64-28V under AASHTO M320 Table 1. The addition of sulfur cross-linker had no effect on the properties of the control binder with 3% SBS. The addition of the 0.5% PPA to the control changed the grade from the 64-28V to a 64-28E. The addition of the PPA and sulfur had a major change on the binder stiffness. Were the sulfur alone had no effect on the binder properties, the sulfur and PPA worked together to significantly stiffen the binder and improve the J_{nr} from 0.75 to 0.06. This is shown graphically in [Figure 7](#).

TABLE 2 Venezuelan 58-28 Modification and Test Results

Original PG 58-28 Binder Modification					
Sample ID	SBS	sulfur	PPA	J_{nr} 3.2 kPa-1	MSCR % Rec
1	3%			0.75	31.4%
2	3%	0.06%		0.99	31.2%
3	3%		0.5%	0.17	61.2%
4	3%	0.06%	0.5%	0.06	84.6%

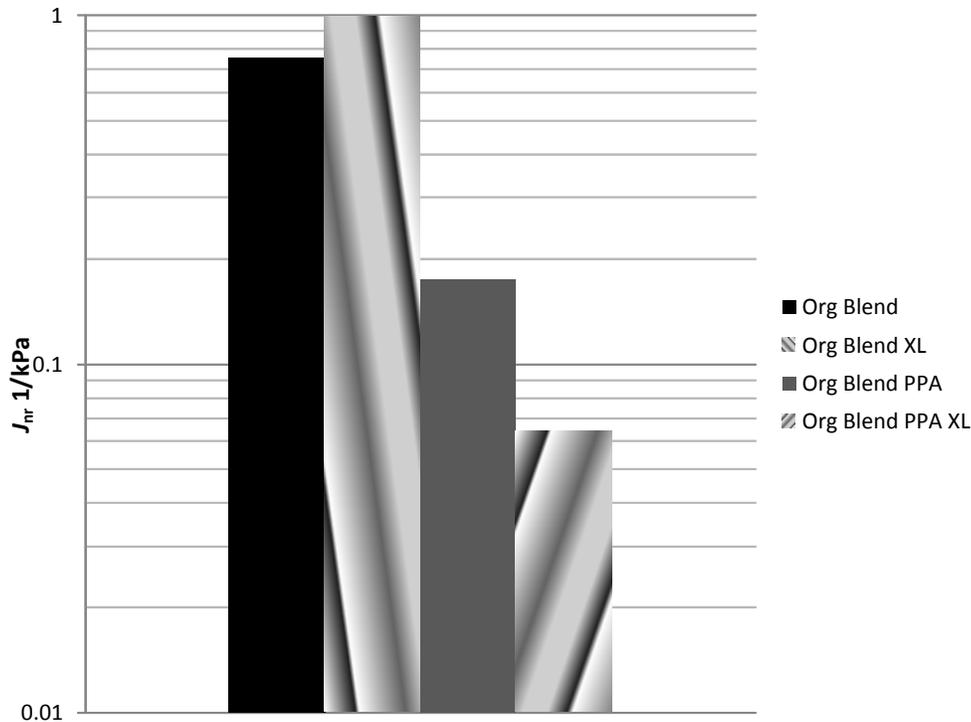


FIGURE 7 Change in MSCR J_{nr} @ 3.2 kPa⁻¹ value of polymer-modified binder with addition of PPA and sulfur cross-linker tested at 64°C.

The change in delayed elastic response of the binder with the addition of PPA modifier is seen by evaluating the percent recovery from the MSCR test. The binder with 3% SBS and 3% SBS with sulfur had almost the same percent recovery of 31%. This indicated that the original mixing process was not improved by the sulfur cross-linker. The addition of the PPA to the 3% SBS blend without sulfur improved the percent recovery to 61% indicating a significant improvement in the polymer network in the binder. The addition of the PPA and sulfur again improved the percent recovery of the binder to 84%. This would indicate that the SBS polymer in the binder is almost completely cross-linked. The improvement of the polymer network in the binder will improve the rut resistance and crack resistance of the binder. This is shown graphically in [Figure 8](#).

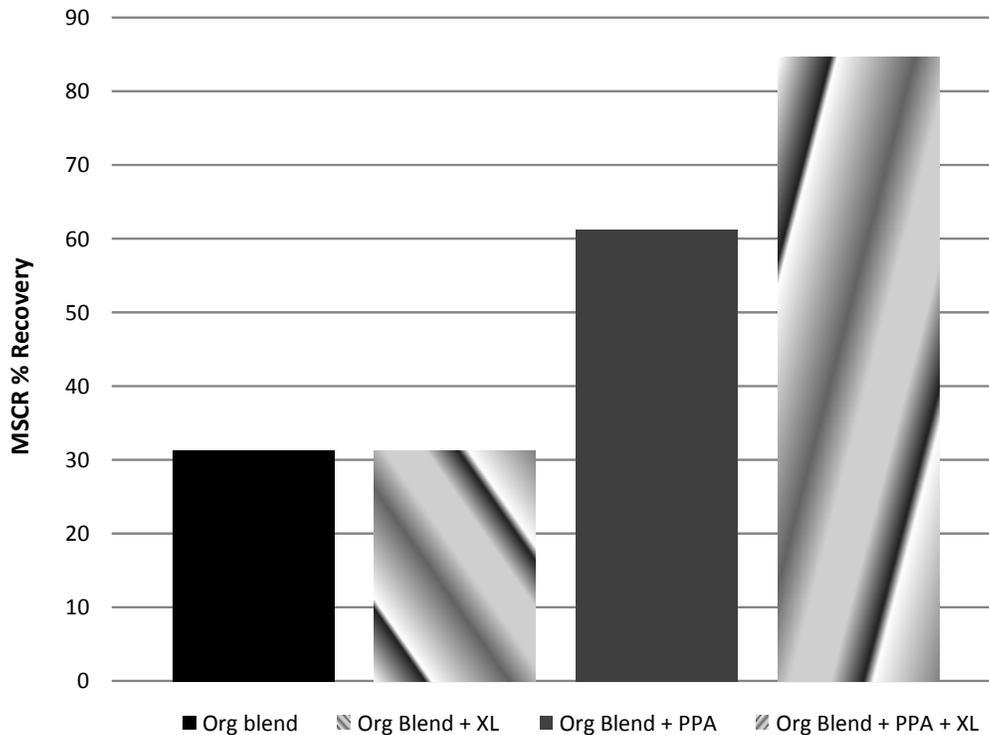


FIGURE 8 Change in MSCR percent recovery @ 3.2 kPa^{-1} of polymer-modified binder with addition of PPA and sulfur cross-linker tested at 64°C .

PPA and Hydrated Lime

Hydrated lime is extensively used as an antistripping additive in hot-mix asphalt. One concern with using PPA as an asphalt binder modifier is that lime would neutralize it and effectively soften the binder. To evaluate if lime would neutralize the PPA, binder testing was done with hydrated lime in the binder.

Hydrated lime is typically added at a rate of 1% by weight of mix. If it is assumed that the mix would have 5% binder content, the 1% lime by weight of mix would be equivalent to 20% lime by weight of binder. The lime has a specific gravity of approximately 2.3, which would equate to a volume of about 9%. With the solids volume less than 10% and the lime particle size less than $75 \mu\text{m}$, dynamic shear rheometer testing with a 1-mm gap for the plates would be valid.

The experiment consisted of testing two binders, a 58-28 and a 64-22 produced from the same crude source. Lion asphalt refined from a Saudi crude was used. The PG 58-28 was modified with 1.2% PPA to increase the grade to a PG 64-22. Then both the original PG 64-22 and the PPA modified 64-22 had 20% by weight lime added. All the samples were PG graded using AASHTO M320 Table 1 and Table 3. The binder continuous grade temperatures are shown in [Tables 3 and 4](#).

TABLE 3 AASHTO M320 Table 1, Continuous Grade Temperatures for the PPA–Hydrated Lime Evaluation

Sample Description	True Grade	Original DSR	RTFO DSR	PAV DSR	BBR S-Value	BBR M-Value
Lion Oil PG 58-28	PG 59.1-28.4	59.8	59.1	19.4	-28.8	-28.4
Lion Oil PG 58-28 Plus HL	PG 63.4-26.1	65.0	63.4	22.5	-26.1	-27.5
Lion Oil PG 64-22	PG 65.2-24.9	66.2	65.2	24.2	-24.9	-25.2
Lion Oil PG 64-22 Plus HL	PG 70.7-21.7	72.2	70.7	28.4	-21.7	-23.4
Lion Oil PG 58-28 Plus PPA	PG 64.1-29.2	64.4	64.1	19.1	-29.3	-29.6
Lion Oil PG 58-28 Plus PPA/HL	PG 67.6-24.9	67.6	66.7	23.3	-24.9	-26.3

TABLE 4 AASHTO M320 Table 3, Continuous Grade Temperatures for the PPA–Hydrated Lime Evaluation

Sample Description	True Grade	Original DSR	RTFO MSCR	PAV DSR	BBR S-Value	BBR M-Value
Lion Oil PG 58-28	PG 58.4-28.4S	59.8	58.4	19.4	-28.8	-28.4
Lion Oil PG 58-28 Plus HL	PG 62.8-26.1S	65.0	62.8	22.5	-26.1	-27.5
Lion Oil PG 64-22	PG 65.1-24.9S	66.2	65.1	24.2	-24.9	-25.2
Lion Oil PG 64-22 Plus HL	PG 69.5-21.7S	72.2	69.5	28.4	-21.7	-23.4
Lion Oil PG 58-28 Plus PPA	PG 63.3-29.2S	64.4	63.3	19.1	-29.3	-29.6
Lion Oil PG 58-28 Plus PPA/HL	PG 64.7-24.9S	67.6	64.7	23.3	-24.9	-26.3

The binder grading data for the neat binder, PPA and hydrated lime study was almost identical for both AASHTO Table 1 and Table 3. There were only very minor differences in the continuous grading temperatures of typically less than 1°C. In order to avoid repetition, only the MSCR AASHTO Table 3 data will be discussed, however, the AASHTO Table 1 data is shown graphically in [Figure 9](#).

The addition of the 1.2% PPA to the PG 58-28S binder increased the high-temperature grade 5°C to 63.3°C with only a 0.5°C loss on the low-temperature end of the grade. This was 80% of a full grade increase on the high-temperature side. The addition of 20% lime to the 58-28S increased the high-temperature grade 4.5°C to 62.8°C. However, the addition of the lime caused a loss of 3.8°C on the low-temperature end. The addition of the lime to the PG 64-22S had almost the identical effect as on the addition to the 58-28S. It would be assumed that if there was no interaction between the lime and the PPA that together their effects would be additive and the high-temperature grade would increase by up to 9°C. However, the increase in high-temperature grade with both PPA and lime in the binder was 6.3°C. This increase is greater

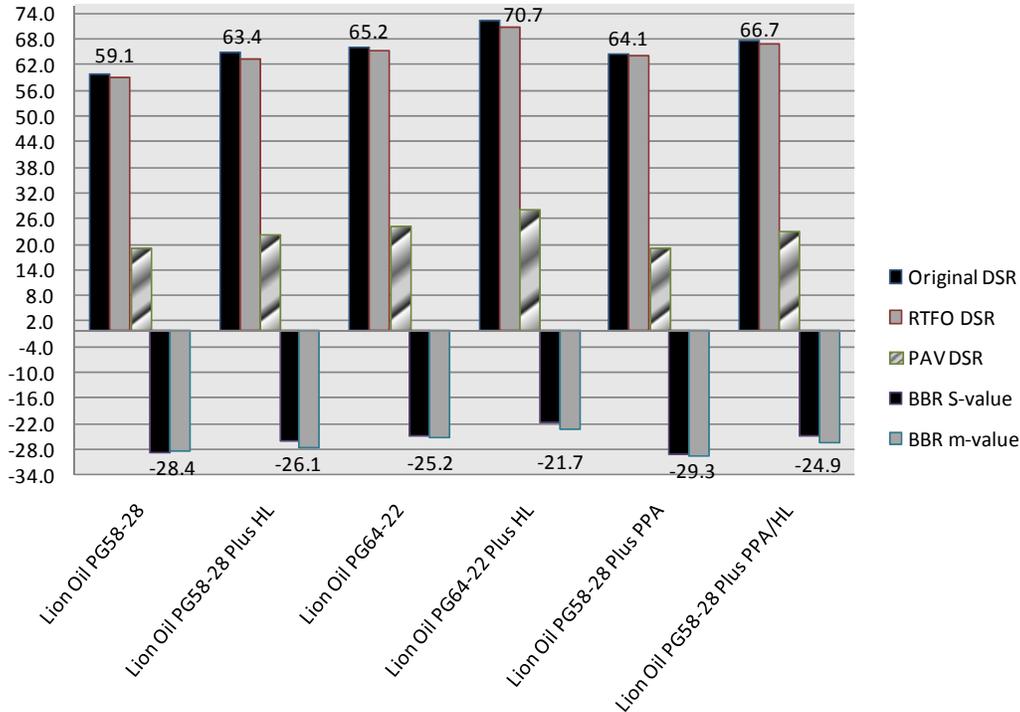


FIGURE 9 AASHTO M320 Table 1, binder properties of Lion asphalt with PPA and hydrated lime added in the binder.

than either PPA or lime by itself, but not directly additive. It would appear that there is some interaction between the lime and the PPA, however, lime could not neutralize the PPA but only reduce its stiffening effect slightly. The PPA-modified 58-28S would still easily meet a PG 64-22S grade. The lime still caused a loss in the low-temperature grade of almost 5°C. This data is shown graphically in [Figure 10](#).

CONCLUSIONS

PPA does stiffen asphalt binders. The stiffening effect is dependent on the crude source or chemical make-up of the binder. For a Boscan Venezuelan binder only 0.5% is needed to increase one full high-temperature grade. For the Saudi light crude source binder 1.2% PPA is needed for a grade increase and for the California Valley crude binder up to 3% PPA would be needed to increase by only half a grade.

The stiffening effect of PPA in combination with a polymer modifier such as SBS is more than just additive. For a Saudi crude binder that requires 1.2% PPA to increase the high temperature one full grade, only 0.5% PPA was needed to increase one full grade in combination with SBS. The effect on the delayed elastic response of the binder was even greater than just the stiffening effect. This was demonstrated by the significant increases in the percent recovery from the MSCR test. The data indicates that PPA in combination with SBS helps in the cross-linking improving the binder stiffness and delayed elastic response of the binder.

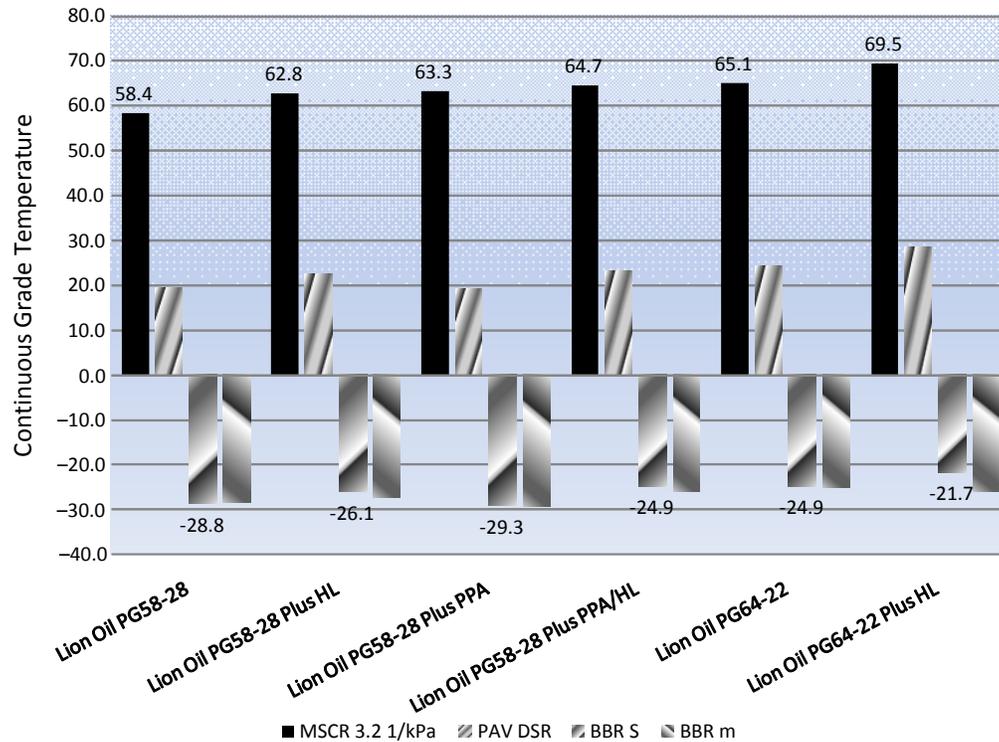


FIGURE 10 AASHTO M320 Table 1, binder properties of Lion asphalt with PPA and hydrated lime added in the binder.

In this study, hydrated lime, when added directly to the asphalt binder, did not neutralize the stiffening effect of the PPA. This was true even when chemically 20% by weight of lime could completely overwhelm the 1.2% PPA in the binder.

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NOTE

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Use of Phosphoric Acid as Modifier for Hot-Mix Asphalt

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The use of polyphosphoric acid (PPA) to stiffen paving asphalt has become quite ubiquitous. Recently, several premature paving failures have been attributed to its usage; however much of this has been based on incomplete information or speculation. Subsequently this has created uncertainty regarding hidden pitfalls surrounding its use. The primary concerns are the effect of different grades of phosphoric acid, the reactivity of asphalts from different sources and whether PPA accelerates aging, or increases the moisture sensitivity of binders.

This paper discusses research conducted to address many of these issues. Data are presented to show the effect of increasing levels of acid modification on moisture sensitivity. Both the absorption of moisture into the binder and mastic samples were examined.

Preconceived notions about the use of phosphoric acid with alkaline antistripping additives are also addressed. Use with antistripping additives is perfectly feasible if the proper screening tests are conducted before use.

BACKGROUND

Phosphoric acid has been used to stiffen paving asphalt for many years. Experienced industry practitioners have found that the addition of small amounts (ca 0.5%) of PPA to polymer-modified binders improved both their handling and performance. When used with styrene-butadiene-styrene polymers it enables suppliers to achieve higher Superpave PG while improving the mixing and compaction characteristics. With ethylene terpolymers, it catalyzes the reactivity of the glycidyl methacrylate groups. Both types of polymer-modified binders have shown the addition of PPA to increase rut resistance of the binder. More recently, the increasing popularity of PPA has led to its use as a partial replacement for polymer modification.

Exacerbated by several apocryphal reports on highway failures attributed to the use of phosphoric acid, the unknowns associated with its use have raised questions at many state agencies. The unknowns have led some agencies to ban phosphoric acid while others continue its use. Issues include the effect of acid grade, asphalt type, asphalt oxidation, [since it is used as a blowing catalyst in preparing asphalt for roofing applications (1)], increased moisture sensitivity and reaction with commonly used antistripping additives such as lime and amines.

BACKGROUND ON PPA

Several grades of phosphoric acid containing different amounts of orthophosphoric acid are commercially available. They contain 50% ("green acid"), 75%, 85%, and 100%

orthophosphoric acid. Two other grades superphosphoric and PPA contain 105% and 115% orthophosphoric acid and are mixtures of pyrophosphoric acid, triphosphoric, and higher acids. Green acid, the precursor of the purified grades, produced by treatment of ground phosphate rock with sulfuric acid, contains strongly acidic impurities, mainly sulfuric and hydrofluoric acids, which may be present at levels up to 2%.

EFFECT OF PPA GRADE ON ASPHALT STIFFNESS

To ensure consistency in comparing the different acid grades, the addition levels are normalized to 100% orthophosphoric acid. For example, 2% by weight of green acid (containing 50% orthophosphoric acid) yielded a phosphoric acid concentration of 1% in the asphalt.

The stiffening effect of different phosphoric acid grades was determined by modifying four SHRP reference asphalts and measuring the Superpave high-temperature stiffness ($G^*/\sin\delta$ at 64°C) using a dynamic shear rheometer (DSR).

The asphalt was heated to 165°C, stirred with a mechanical stirrer running at 450 rpm while adding the acid. Stirring continued for a further 20 min while the binder temperature was maintained at 165°C. Samples were immediately taken and the stiffness measured.

As shown in [Figures 1 through 4](#), all grades of purified phosphoric acid yielded similar increases in stiffness. Crude green acid gave the biggest increase in stiffness. This is attributed to the presence of strong acids (hydrofluoric and sulfuric acid). The corrosive nature of this acid and the likely variability of the crude product are liable to preclude its use in the asphalt industry. Since all the purified grades behaved similarly, all subsequent tests were carried out using 115% PPA. The water boiling off when 85% and weaker acids were added to hot asphalt caused some foaming problems on a laboratory scale. This could become a major issue in full-scale production.

To observe some indication of the rate of reaction of phosphoric acid with asphalt the samples were oven aged overnight at 165°C and the stiffness measured again. The results are shown in [Figure 5](#). There is a slight change following oven aging for 24 h; the bulk of the stiffening takes place almost immediately upon the addition of acid to the hot asphalt.

EFFECT OF ASPHALT FROM DIFFERENT SOURCES

The stiffening effect of phosphoric acid was found to be dependent on the particular asphalt being modified. Asphalt binders from eight different sources were tested: AAD-1, AAK-1, AAM-1, ABM-1, two asphalts from Venezuela provided by Citgo (a 60% Bachequero and a 94% Bachequero), an asphalt from BP Whiting Refinery and one from Holly Corporation. The measured high-temperature Superpave performance continuous grades in degrees centigrade plotted against the PPA addition level are shown in [Figure 6](#). Of these binders, AAK-1 (Boscan) exhibited the greatest reactivity to phosphoric acid, whereas ABM-1 (California Valley) was the least reactive and showed only a very slight increase in stiffness even at high dosage levels. Some of the acid addition levels evaluated are unrealistically high for practical use in paving applications. They are shown merely to demonstrate the stiffening trend.

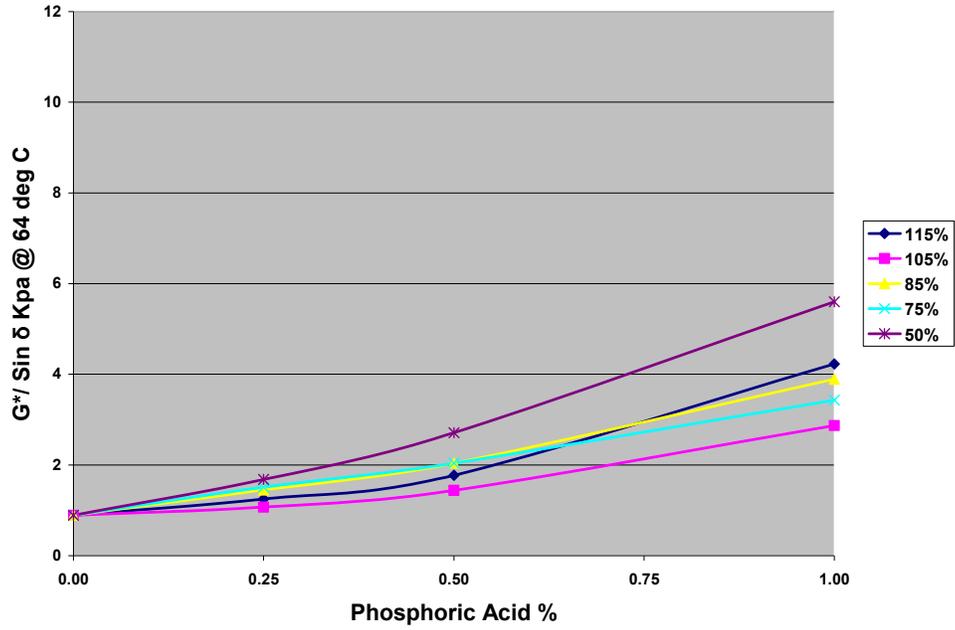


FIGURE 1 Stiffness of asphalt AAD-1 modified with different phosphoric acids.

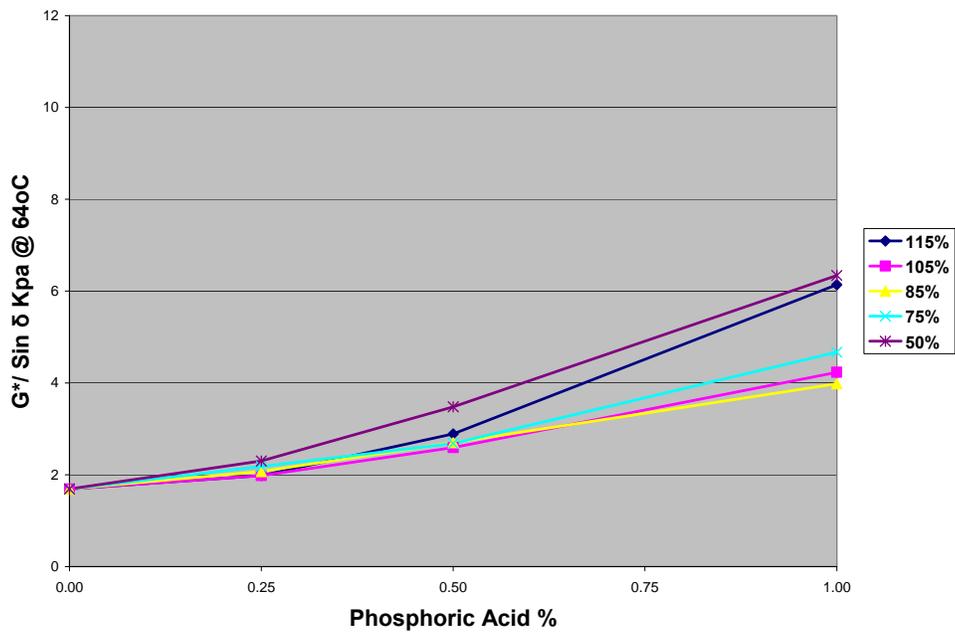


FIGURE 2 Stiffness of asphalt AAM-1 modified with different phosphoric acids.

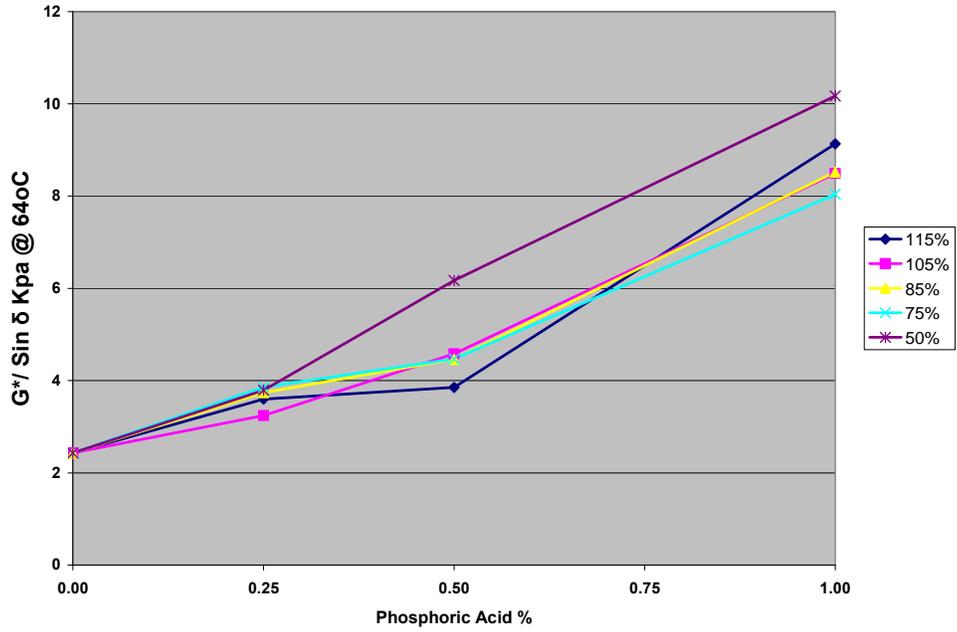


FIGURE 3 Stiffness of asphalt AAK-1 modified with different phosphoric acids.

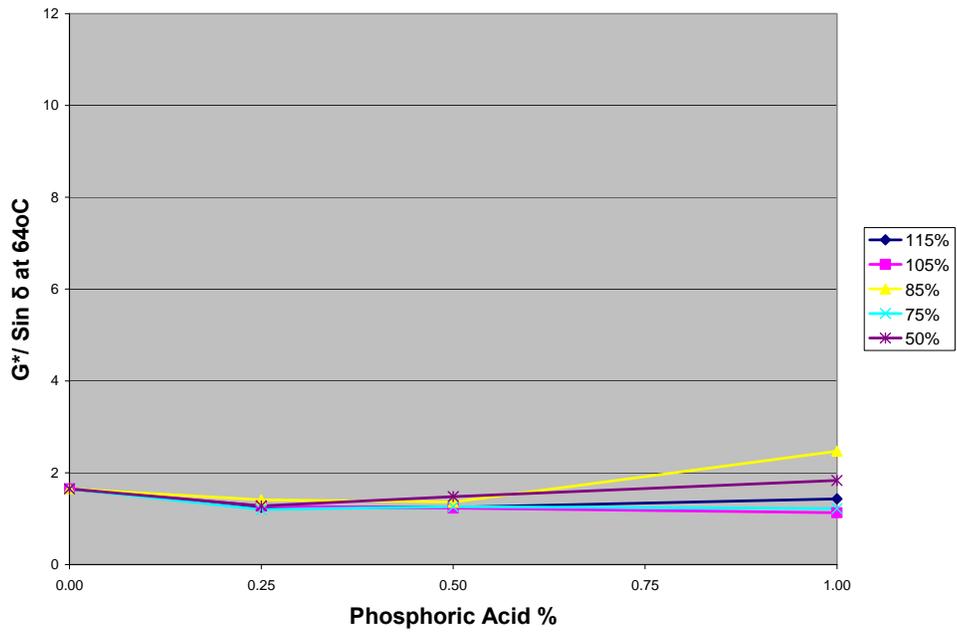


FIGURE 4 Stiffness of asphalt ABM-1 modified with different phosphoric acids.

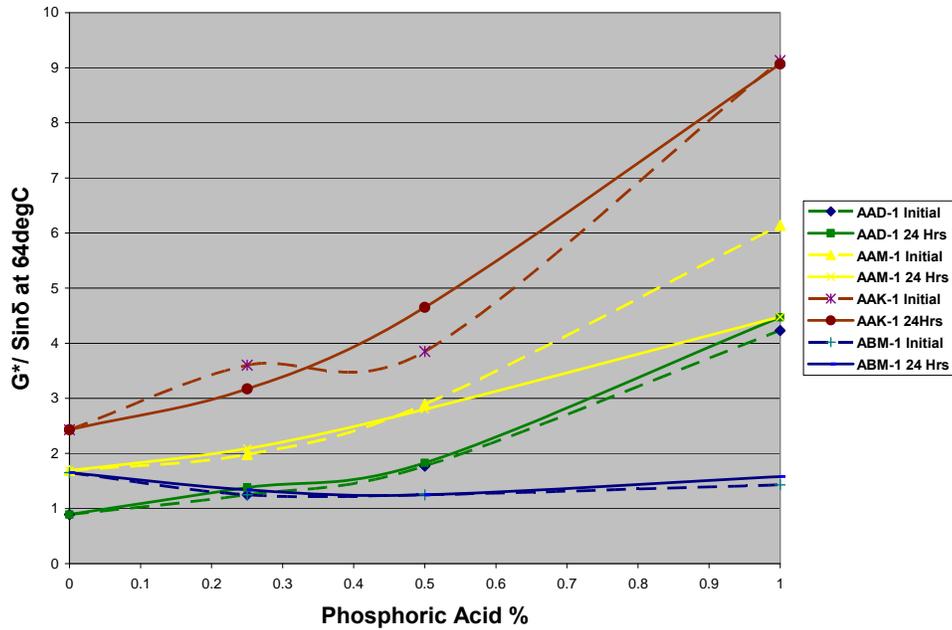


FIGURE 5 Relationship between modification levels and stiffness following 24-h aging at 165°C on the PPA-modified asphalt.

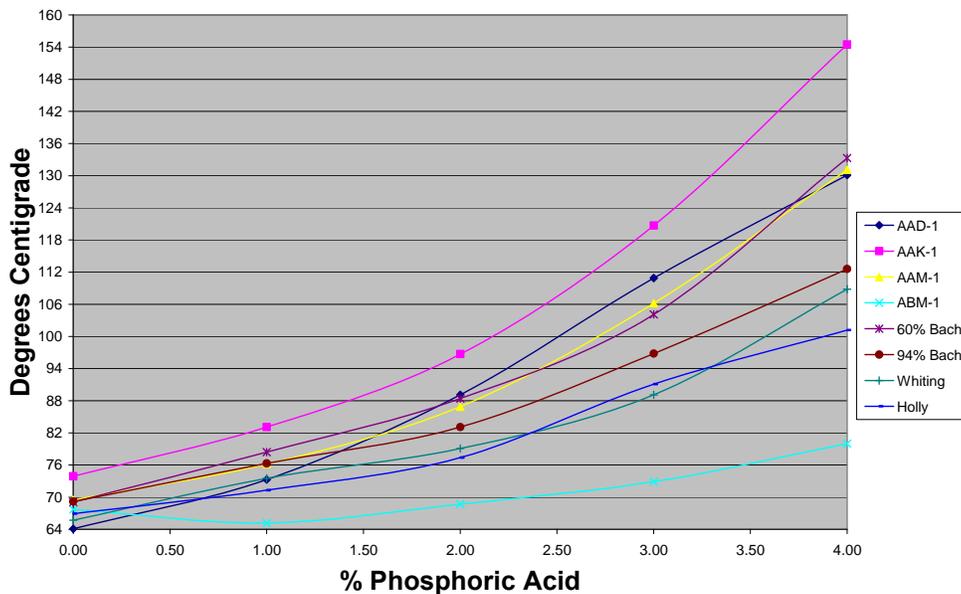


FIGURE 6 Superpave performance grading of asphalts modified with PPA.

For these eight binders, the amount of PPA required to increase the Superpave grading by one and two steps is shown in Table 1. All yielded a one-grade increase with 0.7% or less acid addition with the exception of ABM-1 (California Valley). This sol-type asphalt (2) is insensitive to modification with PPA.

TABLE 1 Amount of PPA Needed to Increase High-Temperature Grade One and Two Steps

	PG 70	PG 76	PG 82
AAK-1	0	0.25%	0.9%
60% Bachequero	0.1%	0.75%	—
94% Bachequero	0.1%	1.0%	—
AAM-1	0.1%	1.0%	—
Whiting	0.5%	1.5%	—
AAD-1	0.7%	1.2%	—
Holly	0.7%	1.8%	—
ABM-1	2.4%	3.4%	—

EFFECT OF PPA ON THE HEPTANE INSOLUBLE FRACTION

In order to understand the relationship between chemical composition of the binder and the stiffening effect, several phosphoric acid-modified asphalts were separated into four fractions (asphaltenes, resins, cyclics, and saturates). This employed a solvent separation technique in conjunction with the use of the Iatrosan (Iatron Laboratories, Inc.). Separation of the binders into asphaltene and maltene fractions was accomplished using ASTM method D3279: Standard Test for n-Heptane Insolubles. The maltene fractions were further separated using a method provided by Gaylon Baumgardner of Paragon Technical Services, Inc. (3). This latter technique involves deconvolution of the less polar fractions on thin silica coated quartz rods. After injecting microgram quantities of the maltene solution on the rods, development is carried out with n-pentane followed by a second development using a mixture of 90% toluene and 10% chloroform. Detection of organic fractions on the rods was by flame ionization.

In each case, the level of the n-heptane insoluble asphaltenes increased with increasing acid concentration. This was accompanied by a corresponding decrease in the resins. ABM-1 (California Valley) showed the same increase in asphaltenes although this was not accompanied by a corresponding increase in stiffness. The results for asphalts AAD-1 and ABM-1 are shown in [Figures 7 and 8](#).

EFFECT OF PPA MODIFICATION ON MOISTURE SENSITIVITY

Phosphoric acid is a strongly hydrophilic material. Its use as an asphalt modifier raises the issue of there being an increased sensitivity to moisture as well as potential environmental consequences resulting from the leaching of phosphoric acid from the highway into the groundwater. These hypotheses were tested in two ways. One was to determine the absorption of moisture by binder and mastic samples and the second method was to measure the leaching of phosphoric acid from asphalt concrete specimens immersed in water.

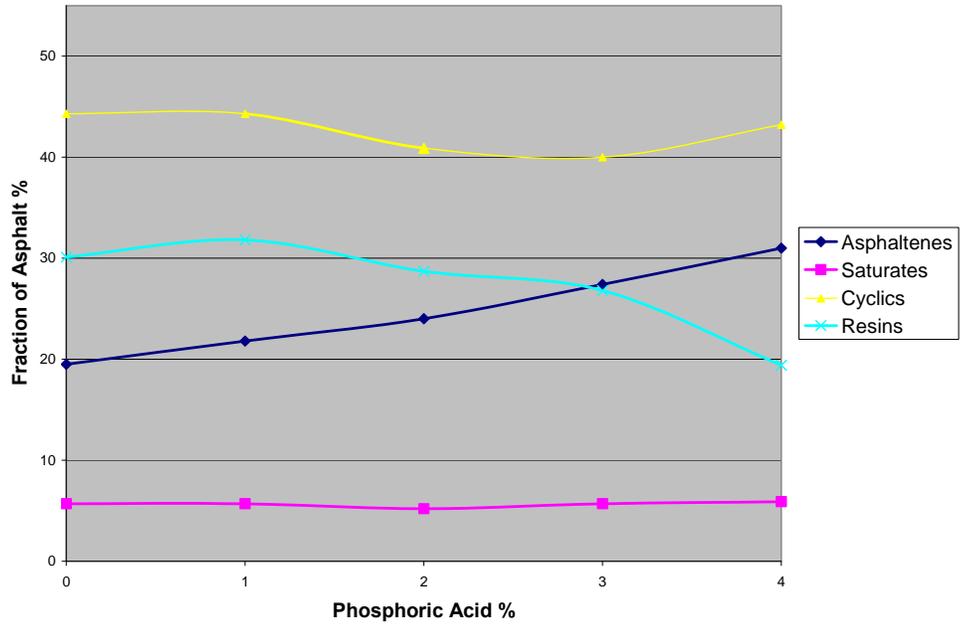


FIGURE 7 Effect of 115% PPA modification on the AAD-1 solvent fractions.

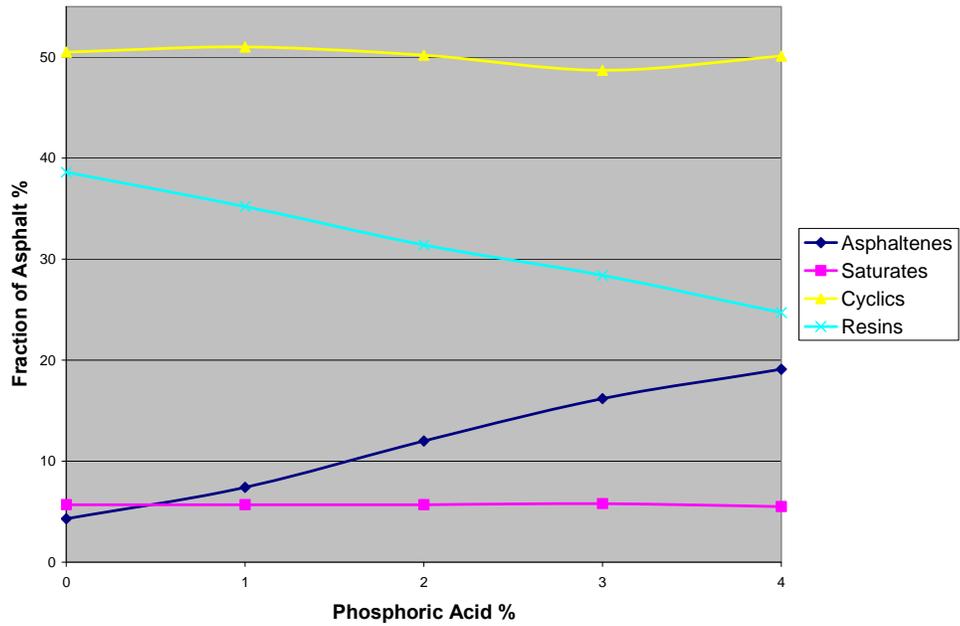


FIGURE 8 Effect of 115% PPA modification on the ABM-1 solvent fractions.

Effect of Moisture on Binders and Mastics

Samples of neat binders and mastics containing 50% by weight of aggregate fines were cast into both direct tension dog bones and bending beam rheometer (BBR) silicone rubber molds. The samples were weighed and then immersed in a water bath held at 45°F. The samples were reweighed at intervals over the next 245 days and the amount of water absorbed determined. All tests were done in duplicate. As shown in Figure 9, all the binders tested, except those modified with more than 1.5% PPA, exhibited an initial slight loss of weight. The most likely cause is the extraction of salts originating from the crude oil. This appears to be borne out by analyses of the soak water from the gyratory specimens that showed the presence of sodium and calcium ions. At PPA modification levels of 0.5%, the water absorption is similar to that of the control that had no PPA. With 1.0% PPA there is evidence of water absorption (increase in weight) and this continues with increasing levels of phosphoric acid.

Some of the soaked samples were dried and their stiffness measured using the DSR. At PPA levels of 1% or less, there was no change in stiffness. At higher levels of modification, loss in stiffness becomes apparent as shown in Figure 10.

The soaking tests were also carried out on 50% mastics using dog bone-shaped specimens. Mastics were made using sand, diabase, gravel, and montmorillonite. The former three mastics showed very similar results. The diabase behavior shown in Figure 11 exemplifies this. At levels of approximately 0.5% to 1.0% the absorption was similar to the unmodified control. At higher modification levels, the water absorption increased in all cases except for mastics made with montmorillonite. The combination of this water absorbing expansive clay and phosphoric acid was expected to result in a very water sensitive mastic. In fact, the opposite was observed. The sample of the unmodified montmorillonite mastic swelled significantly whereas the acid modified samples did not swell at all. The unmodified control absorbed 105% moisture whereas the PPA modified samples only 3% to 4%. These results for the mastics made using montmorillonite and BP Whiting asphalt are shown in Figure 12.

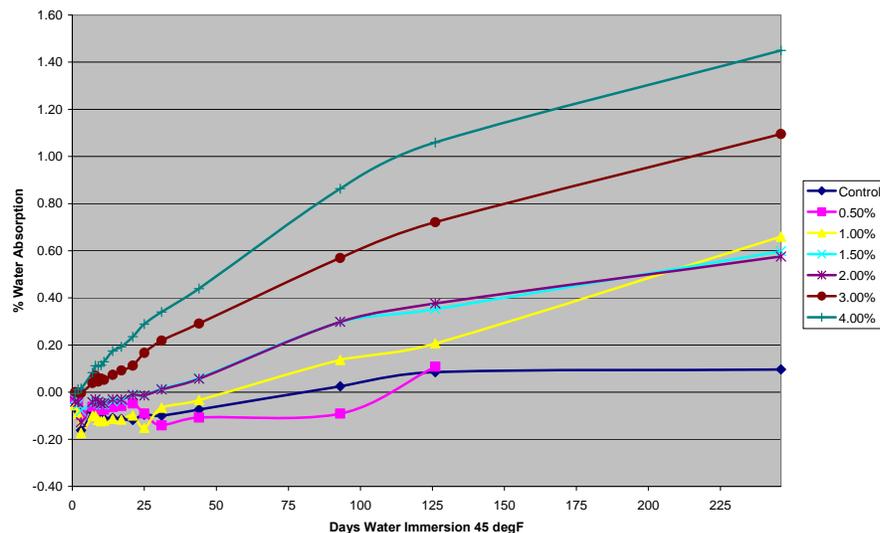


FIGURE 9 Water absorption of Citgo asphalt BBR beams modified with 115% PPA.

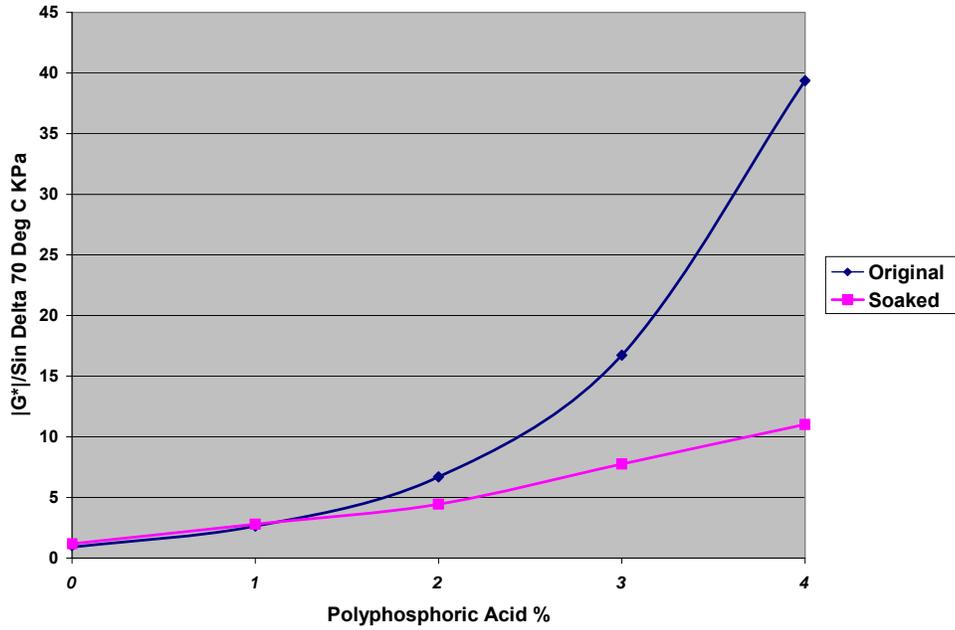


FIGURE 10 Loss of stiffness of PPA-modified Citgo asphalt after 245 days water immersion.

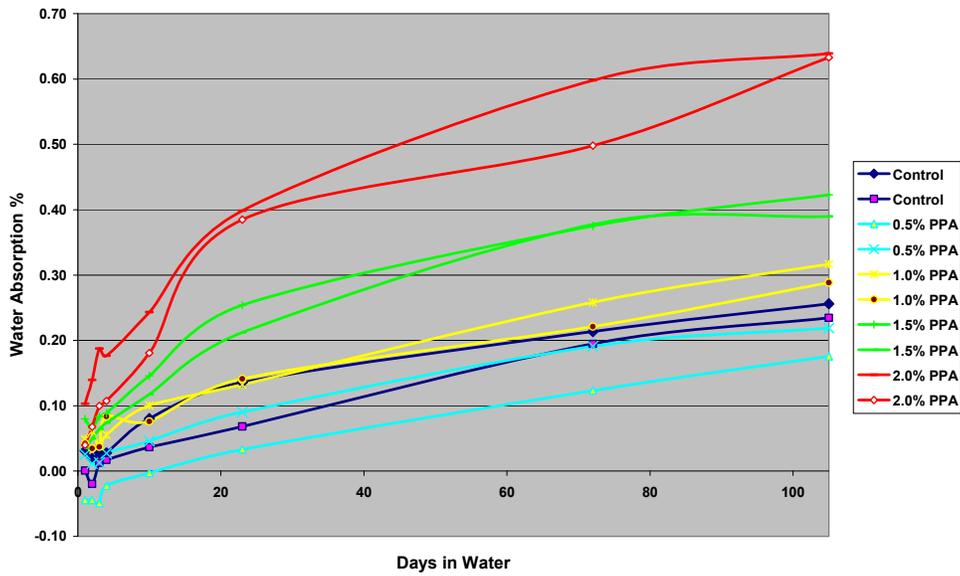


FIGURE 11 Water absorption of 50% diabase-modified Boscan asphalt mastics.

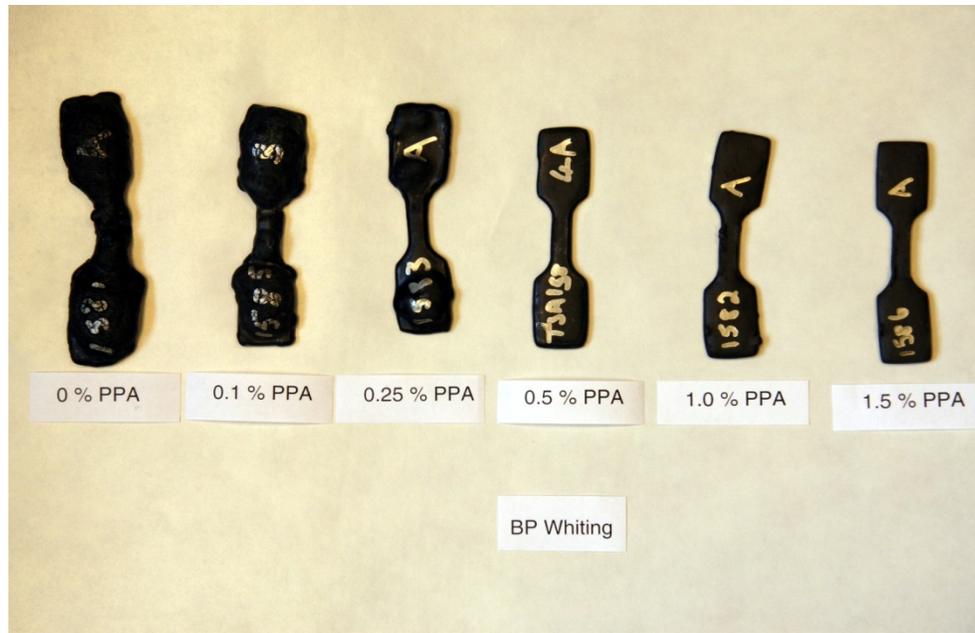


FIGURE 12 Water absorption of 50% Montmorillonite mastics, BP Whiting Asphalt.

USE OF PPA-MODIFIED BINDERS WITH ANTISTRIP ADDITIVES

A common misconception exists that phosphoric acid-modified asphalt cannot be used with lime-treated aggregates or amine antistrip additives since they are alkaline and would react with the phosphoric acid, whereas a neutral antistrip like Innovalt-W (2-ethylhexylphosphate) could be used. This theory was tested on gyratory specimens using the Hamburg rut tester. Duplicate tests were run on specimens soaked at 50°C and the rut depth measured; the criterion for pass-fail was 20-mm rut depth in less than 20,000 cycles. Three aggregates were used: limestone, granite from Georgia, and a sandstone aggregate from Maryland known to be a stripping aggregate. All tests were conducted with a PG 64-28 binder supplied by Citgo.

Lime is normally added to mixes at a rate of 1% of the aggregate whereas the PPA is added at 0.5% to 1% of the binder. Stoichiometric calculation shows that if the binder contains 1% of PPA, then it is overwhelmed chemically 25:1 by the lime.

To prepare the lime treated samples, lime as a 50% water slurry was added to the aggregate. The liquid antistrip additives were added to the binder at 0.5% by weight of the binder. The results are given in Table 2. All the lime treated aggregates exceeded 20,000 cycles and were unaffected by PPA modification.

The tests with liquid antistrip additives showed very mixed results. These are also presented in Table 2. Here the Hamburg results indicate an aggregate and antistrip additive dependence. This clearly demonstrates the need for thorough testing before using a particular asphalt–aggregate–antistrip combination. Generally the acid modification made the stripping worse, but not in every case. The nonamine antistrip worked with some aggregates and not others.

TABLE 2 Hamburg Testing of Lime and Liquid Antistrip Additives for Citgo PPA-Modified Asphalt

PPA %	Aggregate	Antistrip	Cycles to Failure	Is PPA Better or Worse?
0	Granite	Innovalt-W	>20,000	
1	Granite	Innovalt-W	>20,000	Same
0	Sandstone	Innovalt-W	>20,000	
1	Sandstone	Innovalt-W	12,600	Worse
0	Limestone	Innovalt-W	13,000	
1	Limestone	Innovalt-W	14,700	Better
0	Granite	Lime	>20,000	
1	Granite	Lime	>20,000	Same
0	Sandstone	Lime	>20,000	
1	Sandstone	Lime	>20,000	Same
0	Limestone	Lime	>20,000	
1	Limestone	Lime	>20,000	Same
0	Granite	LOF 65-00	>20,000	
1	Granite	LOF 65-00	>20,000	Same
0	Sandstone	LOF 65-00	19,000	
1	Sandstone	LOF 65-00	>20,000	Better
0	Limestone	LOF 65-00	14,200	
1	Limestone	LOF 65-00	9,300	Worse
0	Granite	LA-2	>20,000	
1	Granite	LA-2	>20,000	Same
0	Sandstone	LA-2	15,500	
1	Sandstone	LA-2	11,700	Worse
0	Limestone	LA-2	13,700	
1	Limestone	LA-2	8,100	Worse

CONCLUSIONS

All of the commercially available grades of phosphoric acid can be used to increase the high-temperature Superpave PG of asphalt binders.

The stiffening effect of phosphoric acid is very dependent upon the binder being modified. Most binders reacted well to the addition of phosphoric acid. One binder, California Valley, showed little stiffness increase with acid modification and was not very responsive. Generally, a one-step increase in the Superpave PG was obtained with less than 0.7% acid.

Acid modification of the asphalts resulted in an increase in the asphaltene (n-heptane insoluble material) and a corresponding decrease in the resin fraction. The asphaltene increase was not necessarily accompanied by an increase in stiffness.

The sensitivity of binders to moisture uptake was affected by acid modification. This is probably not an issue at acid addition levels of 0.7% or less. At higher levels, the sensitivity both to moisture absorbed into binders and mastics and acid leaching from gyratory cores and loose mixes increased with increasing levels of acid modification. The high moisture sensitivity of a montmorillonite mastic was almost completely mitigated by phosphoric acid modification. The samples of neat binders with acid modification levels above 1% lost stiffness after soaking in

water for an extended period. There was a loss of stiffness after extended soaking for acid levels above 1%.

Based on the Hamburg results, cores of PPA-modified asphalt containing lime-treated aggregates did not exhibit any potential for moisture damage. Liquid antistrip performance, both amine and nonamine, was aggregate and asphalt dependent and clearly demonstrates the need for thorough testing.

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Analytical Procedures for Determining Phosphorus Content in Asphalt Binders and Impact of Aggregate on Quantitative Recovery of Phosphorus from Asphalt Binders

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Polyphosphoric acid (PPA) has been increasingly used as a means of producing modified binders for the past 10 to 15 years in North America. While there have been reports of isolated use of phosphoric acid and PPA prior to the advent of Superpave Performance Grade (PG) binders, the increased demand for high-performance binders resulting from the adoption of PG binders stimulated more widespread research into the means by which PPA could effectively and economically enable binder suppliers to meet these demands. Consequently, asphalt suppliers in all regions of the United States and Canada turned to PPA to meet the new specifications. It was found that PPA, when used at levels as low as 0.5% by weight of binder, could increase the high-temperature PG grade of some binders by one full grade. Most binders required approximately 0.8% to 1.2% PPA by weight of binder and some required considerably more, sometimes more than 2%. Still other asphalt suppliers found that the addition of low levels, typically less than 0.5% by weight, of PPA to polymer-modified binders enabled them to reduce polymer loading without negatively impacting mixture performance and in some reported cases enhancing mixture performance. The growing realization by user agencies that they were or might be receiving binders containing PPA led to several reactions. Some agencies banned the use of the material, although there was no standardized procedure for measuring the acid content in binder. Other agencies wanted to be able to determine the amount, if any, of acid present in their binders. Still others who had used PPA-modified binders for several years with no obvious ill effects paid the entire issue little heed. FHWA implemented a wide-ranging multi-year investigation into the impact of PPA levels, ranging from 0.2% to 4%, on the physical and moisture sensitivity properties of binders as well as the performance characteristics of mixtures produced using those acid containing binders. At MTE Services, Inc., a decision was made to develop a rapid, reliable technique for determining the amount of phosphorus in asphalt binders. This task was undertaken to fill an obvious need in the industry. In some areas PPA was being blamed for project failures with no analytical evidence or supplier acknowledgment that the acid had been used in the binder. Any projects that did use acid and exhibited problems would certainly be worthwhile evaluating to determine the amount of acid used in the binder and the extent to which that acid content caused the problems. Further motivation came in 2008 when world crude prices spiraled out of control and the supply of butadiene needed to produce SBS polymers decreased precipitously. Under these circumstances some agencies came to the realization that a modest amount of PPA could help to stretch the SBS supply. With a reliable tool for determining the amount of phosphorus in the binder it would be possible to establish limits on the amount of PPA that would be acceptable to the agency. Still more recently some researchers have suggested that pavement problems attributed to PPA may actually be due to the use of the bottoms from the re-refining of engine oils, so-called REOB or reclaimed engine oil bottoms. Lube oils contain fairly high quantities of zinc dithiophosphate and the phosphorus that

shows up in some asphalt binders may actually come from REOB and not PPA. It is against this complex background of factors that the work reported herein has been conducted.

INTRODUCTION

Asphalt does not naturally contain phosphorus. It is not possible to measure the amount of phosphoric acid or PPA present in an asphalt material; it is only possible to determine the amount of phosphorus present in the asphalt binder. If the assumption is made that all of the phosphorus came from PPA, then it is possible to calculate the theoretical amount of PPA used to produce the binder if an assumption as to the concentration of PPA used to produce the binder is known or assumed (1). It is a peculiarity of the production of PPA that concentrations of greater than 100% can be obtained (1). In the past 5 years at least two companies have offered phosphate ester antistripping additives to the industry. While phosphate esters have been used almost exclusively by suppliers of PPA-modified binders they still represent another source of phosphorus that is not derived from PPA. If not all or if none of the phosphorus in a binder is derived from PPA then seriously incorrect conclusions can be drawn as to the amount of PPA present in the binder. Recently Soleimani et al. (2) reported research in which they asserted that pavement performance problems ascribed to PPA, based on measurements of phosphorus in the binder, might actually be caused by the addition of REOB, based upon zinc as well as phosphorus measurements. Because lubricating oils contain both zinc and phosphorus it is possible to determine if the additive in an asphalt binder contained lube oil or PPA. However, given the complexity of this problem it would be difficult to ascertain whether a given binder was modified with only lube oil bottoms or only PPA. With some effort it would be possible to establish criteria for typical levels of zinc relative to phosphorus for lube oil bottoms-treated binders only. However, with many different techniques for re-refining waste engine oil and with different levels of zinc dithiophosphate used in different types of oils there will be no precise value for the ratio of zinc to phosphorus in these products.

DESCRIPTION OF TEST PROCEDURE

There are several approaches to quantitatively determine the amount of phosphorus in an oil matrix. Among these are graphite furnace atomic absorption spectroscopy (Furnace AA), inductively coupled plasma spectroscopy (ICP) (3), energy dispersive x-ray fluorescence spectroscopy (EDXRF) (4), and wavelength dispersive x-ray fluorescence spectrometry (XRF) (5). There are also wet chemistry methodologies available, but these appear to be mainly used in nonoil matrices. One of the drawbacks of ICP and AA is that sample preparation is required to reduce the oil to a low enough viscosity so that it can be sprayed through a nebulizer into a flame. The x-ray fluorescence approach requires no sample preparation and the phosphorus can be directly determined in the matrix as received. Although there are standardized XRF methods available for determining the amount of phosphorus in oil matrices (4, 5), there are no standardized XRF methods available for making the determination in an asphalt matrix. In reality there are no standardized methods for determining phosphorus with other instrumentation methods and if AA or ICP is used, existing methods are used as the starting point for preparing samples to run in those instruments.

Adding to the difficulty of testing an asphalt sample for phosphorus is the fact that the asphalt sample must be liquefied through heating and stirring before it can be poured into the sample cup. The sample cup consists of two open polyethylene cylinders, slightly different in diameter, such that a thin film of polypropylene can be secured to form the bottom of the smaller diameter cylinder. The prepared sample cup is placed on a flat heat sink, such as a metal counter top or metal plate, and then the asphalt sample is poured directly onto the surface of the polypropylene film and allowed to cool on a flat surface so that a flat layer of asphalt is formed (Figures 1a and b and 2). Pouring of the sample requires some practice and technique. If the asphalt sample is too hot it will melt or warp the polypropylene film; if it is too cool it will not flow evenly and air bubbles will be trapped between the asphalt sample and the film. These air bubbles will confound the results. Because the XRF test procedure only penetrates a few molecules into the sample, it is essential that the film be as thin as possible and test specimen be flat and uniform.



FIGURE 1 (a) Two cup halves and film and (b) assembling cup halves to form test cup.



FIGURE 2 Assembled cup with sample poured, top and bottom view.

In addition to the potential difficulties with pouring the sample, sulfur present in the asphalt is a confounder in determining the phosphorus concentration. The confounding issue of sulfur is shown in Figure 3. Electrons of specific energies are produced when x-rays impinge on the target element in the spectrometer. In the case of the Panalytical Epsilon 5 used at MTE, the x-rays are produced using a gadolinium (Gd) anode. When x-rays impact a specific element they kick electrons out of the electron shells of those elements, and when electrons drop back to the ground state to replace those ejected by the x-rays, energy is given off which is measured. It is this emitted energy that is the characteristic fluorescence of each specific element. Every element has specific energy values required for electrons to be ejected from their inner shells. The higher the concentration of the element from which the electrons are ejected, the greater will be the level of fluorescence. One of the difficulties of determining phosphorus in asphalt is that phosphorus and sulfur require very similar energy values to eject electrons from their inner most shell. Those electrons are referred to as the $K\alpha$ (pronounced K alpha) electrons. Figure 3 shows that the $K\alpha$ energy for phosphorus is 2.0 keV (thousand electron volts) and the $K\alpha$ energy for sulfur is 2.3 keV. Furthermore, as Figure 3 shows, even though there is a peak or optimum energy for causing electron fluorescence for these elements, there is a range on either side of the peak energy that will also produce fluorescence. It is this overlap in fluorescing energies that causes the relatively high concentration of sulfur in most asphalt materials to confound or interfere with an accurate determination of the amount of phosphorus in the sample.

Analytical software provided with current equipment will aid in the deconvolution of the interfering signals from two overlapping elements' fluorescing energies, but to accomplish this the standards covering the conceivable range of concentrations of both elements that are expected to exist in asphalt binders of interest need to be used. Consequently, while running the test for phosphorus is quite easy, the upfront work to prepare and test the standards is quite involved. Table 1 shows the range of concentrations that were prepared and tested at MTE. The

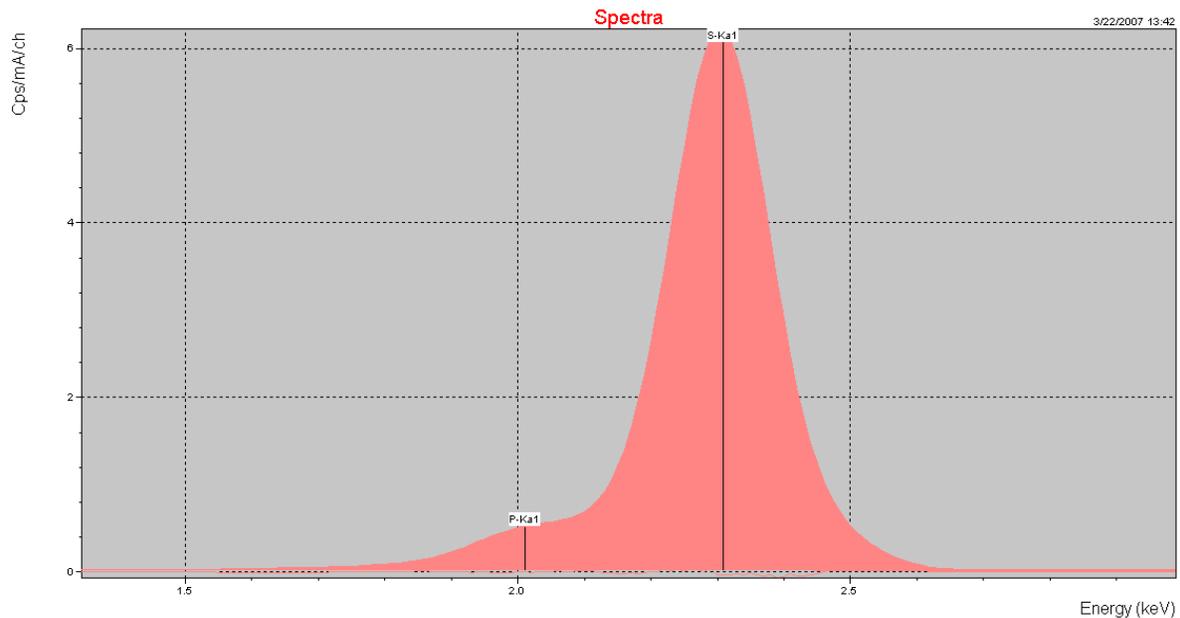


FIGURE 3 X-ray spectra showing $K\alpha$ absorption for phosphorus and sulfur.

Sulfur standards were prepared by blending high and low sulfur binders. Varying levels of PPA were gravimetrically added to these base blends to produce the standards shown. The calibration curve generated by these standards in an asphalt matrix is shown in Figure 4. Also shown in Figure 4 is a phosphorus calibration curve for an oil matrix. These two calibration curves emphasize the importance of using the appropriate sample matrix when generating the calibration curve. If the amount of phosphorus in a re-refined lube oil bottom sample is being measured, the correct result cannot be obtained by using the calibration data from an asphalt matrix. Table 1 does not show all of the standards prepared, but it does show all of the standards that were used to generate the calibration curve.

TABLE 1 Standards for Phosphorus and Sulfur

Standard ID	% Phosphorus	% Sulfur	Standard ID	% Phosphorus	% Sulfur
0	0.000	4.15	23	0.134	3.434
1	0.544	4.15	25	0.170	3.369
3	0.284	4.15	26	0.353	3.369
4	0.247	4.15	27	0.0588	3.369
5	0.116	4.15	29	0.434	4.360
6	0.0457	4.15	30	0.0603	4.360
17	0.0966	1.81	31	0.156	4.360
18	0.266	1.81	34	0.9052	3.72
19	0.219	1.81			

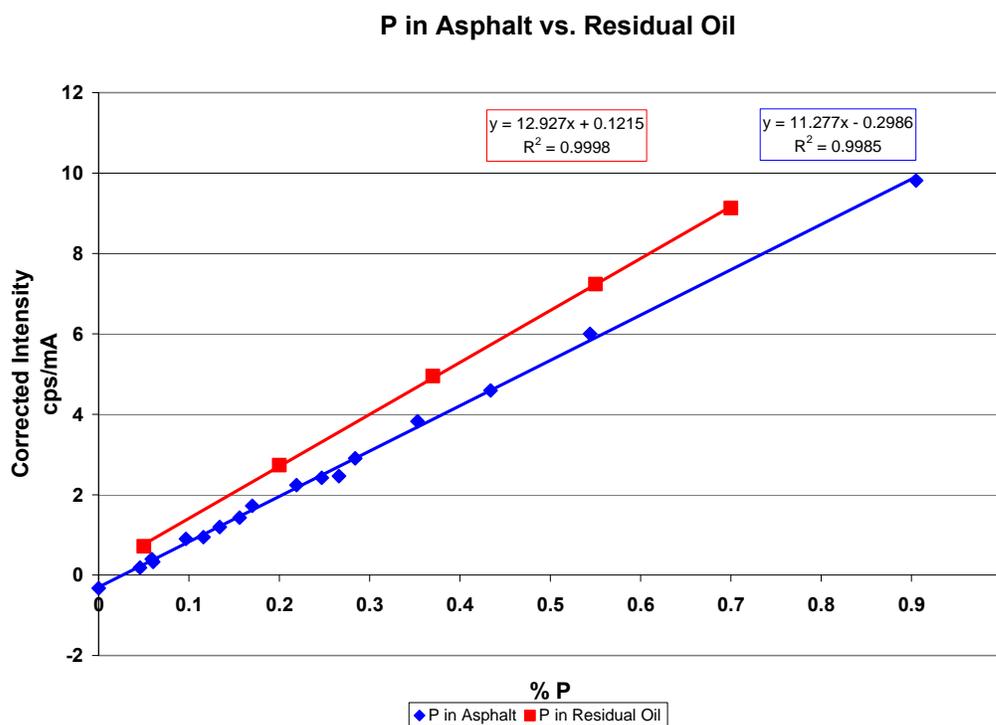


FIGURE 4 Calibration curve for determining amount of phosphorus in sample.

Confirmatory Tests Conducted on Binder Specimens

To evaluate the usefulness of the developed test method and calibration data, a commercially produced tank sample containing sufficient PPA to have a resultant phosphorus concentration of 0.109% P was tested in quadruplicate. The results are shown in [Table 2](#).

BINDER APPLICATIONS

There are several areas in the asphalt supply and paving industry where there is an interest in knowing whether or not phosphorus is present. These include but are not limited to identifying the possibility that PPA was used to modify the asphalt, identifying the possibility that reclaimed lube oil bottoms were used to modify the asphalt, testing to assure compliance with permitted levels of PPA allowed in some states, and forensic analysis of recovered binders from problem pavements. Testing the original binder for the presence of phosphorous is a straight forward procedure as discussed above. The calculation of the theoretical amount of PPA is simply a matter of dividing the measured phosphorous concentration by 0.364 to obtain the theoretical amount of 115% PPA used in the binder. If you divide the phosphorous concentration by 0.33 the theoretical amount of 105% PPA used in the binder is obtained. Given the current propensity of asphalt suppliers to use re-refined lube oil bottoms to modify their binders, it is also a good idea to test the binder for the presence of zinc, especially if the calculated amount of PPA is greater than 1.2%. Not many binders require more than 1.2% PPA to change one full PG and a high theoretical level of PPA could be evidence that re-refined lube oil bottoms are the source of the phosphorus or it is possible that both PPA and re-refined lube oil bottoms have been used in the binder. If you are going to determine the zinc content of a binder you will need to prepare or purchase quantitatively prepared standards containing organo zinc compounds in an oil matrix.

Confirmatory Tests for Binders

MTE was contacted by the Port Authority of New York and New Jersey (PANYNJ) to test and identify the presence of phosphorus and estimate the amount of PPA in a series of samples. The sample set is listed in [Table 3](#).

TABLE 2 Repeatability Test Results

Run Number	% P
1	0.113
2	0.106
3	0.119
4	0.117
Average	0.114
Std dev	0.0057

TABLE 3 Phosphorous and PPA Results Obtained on Samples from Port Authority of New York and New Jersey Laboratory

Sample #	PG Grade of Submitted Sample	wt % Phosphorus Measured	Weight % of 105% PPA in Binder Reported	Weight % Sulfur	Weight % of 105% PPA Added by PANYNJ
A	64-22	0.012	no PPA	4.39	0
B	64-22	0.294	0.886	4.29	0.944
C	76-22 +SBS	0.116	0.350	4.11	0
D	76-22 +SBS	0.333	1.004	4.21	0.645
E	76-22 +SBS	0.015	no PPA	4.18	0
F	76-22 +SBS	0.105	0.317	4.05	0.371
G	70-22	0.016	no PPA	4.51	0
H	70-22	0.235	0.708	4.30	0.739

Technicians at the PANYNJ spiked several binder samples with 105% PPA and also submitted untreated samples. The samples were provided in coded forms. Only after the phosphorus testing had been completed and estimates of PPA levels reported to the Port Authority was information on PG and weight percent of PPA that the technicians at the Port Authority had added to the binder samples reported to MTE; samples C and D are of particular interest with respect to this report. The Port Authority reported that no PPA had been added to sample C and yet an amount of phosphorous equivalent to 0.35% PPA was identified. Furthermore sample D was prepared by adding PPA to sample C. According to the Port Authority technicians 0.645% PPA was added to sample C. Adding 0.645% PPA to the 0.350% PPA that was found in sample C, the total amount of PPA in sample D is determined to be 0.995% PPA as compared to the 1.004% PPA that was reported. In this instance the XRF procedure identified that the original PG 76-22 made with SBS also contained a moderate amount of PPA. Furthermore the Port Authority technicians reported that the PPA used to spike the binder samples was partially crystallized and that some of the crystals adhered to the spatula during the sample preparation procedure. Given this consideration, which would result in lower measured values compared to theoretical, the results in [Table 2](#) are quite accurate.

In another comparative investigation six samples were prepared and tested by the Illinois Department of Transportation (DOT) chemical laboratory in Springfield. Those samples were submitted to MTE coded as samples 1 through 6. MTE determined the phosphorus content and then calculated the amount of 105% PPA required to provide the measured level of phosphorus. The comparative results are shown in [Table 4](#). These results compare quite favorably with the exception of sample 4 and in that case while the percent difference is quite high at 60%, the actual reported values are quite low for both laboratories. In the range of typical usage within the industry (0.2% to approximately 1.5% PPA) the variability between laboratories and equipment type is very good.

TABLE 4 Comparative Testing of Samples: Illinois DOT Laboratory

Sample ID #	Percentage of 105% PPA	
	EDXRF (MTE)	WDXRF (IL DOT)
Sample # 1	0.14	0.14
Sample # 2	0.19	0.17
Sample # 3	0.50	0.45
Sample # 4	0.16	0.10
Sample # 5	1.02	0.94
Sample # 6	1.06	0.97

NOTE: Illinois used a wave dispersive XRF (WDXRF) spectrometer for their analysis. The spectrometer used a fixed channel for phosphorus detection comprised of a monochromator and detector specifically calibrated for phosphorus.

FORENSIC INVESTIGATION OF MIXTURES

Another area of interest for the determination of phosphorus in binders is the measurement of phosphorus in binders recovered from bituminous mixtures. In some instances projects have been placed which exhibit pavement performance problems and there is speculation that these problems are related to the use of PPA in the binder. In other instances there is a desire on the part of agencies to know whether or not PPA is being used in mixes placed in their state. MTE has performed extensive investigation into the extraction of PPA-modified binders from mixtures. There are three factors that can confound accurate removal of PPA-modified binders:

1. Some extraction solvents may contain additives that neutralize acid.
2. Complete removal of phosphate from aggregate has proven to be impossible.
3. Silicon ions removed during extraction can interfere with quantification of phosphorus.

Each of these factors have implications for correctly identifying the amount, if any, of PPA added to the binder as well as whether or not neutralization of the acid modification of the binder occurred in the bituminous mixture on the road.

Neutralization of Acid by Extraction Solvent

Industrial grades of extraction solvents such as trichloroethylene and n-propyl bromide contain acid scavengers to stabilize the solvents. These typically used extraction solvents will over time form hydrochloric acid (HCl) or hydrobromic acid (HBr) unless a chemical is added to the solvent to scavenge the acid. Without the acid scavenger the acid concentration can increase in the solvent to the extent that there can be corrosion in vacuum and centrifugal extraction equipment. The acid concentration, if high enough, will also cause hardening of the asphalt during Abson recovery. The acid scavenger used is typically 1,2 epoxybutane, the molecular structure of which is shown below in [Figure 5](#).

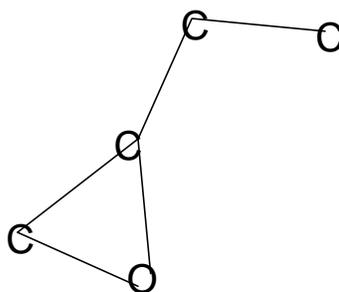


FIGURE 5 Molecular structure of 1,2 epoxybutane.

In 1,2 epoxybutane the oxygen bridges the two carbons on the butane molecule thus forming the epoxy ring. When acid in the form of HBr or HCl reacts with the oxygen in the epoxy ring the ring opens and the acidic hydrogen ion (H^+) reacts with the oxygen ion. The acidic hydrogen is effectively removed from the solvent thus eliminating its ability to cause corrosion to extraction equipment and artificially stiffen the binder. Unfortunately the 1,2 epoxybutane molecules do not differentiate as to the source of the H^+ ions with which they react. If there is acid present in the binder in the form of PPA the 1,2 epoxybutane should also react with and neutralize those acidic ions, which would result in a reduction in the stiffness of the extracted binder. The use of lab-grade n-propyl bromide or trichloroethylene or the use of toluene will eliminate these proposed neutralization issues.

The first indication of a severe problem recovering PPA-modified asphalt from bituminous mixtures occurred when working on recovering binders from cores from a 2007 New York paving project on which a PPA-modified PG 64-28 had been used. According to the supplier of the PG 64-28, who was also the source of the cores for testing, approximately 0.8% of a 115% PPA had been added to a PG 58-28 to produce the PG 64-28. Two cores labeled B and C were extracted using a reclaimed sample of n-propyl bromide and a virgin sample of n-propyl bromide respectively. The recovered binders from those two samples were tested at 64°C for stiffness as determined by $G^*/\sin(\delta)$. The results were 0.977 kPa for core B and 0.455 for core C. These data indicated that the reduction in binder stiffness due to the use of limestone aggregate in the mixtures might have been a problem. However, further investigation led to the identification of the presence of 1,2 epoxybutane as a scavenger in the solvent. To investigate the situation, PG 64-28 produced with PPA was mixed with three different solvents and the binder recovered using a rotary evaporator according to ASTM D5404. To 1 L of solvent 170 g of binder was added and then recovered. The data is shown in [Table 5](#).

The reclaimed n-propyl bromide is obtained by distilling the asphalt and solvent recovered from the extraction of bituminous mixtures. The reclaimed n-propyl bromide may have been through one or more distillation cycles and each time the solvent is used more of the acid scavenger is depleted. The data in Table 5 show that the acid scavenger in the virgin n-propyl bromide has reduced the binder stiffness by approximately 50% whereas the reclaimed n-propyl bromide has reduced the binder stiffness by 27%. The binder recovered from the toluene, which contains no acid scavenger, had an 11% reduction in stiffness. This reduction may be testing variability or the result of a small amount of solvent left due to the higher boiling point of toluene compared to that of n-propyl bromide. It is clear from Table 5 that a solvent, which

TABLE 5 Results of Recovery of PPA-Modified Binder from Different Solvents

Binder Source	Binder type	$G^*/\sin(\delta)$ @ 64°C of binder, kPa	$G^*/\sin(\delta)$ @ 64°C of recovered binder, kPa	Comments, solvent type
Lab sample	PG 64-28 (0.75% PPA)	1.76	1.28	Reclaimed n-propyl bromide
Lab sample	PG 64-28 (0.75% PPA)	1.67	0.825	Virgin n-propyl bromide
Lab sample	PG 64-28 (0.75% PPA)	1.67	1.49	Toluene

does not contain acid scavenger, is needed to obtain recovered binders that are not neutralized by the extraction and recovery procedure. Subsequent extraction and recovery of additional cores from the problematic New York project resulted in the data shown in Table 6. Extractions were performed using centrifugal extraction and recoveries performed using a rotary evaporator with modified ASTM D5404.

The data shown in Table 6 provides strong indication that when PPA-modified binders are recovered using solvent which does not have the ability to scavenge acid that there is no loss in PG grade of the binder even when limestone aggregates are used. The data for core 15°C, while still a PG 64, is lower in stiffness than should be expected for a mix that has been through a hot mix plant and that has been in service for several months. However all of the group 15 cores were taken transversely across the pavement lane at the same location and the single result for 15°C appears to be an erroneous result compared to all of the other samples recovered using toluene.

TABLE 6 Recovered Binder Properties from New York Cores

Source	Binder type	$G^*/\sin(\delta)$ @ 64°C, kPa	Solvent
New York 2007 mix, Core 12B	PG 64-28 produced using 0.8% PPA	0.977	Reclaimed n-propyl bromide
New York 2007 mix, Core 12C	PG 64-28 produced using 0.8% PPA	0.455	Virgin n-propyl bromide
New York 2007 mix, Core 12A	PG 64-28 produced using 0.8% PPA	1.93	Toluene
New York 2007 mix, Core 3C	PG 64-28 produced using 0.8% PPA	2.66	Toluene
New York 2007 mix, Core 15C	PG 64-28 produced using 0.8% PPA	1.15	Toluene
New York 2007 mix, Core 15B	PG 64-28 produced using 0.8% PPA	2.32	Toluene
New York 2007 mix, Core 15A	PG 64-28 produced using 0.8% PPA	1.96	Toluene

NOTE: Cores taken in October 2007 from mix placed in summer 2007.

QUANTIFICATION OF RECOVERY OF PHOSPHORUS FROM BITUMINOUS MIXTURES

In other forensic work there is sometimes a desire to identify whether PPA was used in the binder used to produce bituminous mixtures that may be exhibiting performance problems. The research work performed to investigate the quantitative recovery of phosphorus from bituminous mixtures has not been encouraging. An experimental design used three distinct types of aggregate combined with a PG 64-28 binder produced with 0.746% of 115% PPA blended with a PG 58-28. The three aggregates were a granite, a siliceous gravel, and a limestone. The mixes were prepared using 100 g of aggregate passing the 4.76-mm sieve, blended with 6% of the PG 64-28 by weight. The mixes were then cured in a covered container overnight in a 100°C oven. The binders were extracted from the mix using a Soxhlet extractor and recovery was performed using a rotary evaporation procedure following ASTM D5404. The recovered binder was then tested for phosphorus using the XRF procedure discussed in this paper. The binder sample prepared with a measured amount of 0.746% of 115% PPA theoretically contained 0.271% phosphorus. When the binder sample was tested for phosphorus content using the XRF procedure 0.269% phosphorus was determined. Table 7 shows a summary of the results obtained for recovered phosphorus from each of the mixtures. For each aggregate and extraction solvent combination the measured amount of recovered phosphorus is shown and in parenthesis the percent of actual phosphorus recovered is shown.

The data in Table 7 demonstrates that regardless of the aggregate type the quantitative recovery of phosphorus from bituminous mixtures with solvents typically used for such recovery testing is not feasible. In this investigation n-propyl bromide was used because the investigative effort was to recover phosphorus without concern for acid neutralization. The n-propyl bromide was no more successful in recovering phosphorus than was the more polar toluene/ethanol blend or the THF. In the case of the THF extraction, the original binder stiffness was determined as was the stiffness of the recovered binders from the granite and the limestone mixes. The increased DSR stiffness for both the granite and the limestone mixes reflects the mixing and curing time of the mix, but also serves to make the point that the binder stiffness is due to the

TABLE 7 Percent Phosphorus in Binders Recovered from Different Types of Aggregate

Solvent Used to Extract	Granite Aggregate	Siliceous Gravel Aggregate	Limestone Aggregate
Phosphorus content in binder	0.269% P (100%)	0.269% P (100%)	0.269% P (100%)
n-propyl bromide #1 test	0.103% P (38.3% recovered)	0.211% P (78.4% recovered)	0.149% P (55.4% recovered)
n-propyl bromide #2 test	0.073% P (27.1% recovered)	0.160% P (59.5% recovered)	0.177% P (65.8% recovered)
85% toluene and 15% ethanol	0.029% P (10.8% recovered)	0.151% P (56.1% recovered)	0.017% P (6.3% recovered)
THF DSR stiffness of original binder = 1.32 kPa @ 64°C	0.122% P (45.3% recovered) DSR stiffness of recovered binder = 1.88 kPa @ 64°C		0.102% P (37.9% recovered) DSR stiffness of recovered binder = 1.77 kPa @ 64°C

acid content of the PPA and not the phosphorus content. At best the recovery of binder from a mixture can provide some information as to the presence of PPA in the binder used to produce the mix, but is very unlikely to provide data capable of reflecting the actual amount of PPA used in the binder. Simply stated it is the acid functionality in the PPA that stiffens the binder and the phosphorus in the PPA is THE means by which the acid is delivered.

Other Sources of Phosphorus in Binders

Within the last two years there has been a growing interest in the asphalt blending community to utilize the bottoms from re-refining of recovered drain oil from cars and trucks (2). These bottoms are produced via a number of refining processes, generally by regional collectors of used motor oil. There are no standards nor are there specifications for these bottoms, however, generally the addition of 5% to 10% of these bottoms can improve the low-temperature grade of a binder by 6°C to 12°C. These bottoms contain approximately 0.5% phosphorus, an amount that varies depending on the lube oil collected and the re-refining process used. The phosphorus source in the lube oil bottoms is zinc dithiophosphate which is added to lube oils for anti wear properties, as corrosion inhibitors, and as antioxidants. Zinc dithiophosphate is also added to greases and gear oils, and these materials can often find their way into the drain oil holding tank. Binders modified with re-refined lube oil bottoms will contain zinc dithiophosphate and will show the presence of phosphorus in recovered binders. A re-refined lube oil sample that contains 0.5% phosphorus and that is used at the 10% loading level would yield 0.05% phosphorus by XRF analysis which would calculate to 0.137% of 115% PPA. While this is a low theoretical level of PPA, if one is not able to determine the source of the phosphorus in the binder, an unknowledgeable investigator might conclude that PPA had been used in the binder. If a test for zinc is also performed on the binder, it is possible to ascertain whether the source of the phosphorus was PPA or re-refined lube oil bottoms. Asphalt does not contain zinc nor typically do aggregates and therefore if zinc is present in an asphalt sample it most likely came from the lube oil bottoms.

Due to the presence of surfactants in lube oils, which typically end up in the re-refined bottoms and adversely react with PPA, it is possible but not suggested that PPA and lube oil bottoms be used in the same binder. A sample of PG 64-22 (original DSR stiffness of 1.38 kPa at 64°C) that had been treated with 7.5% re-refined lube oil bottoms had a DSR stiffness of 0.769 kPa at 64°C and 1.63 kPa at 58°C. When 0.5% of 115% PPA was added to this blend the DSR increased to 1.00 kPa at 64°C. A further addition of 0.5% PPA (for a total of 1%) resulted in a DSR stiffness of 1.24 kPa. No further investigation was performed but, as a comparison, a PG 58-28 from the same refiner with a DSR stiffness of 0.629 kPa at 64°C was modified with 0.5% PPA and the DSR stiffness increased to 1.40 kPa at 64°C. In this particular example more than twice as much PPA would be required to achieve the same 64°C stiffness due the presence of the re-refined lube oil bottoms in the binder. From this limited data it appears likely that if a binder contains high levels of phosphorus (in excess of 0.2% phosphorus) as well as zinc then both lube oil bottoms and PPA have been added. Mix produced from this type of binder should be thoroughly investigated for moisture sensitivity as well as permanent deformation performance.

Confounding of Phosphorus by Silicon

Figure 6 shows a test scan of a binder sample recovered from a mix. The scan shows that $K\alpha$ energy level is adjacent to the $K\alpha$ energy absorption of phosphorus. Unless accounted for through calibration with standards containing silicon and phosphorus or through other software techniques, the potentially significant levels of silicon present in some aggregates could overstate the phosphorus levels in the recovered binder. In Figure 6, the blue vertical boxes define a software adjustment called a region of interest (ROI) for both the silicon and the phosphorus measurement. The ROI cuts off the determination at the boundaries of the boxes thus removing the confounding effect of silicon from phosphorus. The level of sulfur in asphalt is so high relative to the amount of phosphorus present in PPA modified binders that even with the ROI set it is necessary to generate a calibration curve that takes into account both the concentrations of sulfur and phosphorus expected in binder samples.

STABILITY OF PPA BLENDED BINDERS

Time Track Storage Study of PPA-Modified Binder

At times there have been concerns expressed by agencies regarding the stability of PPA blended binders. Specifically there is concern that PPA will phase separate from the base asphalt or that the binder will age harden significantly over time. An investigation at MTE was conducted to evaluate the potential for either of these concerns to be realized. Various levels of PPA ranging from 0% to 2.5% were added to a PG 64-22 binder. Approximately 600 g of modified binder at each PPA concentration were prepared. These samples were held in a 325°F oven for 9 days and sampled at varying intervals for determination of their high-temperature stiffness properties.

Table 8 shows the concentrations of PPA added to the PG 64-22 and the temperature

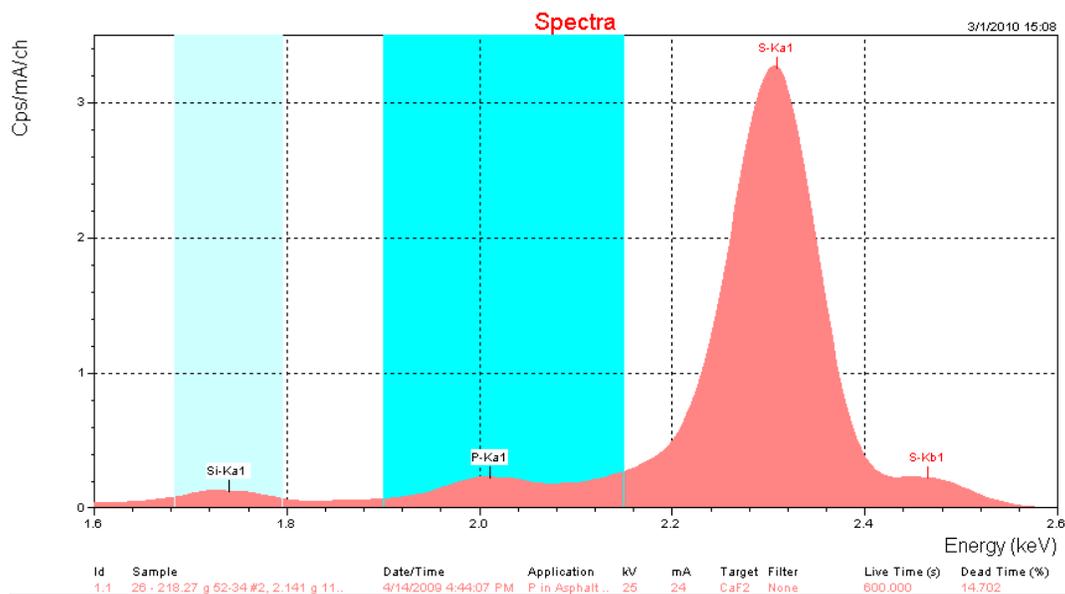


FIGURE 6 Test result showing confounding impact of silicon on phosphorus.

TABLE 8 Blends and Test Temperatures for Time Track Study

Amount of PPA Added	Test Temperature	Amount of PPA Added	Test Temperature
0%	64°C	1.2%	76°C
0.2%	64°C	1.5%	82°C
0.5%	70°C	2%	88°C
0.75%	70°C	2.5%	100°C
1%	76°C		

at which each sample was tracked. Each sample was tracked at a different temperature in an effort to maintain the DSR stiffness value in the range of 1 to 2 kPa. Testing at different temperatures assured that all samples could be plotted on the same scale for easy comparison and also assured that the DSR stiffness values being measured would be in the range typically tested for in the DSR.

The test results for the time track study are shown in Figure 7. These data show that the DSR stiffness immediately after mixing is greater than the stiffness after the samples have been allowed to condition overnight at 163°C. The control PG 64-22 showed a slight decrease after also having been mixed for 1 h prior to being tested on day zero. Figure 7 also shows that the greater the PPA loading the greater the change in stiffness after overnight conditioning. The important data shown in Figure 7, however, is the data from day one through day nine. The DSR stiffness of the PPA blends from 0.2% to 1.2% exhibit stable values over the 9-day testing interval. At levels of 2% and 2.5% there is a definite decrease in stiffness beginning about day two. The data for the 1.5% blend could be said to represent the practical upper limit for this particular binder as there is a stiffness decrease at day two but then the stiffness appears to have leveled off.

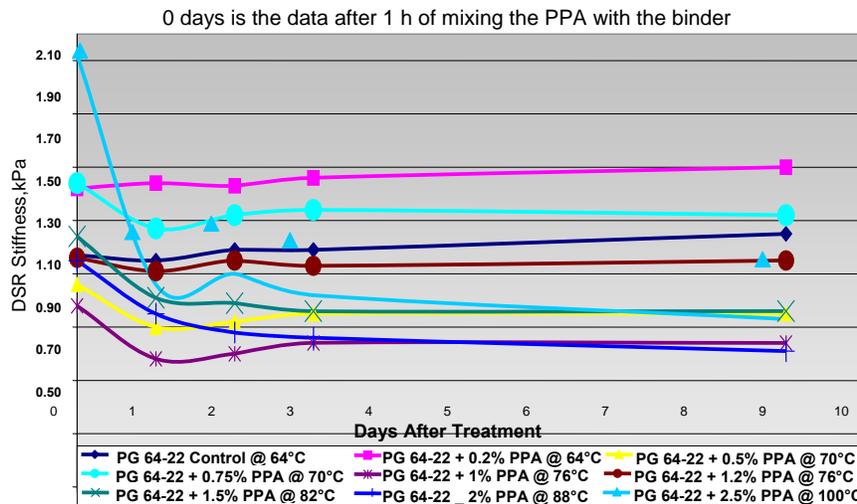


FIGURE 7 Time track study of binders modified with increasing levels of PPA.

In addition to the time tracking test for stiffness, a four day separation test was also performed. Using standard separation test tubes as described in ASTM D7173, a sample of each PPA modified binder was poured and stored in a 163°C oven for 4 days. After 4 days the samples were removed from the oven, chilled to solidify the binder and the tubes cut into thirds. The DSR stiffness and phosphorus content of the binder from the top third and bottom third of each sample tube was determined. Figure 8 is a bar graph comparing the DSR stiffness of the top and bottom third samples of seven blends including the control. Figure 9 is a bar graph plot of the phosphorus content of the top and bottom third samples after four days in the separation tube at 163°C. In both figures the variability in DSR stiffness as well as phosphorus content shows minor and random variations. At PPA concentrations as high as 3%, well in excess of typical usage levels, the variability for both stiffness and phosphorus content are minor. Based on these data it can be concluded that the acid content of binder is not changing or the stiffness would be increasing, nor is the PPA migrating or the phosphorus content would be changing.

FHWA Long-Term PPA-Modified Binder Study

Beginning in 2005 FHWA initiated a long term investigation of the performance behavior of PPA-modified binders. Numerous presentations of this research effort have been presented at industry meetings over the ensuing years (6–8) and a final report on this research is currently in the process of being prepared. One part of this study was to soak beams of PPA-modified binder in water for 245 days. The beams were 12.5 mm wide, 150 mm long, and 6.35 mm thick. A goal of this soaking study was to ascertain whether acid would migrate from the samples during extensive soaking. The data will be provided in the final report.

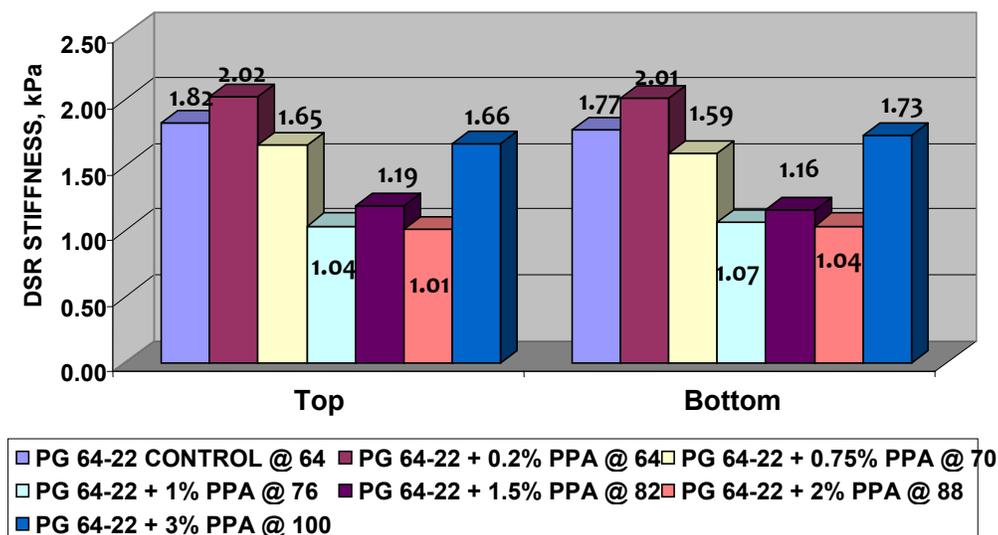


FIGURE 8 Comparison of DSR stiffness of top and bottom samples from a separation test.

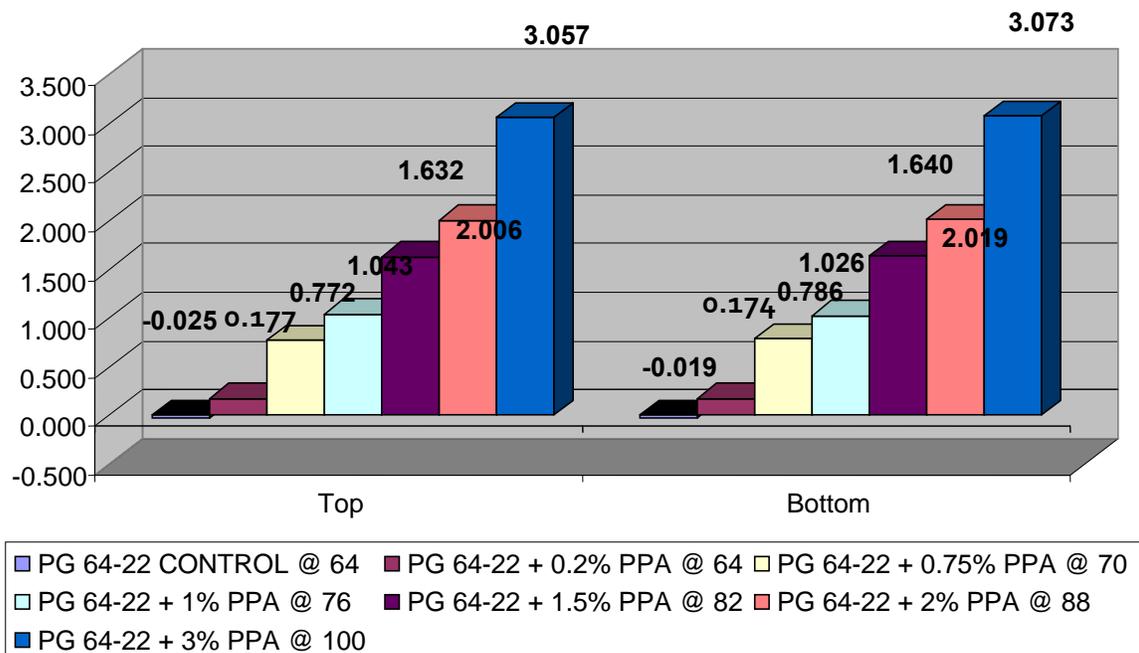


FIGURE 9 Percent of PPA in top and bottom of separation tube samples.

MTE was contacted at the end of the 245-day period and asked to perform an analysis for the phosphorus content of the bars that had been soaked. Table 9 shows the theoretical concentration of PPA that had been added to the quantitatively prepared binders, the theoretical amount of phosphorus that would be in each binder and the percent of phosphorus that was determined to be in each sample after the 245-day soaking period. Examination of Table 9 shows that XRF analysis slightly overstated the percent of phosphorus for the zero, 0.43% and 0.86% PPA loadings. These variations in results could be due to testing variability, variability due to base asphalt source or errors in preparing the original binder samples at the low PPA concentrations where small amounts of PPA would need to be weighed into the binder. At the very least the data in Table 9 shows that there is not a leaching of phosphorus, presumably in the form of phosphate ions into the water. This is an encouraging finding for two reasons: (a) the data speaks to the stability of PPA-modified bitumen to maintain the binder grade and (b) allays concerns that the PPA and, specifically, the phosphate could leach into the environment.

CONCLUSIONS

With proper standards prepared to consider the full range of phosphorus and sulfur contents of binders, it is possible to accurately determine the amount of phosphorus present in an unknown binder sample. While asphalt does not naturally contain phosphorus there are other sources of phosphorus, such as re-refined lube oil bottoms that contain phosphorus that could produce false positive results if the assumption is made that PPA is the only source of phosphorus in asphalt. The PANYNJ testing showed that it was possible to accurately identify not only the

**TABLE 9 Summary of Phosphorus Remaining in Binder
Beam Samples After 245 Days of Water Soaking**

Sample ID	Percent of 115% PPA Added by Weight of Total Blend	Calculated Percent of Phosphorus by Weight of Total Blend	MTE Percent Phosphorus by XRF	Difference in Percent Phosphorus Content (XRF-FHWA)	Amount of 115% PPA Based on XRF Result Remaining in Binder
S7-11-5	0	0	0.034	0.034	0.094
S7-11-4	0.432	0.157	0.178	0.021	0.490
S7-11-6	0.862	0.313	0.355	0.042	0.977
S7-11-7	1.288	0.468	0.479	0.011	1.318
S7-11-1	1.714	0.623	0.620	-0.003	1.706
S7-11-3	2.543	0.924	0.920	-0.004	2.532
S7-11-2	3.361	1.221	1.237	0.016	3.404

phosphorus originally added by the binder supplier, but also the additional phosphorus added by the Port Authority technicians. The comparative testing with Illinois showed that testing between two laboratories, using two different types of equipment and calibrated with different standards, was able to arrive at comparable values for the amount of PPA in the test samples.

Specific conclusions that can be drawn from the investigations reported are as follows:

1. Phosphorus is the element that is determined in the sample, not the acid content. Acid content is calculated based on assumptions that all the phosphorus came from PPA and using an assumed concentration of PPA.

2. Extraction of PPA-modified binders from mixtures can be impacted by stabilizing chemicals in the extraction solvent. Care must be taken to be sure that acid scavengers are not present in the extraction solvents used with PPA containing mixtures. If acid scavenging chemicals are present the stiffening impact of the PPA can be partially destroyed.

3. The testing performed for this report has shown that it is virtually impossible to remove all of the phosphorus from aggregates in bituminous mixtures. If the amount of PPA used in the binder to produce the mix is unknown, there will be no way, via simple binder extraction, to accurately identify the amount of PPA used in the binder.

4. The acid functionality of the PPA is the cause of the binder stiffening and not the phosphorus. Inability to quantitatively recover the phosphorus from a mixture does not mean that the aggregate or other mix components have neutralized the acid reaction with the binder. The acid functionality and the amount of phosphorus recovered are not interdependent when it comes to mixture performance. For example, amines could be added to the binder which could reduce acid functionality and thus reduce binder and mixture stiffness, but the amine addition would have no impact on the amount of phosphorus recovered during an extraction.

5. The time-tracking study has shown that PPA, up to a concentration of 1.5% in binder, produces a stable blend that does not change over time when stored at 163°C. Given that the samples being stored were approximately 700 g in size, any age hardening that might be caused by the presence of PPA should have been observed.

6. PPA does not phase separate from binders. This was shown through lack of marked change in DSR stiffness properties and lack of marked differences in phosphorus content between top and bottom portions in the separation tube conditioning study.

7. Testing of the phosphorus content of the binder beams from the FHWA 245-day soaking study showed that at ambient conditions phosphorus does not leach from asphalt.

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NOTE

This paper was also presented at the Association of Asphalt Paving Technologists Symposium on Polyphosphoric Acid Modification and is included in *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 79, 2010. AAPT gave permission to include it in this document.

Polyphosphoric Acid in Combination with Styrene-Butadiene-Styrene Block Copolymer

Laboratory Mixture Evaluation

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State agencies in the United States have known for years the benefits associated with asphalt binders that are modified with elastomer-type polymers to improve the rutting and fatigue cracking properties of the hot-mix asphalt (HMA). However, in recent years, many asphalt binder suppliers are now using polyphosphoric acid (PPA) in combination with decreased percentages of polymers to meet various performance grade (PG) asphalt binder requirements. This has raised concerns among the state agencies that fear that the combination of PPA and reduced polymer percentages will result in an inferior asphalt binder when compared to the same asphalt binder solely modified by polymer. To help answer this question, a research program was developed to examine and compare the laboratory properties of an asphalt binder modified with and without PPA. Asphalt binder testing, consisting of PG grading and MSCR, and mixture testing, consisting of dynamic modulus and flexural beam fatigue tested at both short- and long-term aged conditions, as well as repeated load testing to evaluate permanent deformation were conducted on a base binder and the base binder modified in two manners: SBS polymer only and reduced SBS polymer + PPA. This paper presents the findings of the binder and asphalt mixture evaluation and shows that the use of PPA in formulation with SBS provides an equal performance, with respect to HMA mixture rutting and fatigue performance, to the highly SBS-modified asphalt binder.

INTRODUCTION

PPA is one of many additives used to modify and enhance paving grade asphalt. The first patent describing asphalt modification with PPA was published in 1973. Since the early 1990s, PPA has also been successfully used across the United States in combination with various polymer modifiers. Even with this fairly extensive use of PPA in asphalt, there is very limited information regarding how PPA modification affects the performance of the HMA.

State agencies in the United States have known for years the benefits associated with asphalt binders that are modified with elastomer-type polymers to improve the rutting and fatigue cracking properties of the HMA. However, in recent years, many asphalt binder suppliers are now using PPA in combination with decreased percentages of polymers to meet various PG asphalt binder requirements. This has raised concerns among the state agencies that the combination of PPA and reduced polymer percentages will result in an inferior asphalt binder when compared to the same asphalt binder solely modified by polymer.

The growing knowledge of PPA usage by state DOTs has raised legitimate questions from engineers in charge of pavement performance and durability. How will a PPA-modified pavement perform over time? Do the initial enhanced binder properties observed in the laboratory with PPA modification change over time on the roadway? Do PPA-modified mixes perform any differently in the field compared to non-PPA mixes with regards to cracking, aging, and moisture-related distresses?

Some states have responded to this lack of understanding in PPA asphalt modification technology by banning the use of PPA through specific clauses in their specifications. Other states have examined the issue and decided that their current PG and PG-plus binder specifications are sufficient to ensure a quality performing binder. Any prohibition on the use of an effective modification technology without valid reasoning can lead to a more expensive product in the marketplace.

The combined use of PPA and polymers is widely used and has become increasingly popular as state agencies move to PG-plus specifications including specifications for items such as elastic recovery and ductility. A broad range of polymers have been claimed to be used beneficially in combination with PPA. Those preferred have been the elastomeric polymers (SBS and SB), which have been used by a wide margin for almost 10 years with PPA. It is now well established that PPA increases the stiffness of the asphalt binder without degrading the performance at low temperature (*I*). However, as PPA does not provide any significant elasticity of the binder, there remain some questions regarding the impact of PPA on the fatigue resistance of the mix.

The paper presents the results of an experimental program developed to examine and compare the laboratory properties of an asphalt binder modified with and without PPA. Asphalt binder testing, consisting of PG grading and MSCR and mixture testing, consisting of dynamic modulus and flexural beam fatigue tested at both short- and long-term aged conditions, as well as repeated load testing to evaluate permanent deformation were conducted on a base binder (PG 64-22) and the base binder modified in two manners: SBS polymer only and reduced SBS polymer + PPA.

OBJECTIVES

The research undertaken encompassed comparing asphalt binder and mixture properties of SBS polymer and SBS polymer + PPA modified to:

- Compare the permanent deformation according to the MSCR test developed by FHWA;
 - Compare the mixture stiffness properties at both short- and long-term aging conditions;
 - Compare the fatigue performance at both short- and long-term aging conditions;
- and
- Compare the permanent deformation characteristics from mixture testing.

MATERIALS SUMMARY

Material Characterization

Asphalt Binder

Three different binders were studied in the research program. Their characteristics at high temperature as well as their composition are reported in [Table 1](#) below. The true PG temperature was measured on the original binder and the RTFOT-aged binder according to AASHTO T240 and T315.

Aggregate Materials and Gradations

The primary aggregate source used to develop the mixture gradation was granitic gneiss from northern New Jersey. The aggregates were used to develop a coarse-graded, 12.5-mm Superpave mix at an N_{design} level of 100 gyrations. Gradation and design volumetric properties are shown in [Figure 1](#).

TABLE 1 True PG High-Temperature of SBS and SBS+PPA Binders

Description	Original True Grade (°C)	RTFOT True Grade (°C)
Neat asphalt	68.4	74.1
4.25% SBS modified	79.8	85.5
0.5%PPA –2.5%SBS modified	82.8	88.4

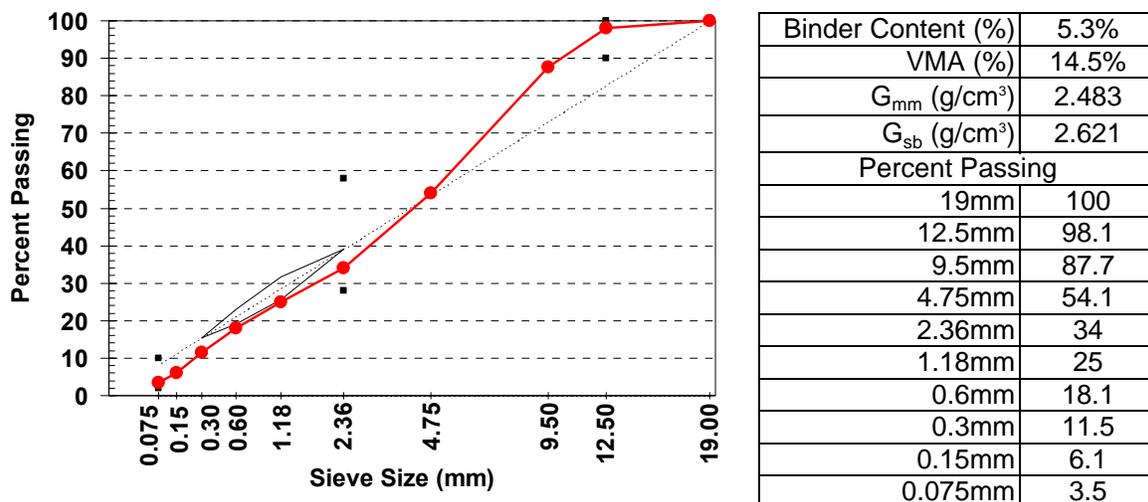


FIGURE 1 Gradation and design volumetric properties.

RESULTS OF LABORATORY PROGRAM

Asphalt Binder Testing: MSCR

Asphalt binder testing consisted of performing the MSCR test developed by FHWA. The MSCR test has been proposed to evaluate the high -temperature performance of asphalt binders since it has been suggested that binders with lower values of accumulated strain should result in asphalt mixes that are less prone to permanent deformation in actual application. The MSCR test procedure is summarized below.

- Specimens 25-mm diameter by 1-mm thick of original and RTFO-aged binder are tested at the true grade temperatures. For this study, these temperatures are reported in [Table 1](#).
- The specimen is subjected to a 1-s application of a 100 Pa stress followed by a 9-s period of zero stress during which the specimen is free to recover a portion of the strain which resulted from the 1-s stress application.
- At the end of the 9-s recovery period another 1-s stress application is imposed followed by another 9-s recovery period.
- The test is conducted until 10 cycles are achieved.
- After the 10 cycles at the 100 Pa stress have been completed, a stress of 3,200 Pa is then applied following the same protocol discussed above. The 3,200 Pa stress is then applied for another 10 load cycles. The lower the cumulative strain after 10 cycles, the higher the resistance to permanent deformation the asphalt mixture is expected to exhibit.

The accumulated strain versus time for the neat, SBS-modified, and SBS+PPA-modified specimens in the MSCR recovery tests were measured on the original aged and RTFOT-aged binder at two different stress levels: 100 Pa and 3,200 Pa ([Figures 2](#) through [5](#)). The three different asphalt binders were tested at their true grade temperatures are reported in [Table 1](#).

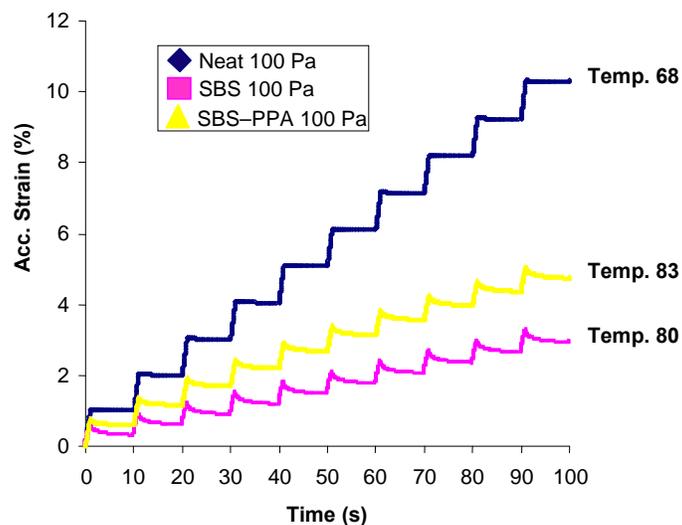


FIGURE 2 MSCR test results of original aged asphalt binders (applied stress = 100 Pa).

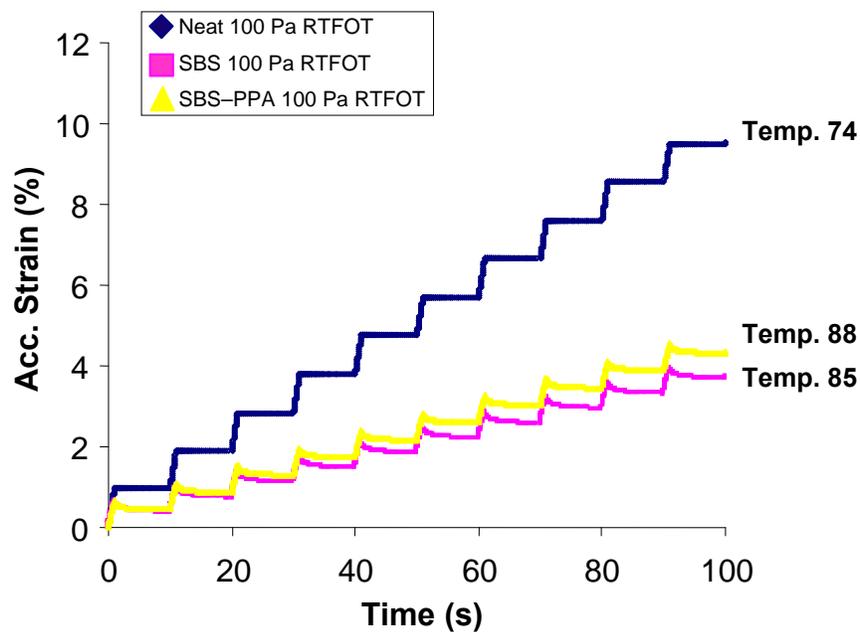


FIGURE 3 MSCR test results of RTFO-aged binders (applied stress = 100 Pa).

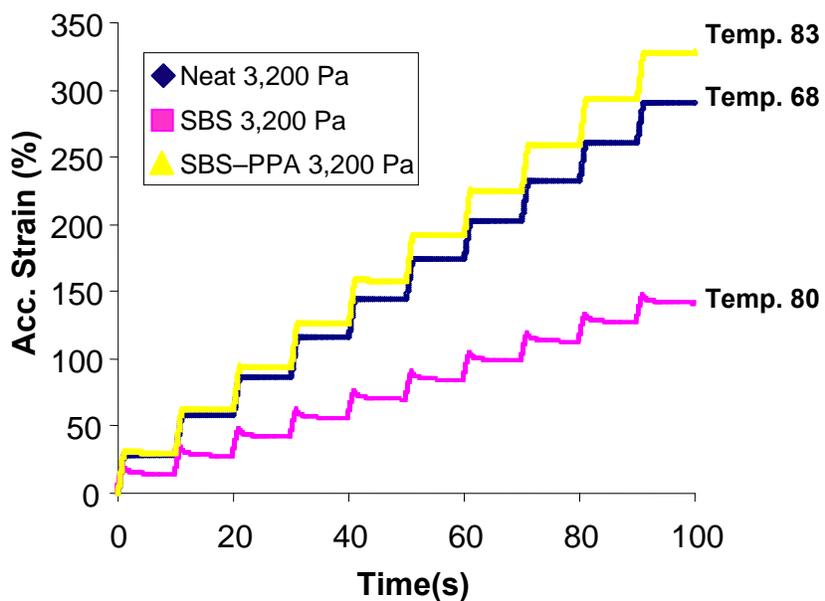


FIGURE 4 MSCR test results of original aged asphalt binders (applied stress = 3,200 Pa).

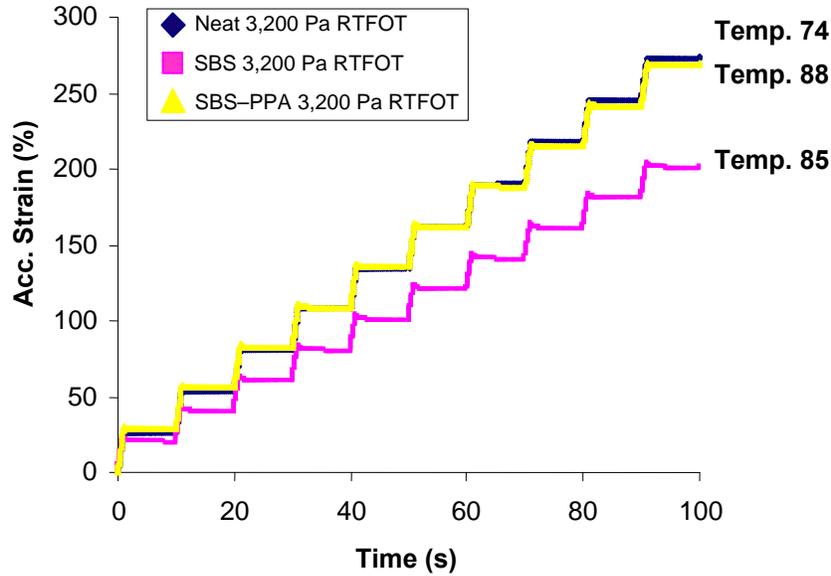


FIGURE 5 MSCR test results of RTFO-aged asphalt binders (applied stress = 3,200 Pa).

As expected, the highest cumulative deformation is achieved with the neat binder, even though the test temperature was 12°C to 15°C lower than the modified binders. The SBS-modified binder is showing a slightly lower permanent deformation than the SBS+PPA-modified binder (Figure 2). A similar observation was made on the RTFO binders, where both modified binder again performed in a similar manner (Figure 3).

As the applied stress increased to 3,200 Pa, the strain response of the asphalt binder seems to be affected significantly, namely with the SBS+PPA-modified binder, where it showed a similar deformation to the neat binder (Figure 4). A threshold limit seems to exist where the microstructure of the asphalt binder is changed drastically. This threshold appears to be apparent at a very high test temperature. These results highlight the critical importance of the temperature conditions during the test. In this case, the SBS+PPA-modified asphalt binder was tested at 15°C above the neat binder and 3°C above the SBS-modified binder. As the binder is aged (Figure 5), the test temperature has been increased and the difference between all binders is lessened.

The comparison of the percentage of recovery of the three asphalt binders at original and RTFO-aged conditions tested at stress levels of 100 Pa and 3,200 Pa are shown in Figure 6.

The percentage of recovery is defined by Equation 1:

$$R = \frac{\sum_{\varepsilon_r=1}^{10} \varepsilon_r(A, N)}{10} \quad (1)$$

where

A = stress level either 100 or 3,200 Pa;

N = number of cycles = 10;

$\varepsilon_r = (\varepsilon_l - \varepsilon_{l0}) * 100/\varepsilon_l$;

ε_l = adjusted strain value at the end of the creep portion = $\varepsilon_c - \varepsilon_0$ for each cycle;

ε_{10} = adjusted strain value at the end of recovery portion of each cycle;
 ε_c = strain value at the end of the creep portion of each cycle; and
 ε_0 = initial strain value at the beginning of the creep portion cycle.

The percentage of recovery is clearly improved by the use of SBS or SBS+PPA modification. As expected, the recovery decreases significantly as the asphalt binder is aged, even more significantly in the case of SBS-modified binder. The SBS- and SBS+PPA-modified binders are showing quite similar behavior after RTFO aging for 100 Pa applied stress. Once again, as the stress increased to the 3,200 Pa stress level, the SBS-modified asphalt binder still obtains the largest recovery.

HMA Mixture Testing

HMA performance testing was conducted on laboratory produced samples. The performance-related laboratory testing included

- Dynamic modulus testing of short-term and long-term oven-aged samples;
- Flexural beam fatigue testing of short-term and long-term oven-aged samples;
- Repeated load permanent deformation testing of short-term oven-aged samples; and
- Moisture sensitivity testing using AASHTO T283: Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage.

Dynamic modulus, flexural beam fatigue, and repeated load samples were evaluated at a target air void level of 6% to 7%, while the moisture sensitivity test samples were evaluated at a target air void level of 6.5% to 7.5%.

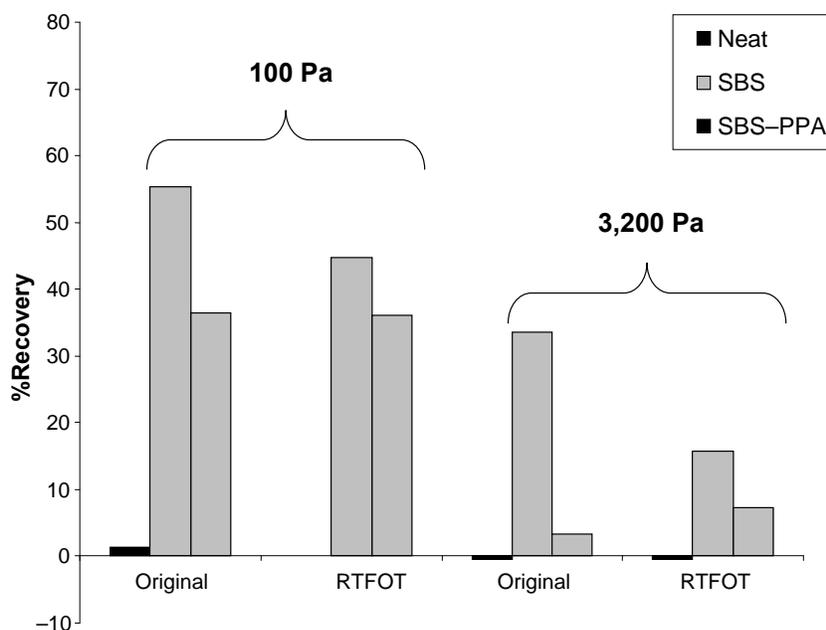


FIGURE 6 Percent recovery comparison of asphalt binders from the MSCR test.

Mixture Stiffness: Dynamic Modulus (E^*)

Dynamic modulus and phase angle data were measured and collected in uniaxial compression following the method outlined in AASHTO TP62: Standard Test Method for Determining Dynamic Modulus of Hot-Mix Asphalt Concrete Mixtures. The data was collected at three temperatures: 4°C, 20°C, and 35°C (for the neat asphalt binder only) and 45°C (for both modified asphalt binders), using loading frequencies of 25, 10, 5, 1, 0.5, 0.1, and 0.01 Hz. Samples were tested in triplicate after short-term and long-term following the procedures outlined in AASHTO R30: Mixture Conditioning of HMA.

The collected modulus values of the varying temperatures and loading frequencies were used to develop dynamic modulus master stiffness curves and temperature shift factors using numerical optimization of Equations 2 and 3. The reference temperature used for the generation of the master curves and the shift factors was 20°C.

$$\log|E^*| = \delta + \frac{(Max - \delta)}{1 + e^{\beta + \gamma \left\{ \log \omega_r + \frac{\Delta E_a}{19.14714} \left[\left(\frac{1}{T} \right) - \left(\frac{1}{T_r} \right) \right] \right\}}} \quad (2)$$

where

- $|E^*|$ = dynamic modulus, psi;
- ω_r = reduced frequency, Hz;
- Max = limiting maximum modulus, psi; and
- δ , β , and γ = fitting parameters,

$$\log[a(T)] = \frac{\Delta E_a}{19.14714} \left(\frac{1}{T} - \frac{1}{T_r} \right) \quad (3)$$

where

- $a(T)$ = shift factor at temperature T ;
- T_1 = reference temperature, °K;
- T = test temperature, °K; and
- ΔE_a = activation energy (treated as a fitting parameter).

The resultant master stiffness curves for STOA and LTOA samples are shown in [Figures 7](#) and [8](#). The STOA results in [Figure 7](#) show that the SBS+PPA-modified asphalt binder obtained higher modulus values at the lower loading frequencies (i.e., at the higher test temperature), while obtaining equivalent modulus values at the higher loading frequencies (i.e., lower test temperature). The neat asphalt binder obtained similar modulus values until approximately 1.0E-2 Hz for the STOA condition, where the modulus values drastically decreased. This was caused by low modulus values at the high test temperature.

The LTOA samples shows a similar trend, except that the SBS-modified asphalt binder obtained modulus values much closer to the SBS + PPA-modified samples when compared to the STOA condition ([Figure 8](#)). This indicates that the SBS-modified samples underwent greater age hardening due to LTOA than the SBS + PPA-modified samples. The extent of aging was

further evaluated by comparing the ratio of LTOA to STOA modulus values (Figure 9) versus the reduced loading frequency from the master stiffness curves. The aging results showed that

- The neat asphalt binder accumulated an average increase in modulus due to LTOA of 20%, with a maximum modulus increase of 65%;
- The SBS-only modified asphalt binder accumulated an average increase in modulus due to LTOA of 9%, with a maximum modulus increase of 18%; and
- The SBS + PPA-modified asphalt binder accumulated an average increase in modulus due to LTOA of 4%, with a maximum modulus increase of 7%.

Flexural Beam Fatigue: Test Results

Fatigue testing was conducted using the flexural beam fatigue test procedure outlined in AASHTO T321: Determining the Fatigue Life of Compacted HMA Subjected to Repeated Flexural Bending. The applied tensile strain levels used for the fatigue evaluation were 250, 400, 600, and 800 micro-strains. Samples were tested in triplicate after STOA and LTOA following the procedures outlined in AASHTO R30: Mixture Conditioning of HMA.

Samples used for the flexural beam fatigue test were compacted using a vibratory compactor designed to compact brick samples of 400 mm in length, 150 mm in width, and 100 mm in height. After the compaction and aging was complete, the samples were trimmed to within the recommended dimensions and tolerances specified under AASHTO T321.

The test conditions utilized were those recommended by AASHTO T321 and were as follows:

- Test temperature = 20°C;
- Haversine waveform;
- Strain-controlled mode of loading; and
- Loading frequency = 10 Hz.

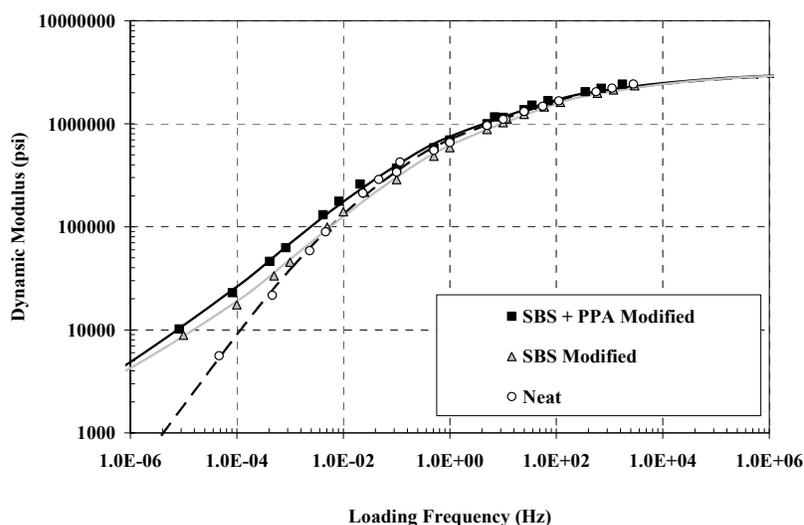


FIGURE 7 Master stiffness curves: STOA.

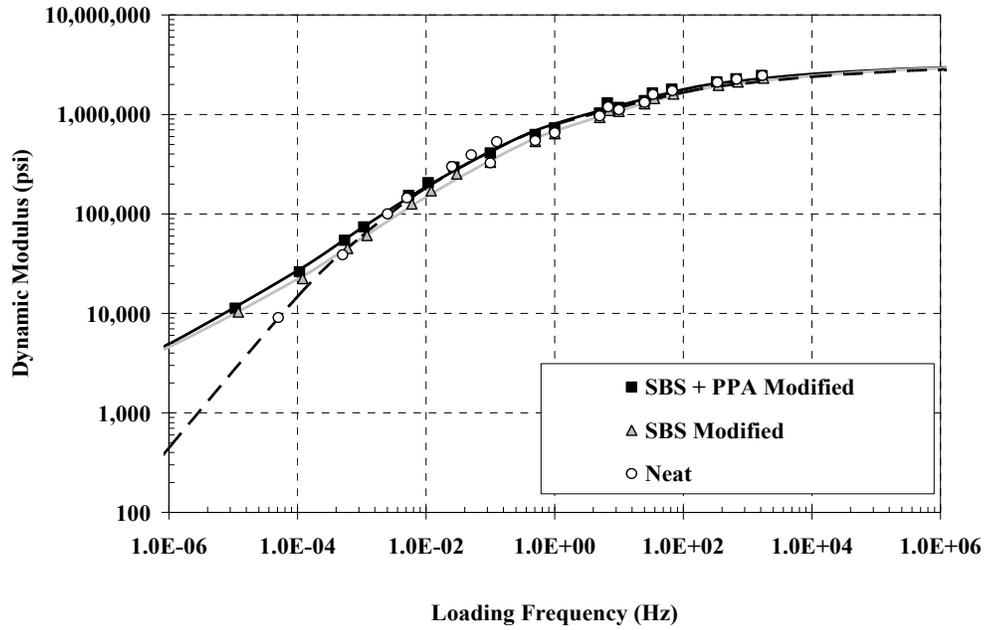


FIGURE 8 Master stiffness curves: LTOA.

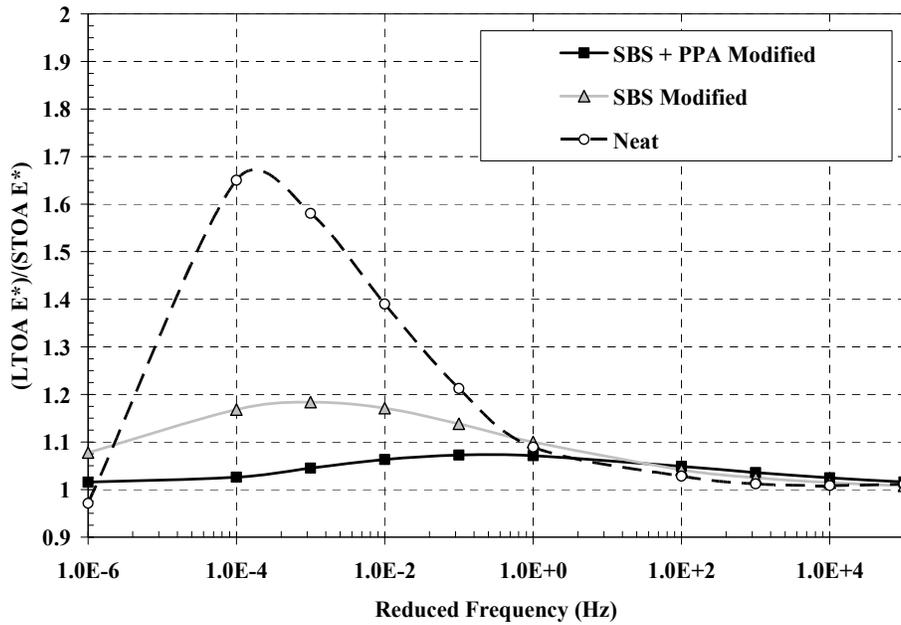


FIGURE 9 Increase in material stiffness due to LTOA.

The results of the STOA and LTOA flexural beam fatigue tests are shown in Figures 10 and 11. Table 2 shows the regression constants used to develop the fatigue life equation, as described by Hudson et al. (2), shown as Equation 4.

$$N_f = k_1 \left(\frac{1}{\varepsilon_t} \right)^{k_2} \left(\frac{1}{E} \right)^{k_3} \quad (4)$$

where

- N_f = number of loading repetitions until fatigue failure (50% of the initial stiffness)
- k_1, k_2, k_3 = regression coefficients depending on material type and test conditions
- ε_t = tensile strain
- E = initial flexural stiffness

A statistical analysis was conducted using a student's *t*-test analysis (two samples assuming equal or unequal variances). The statistical analysis was utilized to determine if the samples were statistically equal or statistically not equal among the common test results and parameters. A 95% confidence interval was chosen for the analysis.

Based on the average (mean) results of the STOA and LTOA samples, the SBS-modified asphalt had a slightly greater fatigue resistance than the SBS + PPA-modified asphalt when comparing the flexural beam fatigue results. However, when statistically comparing the full set of STOA fatigue results from each tensile strain level, the SBS-modified and the SBS + PPA-modified asphalts were shown to be statistically equal at a 95% confidence level using the student *t*-test analysis. When statistically comparing the full set of LTOA fatigue results from each tensile strain level, the SBS-modified and the SBS + PPA-modified asphalts were shown to be statistically equal at a 95% confidence level at the 250 and 600 micro-strain levels. The SBS-modified asphalt had a statistically greater fatigue life at the 400 micro-strain level and the SBS + PPA-modified asphalt had a statistically greater fatigue life at the 800 micro-strain level. In both the STOA and LTOA aged conditions, the neat asphalt binder achieved the lowest fatigue life.

Repeated Load Permanent Deformation: Test Results

Repeated load permanent deformation tests were conducted in uniaxial compression following the procedures outlined in Appendix B of *NCHRP Report 465* (3). The unconfined repeated load tests were conducted with a deviatoric stress of 10 psi and a test temperature of 54.4°C (130°F), which, on average, corresponds to the 50% reliability, 7-day average maximum pavement temperature at a depth of 25 mm for New Jersey (4). Samples were tested in triplicate and were continued to 10,000 load cycles.

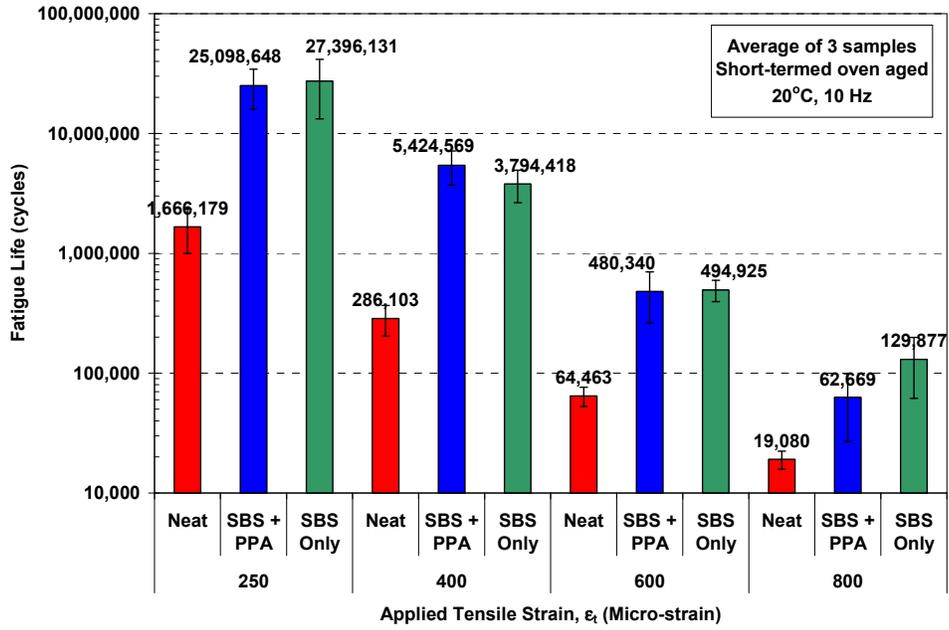


FIGURE 10 Flexural beam fatigue results for STO.

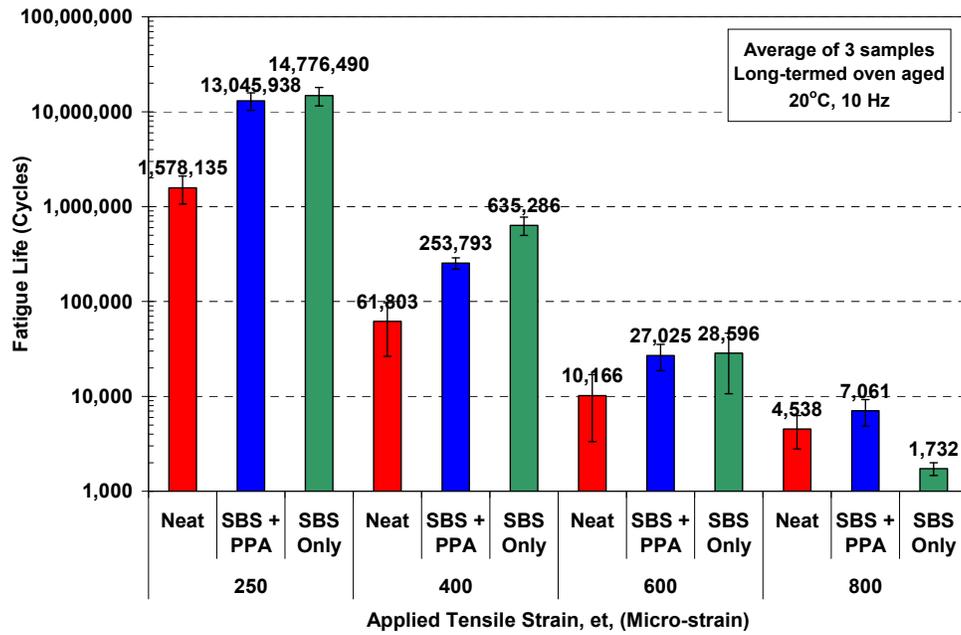


FIGURE 11 Flexural beam fatigue results for LTO.

TABLE 2 Fatigue Life Equation Coefficients

$N_f = k_1 \left(\frac{1}{\epsilon_f}\right)^{k_2} \left(\frac{1}{E}\right)^{k_3}$			
Asphalt Binder Type	STOA		
	k_1	k_2	k_3
Neat	5.23E-07	3.736	0.260
SBS + PPA Modified	2.91E-03	5.207	2.296
SBS Modified	7.10E-02	5.072	2.539
Asphalt Binder Type	LTOA		
	k_1	k_2	k_3
Neat	8.32E-14	5.021	0.250
SBS + PPA Modified	2.15E-15	6.521	0.462
SBS Modified	6.34E-18	7.545	0.699

Figure 12 shows a comparison of the permanent deformation results for the neat, SBS- and SBS+PPA-modified asphalt binders. The permanent deformation plots for the SBS-modified and SBS + PPA-modified asphalts are extremely close to each other, while the neat asphalt binder clearly undergoes tertiary flow failure between 2,000 and 3,000 loading cycles.

The permanent deformation data was also evaluated using preliminary guidelines developed by Advanced Asphalt Technologies for the Maryland State Highway Association (5). The guidelines are based on limiting permanent deformation in the asphalt layer to 10 mm. The results shown in Table 3 indicate that on average, the SBS + PPA asphalt binder performs slightly better than the SBS-modified asphalt. However, when statistically comparing the results using the student *t*-test, the test results are statistically equal at a 95% confidence level. This somewhat contradicts the MSCR test results that had identified the SBS-modified asphalt binder as being more resistant to permanent deformation.

Resistance to Moisture-Induced Damage (TSR): Test Results

Tensile strengths of dry and conditioned asphalt samples were measured in accordance with AASHTO T283: Resistance of Compacted Asphalt Mixtures to Moisture-Induced Damage. The results of the testing are shown in Table 4. The testing shows that the SBS+PPA asphalt samples achieved a slightly higher TSR value than the SBS-modified asphalt, 88.9% and 87.8%, respectively. On average, the tensile strength of the SBS+PPA samples was also determined to be slightly higher than that of the SBS-modified asphalt, although the results were found to be statistically equal. The test results indicate that both mixtures exceed the AASHTO M323 minimum TSR criteria of 80%. Meanwhile, the neat asphalt sample only achieved a TSR value of 76.7%.

SUMMARY AND CONCLUSIONS

PPA has been used successfully in the asphalt field for more than 40 years. Extensive use of PPA either as a solo asphalt binder modifier or in combination with synthetic polymers has been practiced for more than 10 years across North America. This use has grown extensively as the industry has grown more confident in the use, application, and performance of PPA as an asphalt

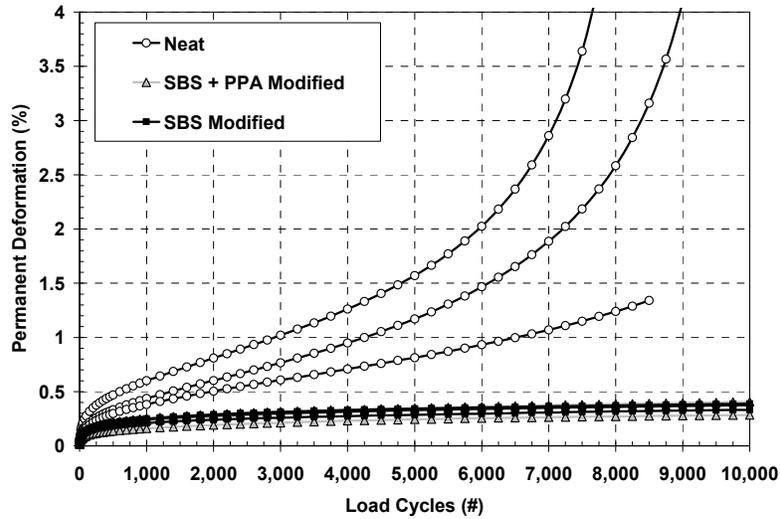


FIGURE 12 Repeated load permanent deformation results.

TABLE 3 Test Data and Rutting Estimates from Permanent Deformation Testing

Sample Type	Sample ID	ϵ_p @ 5,000 Cycles (%)	Estimated Traffic to 10-mm Rut Depth (million ESALs)
Neat	#1	1.57	1.2
	#2	1.17	
	#3	0.82	
	<i>Average</i>	<i>1.19</i>	
	<i>Std. Dev.</i>	<i>0.38</i>	
SBS Modified	#1	0.29	4.3
	#2	0.33	
	#3	0.34	
	<i>Average</i>	<i>0.32</i>	
	<i>Std. Dev.</i>	<i>0.03</i>	
SBS + PPA Modified	#1	0.24	4.5
	#2	0.35	
	#3	0.33	
	<i>Average</i>	<i>0.31</i>	
	<i>Std. Dev.</i>	<i>0.06</i>	

TABLE 4 TSR Test Results

Specimen Type	Average Air Voids (%)	Indirect Tensile Strength (psi)		Average TSR (%)
		Dry	Conditioned	
Neat	7.2	164.6	126.2	76.7
SBS + PPA	6.9	230.5	204.8	88.9
SBS	7.1	221.3	194.4	87.8

binder modifier. PPA-modified asphalt binders have been used to pave roads all across the country under a wide variety of traffic and weather conditions and have performed well. However, many state agencies are still skeptical regarding the durability and overall performance of PPA-modified asphalts. Therefore, continued work in the field of performance studies that incorporates PPA-modified asphalt binders is needed.

To help add to the state of knowledge regarding HMA performance and PPA, a research study was initiated. The work conducted in this research study showed the following:

- SBS+PPA-modified asphalt binders can provide fatigue and durability resistance as well as asphalt binders solely modified with SBS. Flexural beam fatigue test results on STOA and LTOA samples were statistically equal at a 95% confidence level. Meanwhile, results from the TSR tests concluded that the SBS+PPA-modified asphalt achieved a slightly higher TSR value than the SBS-modified samples.
- Dynamic modulus testing conducted on SBS+PPA- and SBS-modified asphalts that were laboratory aged under STOA and LTOA conditions, as specified in AASHTO R30, showed that both modified asphalts provided very similar modulus values after undergoing LTOA. The SBS+PPA-modified asphalt achieved slightly higher modulus values at higher test temperatures at the STOA condition. When evaluating the ratio between LTOA and STOA modulus, the SBS+PPA asphalt achieved slightly lower ratios than the SBS modified asphalt. This may indicate that the SBS-modified asphalt underwent a greater extent of age hardening when compared to the SBS+PPA-modified asphalt.
- Repeated load permanent deformation testing conducted on HMA samples showed that both the SBS and SBS+PPA asphalts achieved almost identical resistances to permanent deformation when tested in uniaxial compression. This was somewhat contradictory to the MSCR test that concluded the SBS-modified asphalt should provide a greater degree of permanent deformation resistance.

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NOTE

This paper was also presented at the Association of Asphalt Paving Technologists Symposium on Polyphosphoric Acid Modification and is included in *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 79, 2010. AAPT gave permission to include it in this document.

Polyphosphoric Acid–Modified Binders and Mixtures

Aggregate and Binder Interactions, Rutting, and Moisture Sensitivity of Mixtures

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Polyphosphoric acid (PPA) has been increasingly used as a means of producing modified binders for the past 10 to 15 years in North America. Reports of isolated or regional use of phosphoric and PPA prior to the advent of Superpave performance grade (PG) binders have been published, but the increased demand for high-performance binders resulting from the adoption of PG binders stimulated more widespread research into the means by which PPA could effectively and economically enable binder suppliers to meet these demands. Consequently asphalt suppliers in all regions of the United States and Canada turned to PPA to meet the new specifications. It was found that PPA, when used at levels as low as 0.5% by weight of binder, could increase the high-temperature PG of some binders by one full grade. Most binders required approximately 0.8% to 1.2% PPA by weight of binder and some required considerably more; sometimes more than 2%. Still other asphalt suppliers found that the addition of low levels, typically less than 0.5% by weight, of PPA to polymer-modified binders enabled them to reduce polymer loading without negatively impacting mixture performance and in some reported cases enhancing mixture performance. Almost simultaneously with the onset of PPA usage, concerns were raised by a cross section of individuals, organizations, and agencies associated with the asphalt production and supply, bituminous paving and governmental sectors. These concerns were manifested by fears of mixture stripping because of the hygroscopic nature of PPA and fears of accelerated aging and adverse effects on low-temperature properties of both binders and their mixtures because of the well-known use of phosphoric acids, PPA, and phosphorus pentoxide to catalyze the production of roofing asphalt during the blowing process. There was also the often unstated but ever-present belief that purchasers of PPA-modified binders were being cheated because they were not receiving polymer when purchasing some premium PG grades. Some of these concerns were justified, many were not. The information in this study will endeavor to put some perspective around these concerns, to show where there might be cause for concern and where there is not. This document does not provide an answer to all questions and it raises a few questions that still need to be answered.

INTRODUCTION

With the implementation of the PG binder system came the good, the bad, and the ugly and in at least one case the absurd. The good, of course, is polymer, specifically elastomeric polymer, modification; a process that had been in use for at least 40 years and suddenly had a new lease on life. All of sudden there were tests that could quantitatively prove the performance values added to binders by polymers and more importantly to mixtures. And as they say, the rest is history.

The bad, or at least the perceived bad, was that every person with an additive that could change the physical properties of asphalt cement was attempting to promote it to someone. This includes, but is not limited to, PPA, oxidation, gelled asphalt, carbon black, ground tire rubber, caustic reacted asphalt, bottoms from the re-refining of used motor oil, natural waxes, synthetic waxes, sulfur (in several forms), and the list goes on. These are categorized as bad because unlike virgin polymer-modified binders the performance improvement characteristics are not necessarily obvious or easily quantified. Someone somewhere has to invest time and money into proving that all of these nonvirgin polymer materials actually deliver. The ugly part of PG binders is the fact that not only could the good additives produce binders that met the specification, but what has been somewhat facetiously called bad additives could as well. This fact generally did not sit well with specifying agencies. Things went from ugly to uglier when SHRP-plus specifications were added in many states to insure that only the good could be used. The absurd case is the presentation at one binder expert task group meeting where it was shown that sawdust added to asphalt could alter the PG of the binder. This paper deals with only PPA containing binders, their interactions with different types of aggregates and how mixtures produced with those binders perform in terms of permanent deformation and moisture sensitivity. In the course of the investigation new information on the interaction of PPA-modified binders with different aggregate types will also be explored.

Outline of Information to Be Covered

Much research has been conducted at MTE over the past 10 years into the impact of PPA-modified binders on mixture performance. The three main areas to be covered in this report are

1. The impact on binder properties resulting from blending PPA-modified binders with aggregates finer than 1.19 mm (16 mesh);
2. Moisture sensitivity of mixtures produced with PPA-modified binders; and
3. Permanent deformation properties of mixtures produced with PPA-modified binders.

Results of Blending Aggregate and PPA-Modified Binders

Anecdotal reports and published studies (1, 2) have identified the impact of blending aggregate components such as hydrated lime and limestone aggregate with PPA-modified binders resulting in neutralization of the acid functionality and consequent reduction in the stiffness of the PPA-modified binder. More recent work by FHWA (3) has presented information that limestone aggregate and lime dust treatment of PPA modified as well as control binders can result in a reduction in the stiffness of the binders when solvent extracted and recovered from the aggregate blends. The surprising aspect of this work was that similar trends were observed whether the binders were PPA modified or neat. Generally the percent of stiffness reduction of the PPA modified binders was greater than that of the neat binders. When the work was repeated without removing the binder from the aggregate fines and in fact keeping the fines suspended the stiffness reductions were not as marked or were eliminated. With this work as a background several blends were produced using limestone and granite aggregates with conventional binders and PPA-modified PG grades produced from those binders. [Figure 1](#) is a graph of the impact of blending a limestone and a granite aggregate with a Flint Hills Refinery PG 64-22 and the PG 64-22 after reaction with PPA to produce a PG 70-22.

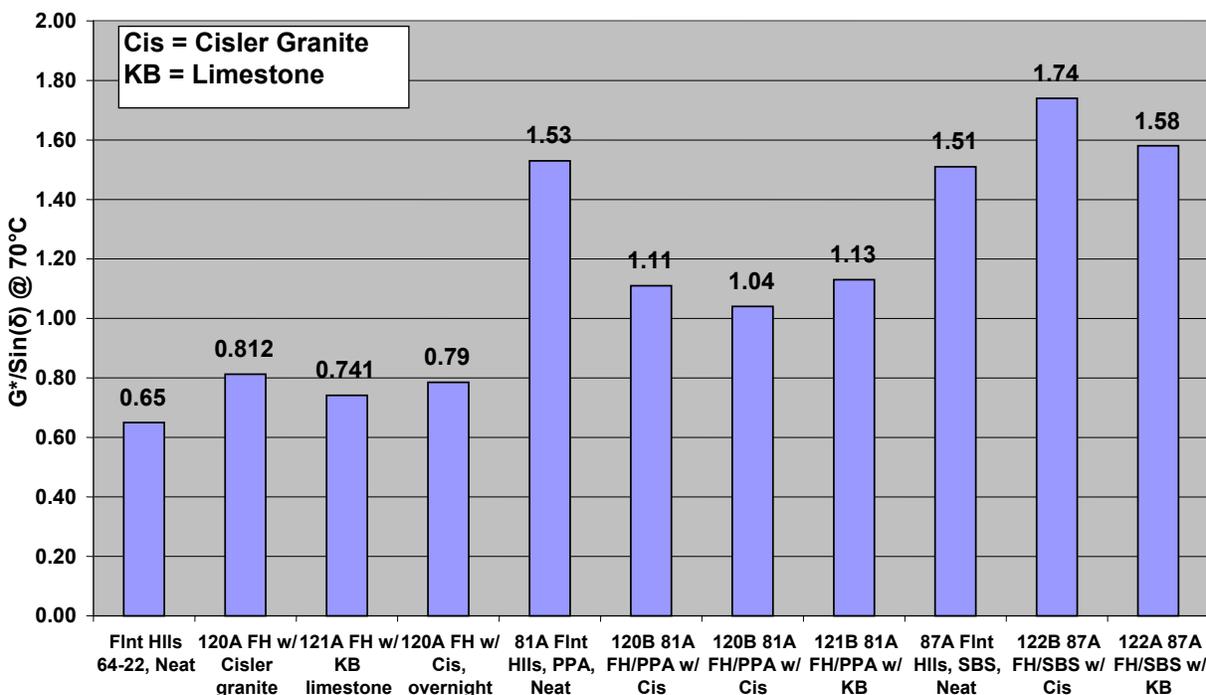


FIGURE 1 DSR stiffness of Flint Hill PPA binder after blending with aggregate ≤ 1.19 mm.

The Flint Hills Refinery is located in the Minneapolis, Minnesota, area and utilizes a blend of Canadian crudes to produce PG asphalts. In the case of Figure 1 the binders were blended with aggregate finer than 1.19 mm (the #16 mesh sieve) in a 1:1 weight ratio of asphalt to aggregate for a period of 30 min. The aggregate binder blends were stored in a 163°C oven and the aggregate was allowed to settle under gravity for at least 2 h and then a sample of the supernatant asphalt was taken and tested for stiffness using a DSR. Figure 1 shows that for the untreated PG 64-22 there is a minor (approximately 18%) increase in DSR stiffness due, most likely, to heating effects on the binder and retention of a small amount of the finest aggregate in the binder sample at the time of testing. In contrast the same binder reacted with PPA to produce a PG 70-22 when treated in the same fashion exhibited a 28% reduction in binder stiffness regardless of aggregate treatment. For further comparison a PG 70-22 produced using an SBS modifier showed an increase in stiffness after treatment with the aggregates. The general conclusion would be to ascribe the reduction in DSR stiffness for the PPA-modified binder and the limestone aggregate to a reaction of the acid functionality with the limestone, but the granite aggregate contains very low levels or no carbonates and hence there should be minimal or no stiffness degrading reaction.

In another experiment, a PG 64-22 from Marathon Refining Company's Detroit, MI, refinery was tested with the same limestone and granite aggregates. A PG 70-22, produced from the PG 64-22 with PPA, was also blended with the same aggregates. Figure 2 shows that there is a very minor increase in DSR stiffness for the PG 64-22 blends, but the PG 70-22 PPA-modified binder exhibited approximately a 27% decrease in stiffness after blending with the aggregates. Once again the granite aggregate resulted in a decrease in stiffness similar to that of the limestone aggregate. While the magnitudes of these differences are similar to those presented by

FHWA (3) there are two differences. The FHWA results showing a reduction in stiffness were for binders solvent recovered from the aggregates blends and only carbonate type aggregates were investigated. The data presented in this study suggest that for two different binders, which were also different than any of the binders employed by FHWA, and for aggregates of completely different chemistry there is an interaction occurring as a result of the PPA modification that causes a reduction in DSR stiffness absent the solvent extraction and recovery step employed by FHWA.

Figure 3 presents data that may provide some insight as to what is taking place. Examining the data in Figure 3 beginning from the left side of the plot, the neat Flint Hills PG 64-22 was blended with granite aggregate, and the binder above the aggregate after settlement was tested.

An XRF scan for phosphorus was conducted and the result corrected for silica that might have remained suspended in the settling. The corrected value shows 0% phosphorus, as should be the case for the neat PG 64-22. The PG 70-22 PPA-modified binder with no aggregate exposure shows the same level of phosphorus with and without silicon correction, as should be the case. When the PG 70-22 is blended with granite and liquid above the settled aggregate tested there is more than a 20% reduction in the phosphorus resident in the binder even with the silicon correction. The PG 70-22 when blended with limestone shows approximately an 18% loss in resident phosphorus, but a minor silicon correction, as expected for a limestone aggregate. The Marathon PPA produced PG 70-22 exhibits approximately 16% and 19% reduction in resident phosphorus for granite and limestone blends respectively. However both the Marathon PG 70-22 and the Flint Hills PG 70-22 blended with silica sand and then tested show only about a 2% or

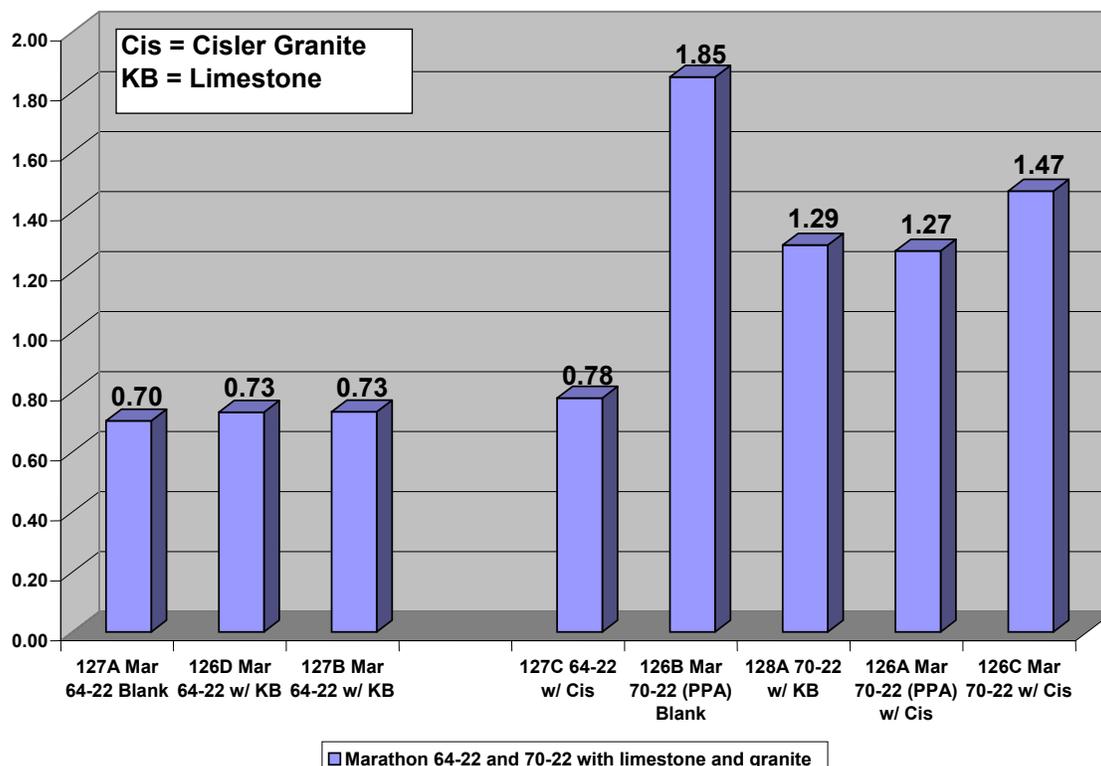


FIGURE 2 DSR stiffness of marathon PPA binder after blending with aggregate ≤ 1.19 mm.

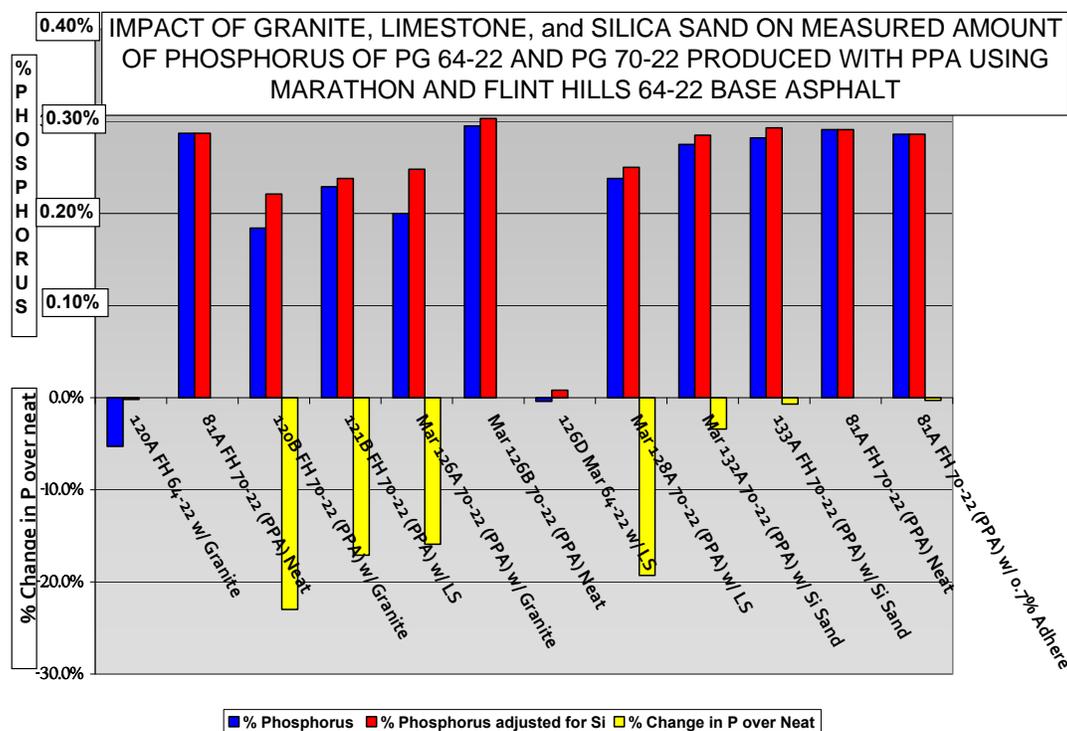


FIGURE 3 Impact of granite, limestone, and silica sand on phosphorus levels in remaining binders after aggregate settlement.

less reduction in resident phosphorus and very minor adjustments for silicon. Comparing the loss in resident phosphorus to the measured reduction in DSR stiffness values shown in Figures 1 and 2 does not provide a 1-to-1 correspondence between the two parameters; nor should that be the expectation. Phosphorus is not the element that produces the stiffness increase in the binder.

What is unknown at this point and requires further investigation is an understanding of the species that remains behind with the aggregate. Phosphoric acid has three levels of dissociation. The first hydrogen ion is fairly reactive, but the $\text{H}_2(\text{PO}_4)^{-2}$ and $\text{H}(\text{PO}_4)^{-1}$ species hold onto their H^+ ions more aggressively. (The pK_a^1 for phosphoric acid is 2.12, pK_a^2 is 7.21 and pK_a^3 is 12.67.) Understanding how much of the $\text{H}_2(\text{PO}_4)^{-2}$ and $\text{H}(\text{PO}_4)^{-1}$ associates with the aggregate after extraction and how much remains with the asphalt could provide an explanation for the reduction in stiffness when PPA-modified binders are solvent recovered from aggregates. The data in Figure 3 shows that the affinity of aggregate for phosphate groups is dependent on the type of aggregate and the binder into which the PPA has been added. In this work there is no opportunity for loss of phosphate because there has been no solvent extraction step; the phosphate is either in the asphalt binder or settled out with the aggregate. Table 1 shows the main chemical composition of the granite and limestone used for the study shown in Figure 3. This compositional analysis shows that the granite and limestone are markedly different in terms of their main chemical constituents and yet the levels of phosphate loss in the binder after aggregate settlement are similar as are the resulting DSR stiffness values. Table 2 summarizes the phosphate found in the asphalt liquid and the DSR stiffness of the binder after the aggregate was allowed to settle out.

The data shown in Table 2 is plotted in Figure 4 and shows a reasonable correlation between the amount of phosphorus and the DSR stiffness.

TABLE 1 Chemical Composition of Granite and Limestone Aggregate

Aggregate	Si as SiO ₂ , %	Al as Al ₂ O ₃ , %	Mg as MgCO ₃ , %	Ca as CaCO ₃ , %
Granite	60.6	13.0	4.2	8.3
Limestone	16.1	3.97	35.1	48.2

TABLE 2 Summary of Phosphorus Resident in Asphalt Sample after Mixing with Aggregate and the DSR Stiffness of the Asphalt after Aggregate was Allowed to Settle Out

Sample Identification	Phosphorus, %	DSR Stiffness @ 70°C, kPa
81A FH 70-22 (PPA) Neat	0.289	1.53
120B FH 70-22 (PPA) w/ Granite	0.221	1.04
121B FH 70-22 (PPA) w/ LS	0.238	1.13
Mar 126A 70-22 (PPA) w/ Granite	0.248	1.27
Mar 126B 70-22 (PPA) Neat	0.303	1.85
Mar 128A 70-22 (PPA) w/ LS	0.25	1.29
Mar 132A 70-22 (PPA) w/ Si Sand	0.285	1.4
133A FH 70-22 (PPA) w/ Si Sand	0.293	1.48

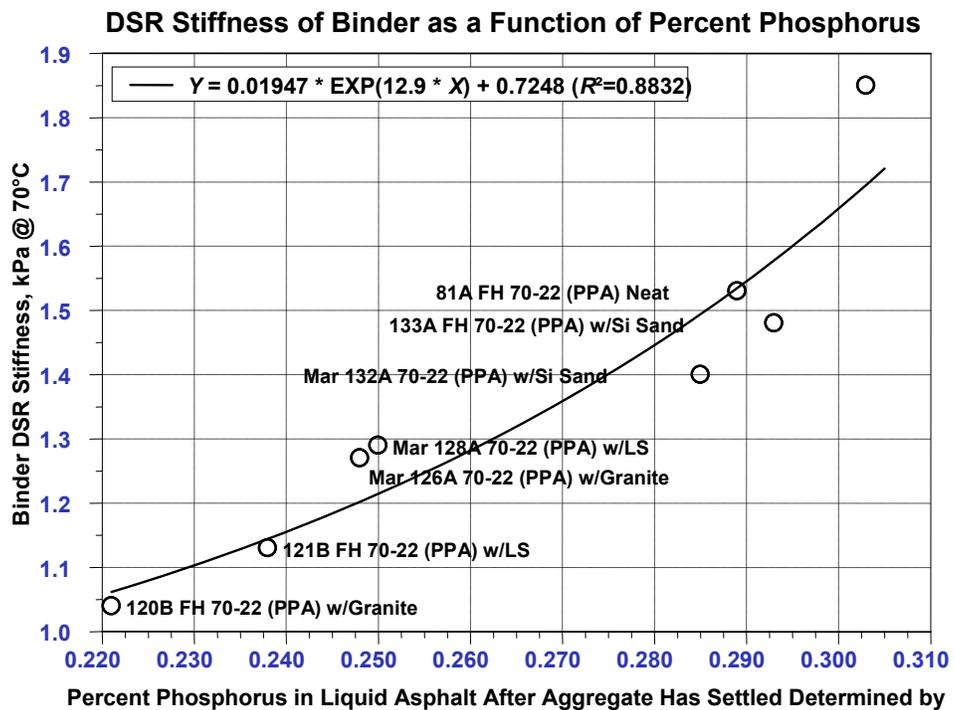


FIGURE 4 Impact of removal of phosphorus from aggregate binder blends on the resulting DSR stiffness of the binder.

The samples labeled as “neat” contained no aggregate and therefore the phosphorus levels and DSR stiffness values are the maximum values for those blends. This is a limited data set and further investigation should be performed to avoid the danger of overinterpreting a trend based on only eight samples. These data, however, do suggest that aggregate source and chemistry can impact the recovered phosphorus content and further suggest that there is some relationship between aggregate removal of phosphorus from the asphalt binder when aggregate and binder are in direct contact and the ultimate reduction of binder stiffness in these blends. This last point, however, is not meant to suggest that the phosphate ions are responsible for the stiffening of asphalt binders to which PPA has been added. A recent paper by Fee et al. (4) provides data showing that simply adding phosphate ions to asphalt utilizing dipotassium hydrogen phosphate (K_2HPO_4) in the form of an aqueous solution is not sufficient to increase the DSR stiffness of the binder. (Dipotassium hydrogen phosphate solution has a pH of 9.) Neutralization of acid functionality is not a likely explanation for this stiffness reduction if one considers the composition of the granite aggregate. Although Miknis (5) has shown that hydrated lime can react with PPA-modified asphalt; in the same report he concluded that “PPA does not appear to react with limestone, $CaCO_3$.” Both the limestone and granite aggregates exhibit similar reductions in phosphorus resident in the liquid asphalt and similar reductions in DSR stiffness. Some other mechanism must explain the removal of a portion of phosphorus from the asphalt binder that has been blended with these aggregates. Additionally Reinke et al. (6) have reported data indicating that PPA modified binders can improve the moisture sensitivity of mixtures produced with granitic type aggregates. The implication of the data presented here and the interpretation advanced is that removal of H^+ ions from the liquid asphalt in the form of $H_2(PO_4)^{-2}$ and possibly $H(PO_4)^{-1}$ through aggregate interaction resulted in the reduction in binder stiffness.

Iatroscan analyses (7) of the binders utilized to produce the results shown in Figure 3 were performed. As previously described, the binders had been blended with the aggregates which had then been allowed to settle out in an oven. The liquid asphalt remaining above the aggregate was then sampled for compositional testing. No solvent extractions of these binders from the aggregates were performed. After removal of asphaltenes using n-heptane according to ASTM D3279, the Iatroscan determination of resins, saturates and cyclics was performed. An adjustment for mineral fine contamination was also performed. Arnold et al. (8) have shown that the addition of PPA to a given binder results in an increase in n-heptane insolubles (asphaltenes) and a corresponding decrease in the resin fraction as determined by the Iatroscan. Similar findings are referenced by Huang, et al. (9) as well. In their paper Arnold et al. show the increase in n-heptane insolubles in binder over the range of zero to four percent PPA in one percent incremental additions of PPA to SHRP binders AAD (California Coastal) and ABM (California Valley). In the current work being reported the asphalts used are derived from predominantly Canadian crude and both the Marathon and Flint Hills binders require approximately 0.75% to 0.8% of 115% PPA to change the PG grade from a PG 64-22 to the PG 70-22s used in the study. The n-heptane insolubles (reported as asphaltenes) and the Iatroscan fractions are plotted in Figure 5. Also shown in this figure are the data for percent phosphorus resident in the asphalt liquid above the settled aggregate and the DSR stiffness of that asphalt. These are the same data values as shown in Figure 4, but are reproduced here to make analysis with the compositional data easier. Since there was only one relatively low level of PPA used to obtain the modified binders evaluated for Figure 5, the impacts of PPA on asphaltenes and resins are not as easily observed as in the work by Arnold et al. but are still apparent. The data plotted in Figure 5 is shown in Tables 3 and 4. While it is easier to observe data patterns in Figure 5, the numerical details are more difficult to ascertain due to the complexity of the plot.

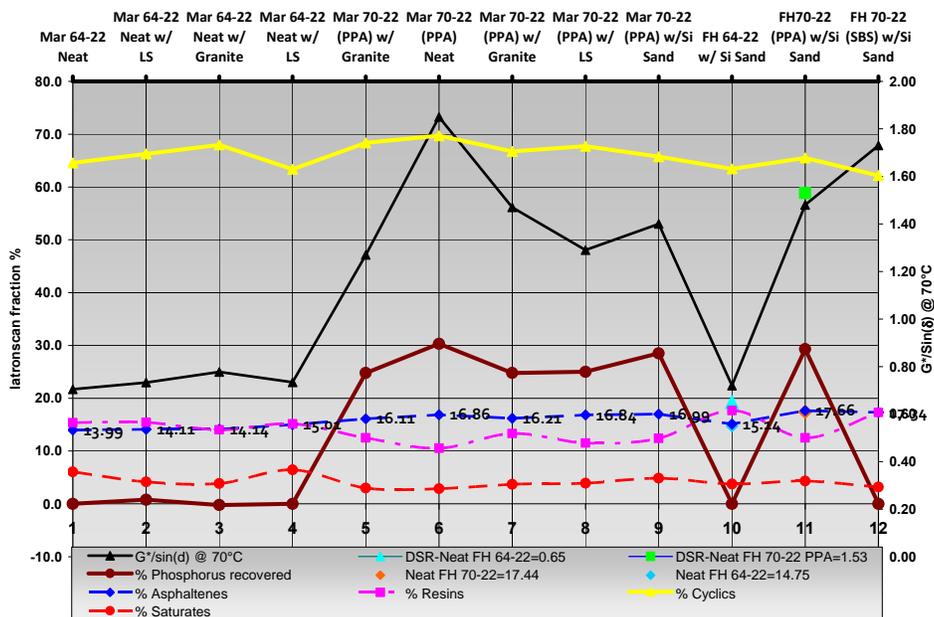


FIGURE 5 Summary of Iatroskan results of PG 64-22, PG 70-22 (PG 64-22 modified with PPA) and blends of those binders with granite, limestone, and silica sand.

TABLE 3 Asphaltene, Iatroskan, and DSR Data

Blend Description	Mar 64-22	Mar 64-22	Mar 64-22		Mar 70-22	Mar 70-22	Mar 70-22
	Neat	Neat w/ LS	Neat w/ Granite	Mar 64-22 Neat w/ LS	(PPA) w/ Granite	(PPA) Neat	(PPA) w/ Granite
Sample number	127 A	126 D	127 C	127 B	126 A	126 B	126 C
% Asphaltenes	13.99	14.11	14.14	15.00	16.11	16.86	16.21
% Resins	15.39	15.45	14.02	15.17	12.52	10.56	13.34
% Cyclics	64.55	66.27	67.97	63.38	68.36	69.71	66.75
% Saturates	6.07	4.17	3.87	6.45	3.01	2.87	3.70
G*/sin(δ) @70°C	0.70	0.73	0.78	0.73	1.27	1.85	1.47

TABLE 4 Asphaltene, Iatroskan, and DSR Data

Blend Description	Mar 70-22	Mar 70-22	FH 64-22	FH70-22	FH 70-22	FH 64-22	FH 70-22
	(PPA) w/ LS	(PPA) w/Si Sand	w/ Si Sand	(PPA) w/Si Sand	(SBS) w/Si Sand	FH 64-22	PPA
Sample number	128 A	132A	133B	133A	133C	NEAT AC	NEAT AC
% Asphaltenes	16.84	16.99	15.14	17.66	17.34	14.75	17.44
% Resins	11.52	12.42	17.67	12.5	17.31	15.65	11.51
% Cyclics	67.73	65.73	63.42	65.5	62.17	65.88	66.45
% Saturates	3.91	4.86	3.77	4.34	3.18	3.72	4.6
G*/sin(δ) @70°C	1.29	1.4	0.72	1.48	1.73	0.65	1.53

Reinke et al. (10) have shown that when the asphalt is extracted from mixtures produced with PPA-modified binders, less than 100% of the phosphorus is recovered in the binder. They also demonstrated that when nonacid scavenging solvents such as toluene are used to extract PPA-modified binders from mixtures, the recovered binder stiffness is comparable to the binder stiffness at the time of mixing, making some allowance for age hardening of the binders during the mixing process. Based on those studies the amount of phosphorus recovered appears to be highly dependent on the type of aggregate used in the mixture and somewhat dependent on the type of solvent used. In the data currently under discussion in Figure 5 there has been no extraction and yet the resident phosphorus contents in the liquid asphalt above the aggregate covers a range of more than 20% reduction to nearly no reduction compared to the neat PG 70-22. The reduction in resident phosphorus appears to be highly aggregate dependent. The DSR stiffness values of these binders are also reduced by varying amounts with a reasonable correlation between phosphorus reduction and reduction in DSR stiffness (Figure 4). The reduction in DSR stiffness should not have occurred based on aggregate chemistry in the case of the granite and silica sand, and based on reports (3, 5, 10) there should have been no significant reduction of DSR stiffness with the limestone aggregate. The reduction in resident phosphorus and the decrease in stiffness imply that acid functionality was in some manner removed from the binder, although neutralization does not appear to be the mechanism based on previously cited work. Giavarini et al. (11) and Orange et al. (12) identified the use of PPA as a mechanism for increasing the n-heptane insolubles in asphalt; as can be seen from the data in Tables 3 and 4, there is a 2.87% increase in n-heptane insolubles between the PG 64-22 the PG 70-22 for the Marathon asphalt and a 2.3% increase for the Flint Hills binders. These n-heptane insoluble levels remain fairly constant for all the aggregate asphalt blends produced with the two PG 70-22 binders. At this point there is no adequate explanation for these results. If neutralization of acid functionality had occurred there should have been a concomitant reduction in n-heptane insolubles and there was not. The moderate correlation between percent phosphorus in the binder and the DSR stiffness is not very reliable considering the sparseness of the data set. Even if the correlation could be shown to hold up with additional data, a sound mechanism linking the reduction in the resident phosphorus in the liquid asphalt to the reduction in DSR stiffness is lacking. A sound mechanism must take into account not only the reduction in resident phosphorus and the loss of acid functionality implied by that reduction, but must also account for the level of n-heptane insolubles in the binder, which are also intimately tied to the acid functionality in the binder. Finally, for such mastic-like mixes the binder must be extracted from a variety of aggregates and PPA prepared binders, and then the phosphorus content, DSR stiffness and compositional values of the asphalt would need to be determined.

MOISTURE SENSITIVITY AND PERMANENT DEFORMATION TESTING OF PPA-MODIFIED MIXTURES

Impact of Different Aggregate Types and PG Binder Grades on Submerged Hamburg Wheel Tracking Tests at 50°C

One of the major areas of concern with respect to the use of PPA-modified binders has been the moisture sensitivity of mixtures produced with those binders.

In a study conducted at MTE, limestone, crushed gravel, and granite mixtures conforming to requirements for 1 million (E-1) and 10 million (E-10) ESAL pavements were investigated for moisture sensitivity using the Hamburg wheel tracking test performed at 50°C submerged in water. Seven binders were investigated: PG 58-28 unmodified, PG 64-28 modified with only PPA, PG 64-28 modified with PPA and containing 0.5% of a phosphate ester antistrip, PG 64-34, PG 64-28, and PG 70-28—all modified with varying levels Elvaloy polymer plus 0.3% PPA, and a PG 76-22 modified with SBS polymer and 0.3% PPA. Rut depth results for E-1 mixes and E-10 mixes at 10,000 wheel passes are shown in Figure 6.

The immediate observation is that for all of the binders the E-1 mixes had greater rutting than the E-10 mixes, which is not unexpected. Within these categories the PG 64-28 PPA modified had approximately the same rutting response as the PG 58-28 control for all aggregate types. However, the PG 64-28 PPA modified binder containing the phosphate ester antistrip had significantly less rutting in this test than did the binder without antistrip. Also the PG 64-28 polymer modified binder compared to the PG 64-28 PPA plus antistrip exhibited less rutting at 10000 passes for all aggregates and mix types except for the E-1 granite mix. The two highly modified binders, PG 70-28 and PG 76-22, both performed extremely well with all aggregates and mixes, but this was anticipated given the high polymer loading. Lastly, the PG 64-34 displayed more rutting than the PG 64-28 polymer modified binder, even though the PG 64-34 contained approximately 50% more polymer. This type of response has been seen in other studies (13) and appears to be more a consequence of the low stiffness modulus of the PG 52-34 base binder used to produce the PG 64-34 than due to any other factor.

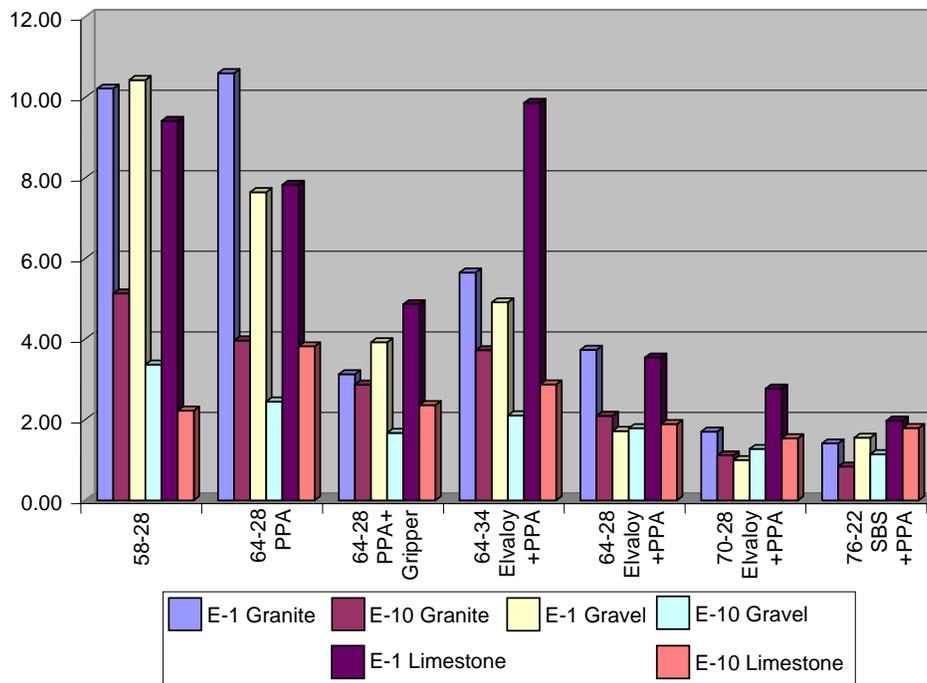


FIGURE 6 Rut depth at 10,000 wheel passes in the Hamburg wheel tracking test, 50°C, submerged samples.

Figures 7 and 8 are plots of the rutting passes to 12.5 mm of rutting for the E-1 and E-10 mixes respectively. All of the E-10 mixes would meet the Hamburg moisture sensitivity requirement for the State of Texas and all but the PG 64-28 PPA modified E-1 mix would meet those requirements as well. It is interesting that the PG 64-28 PPA plus phosphate ester antistrip and the PG 64-28 polymer-modified binders both reached the full 20,000 rut passes before reaching 12.5 mm of rutting, although as noted in Figure 6 the rutting rate for the PPA-plus antistrip mix was somewhat higher.

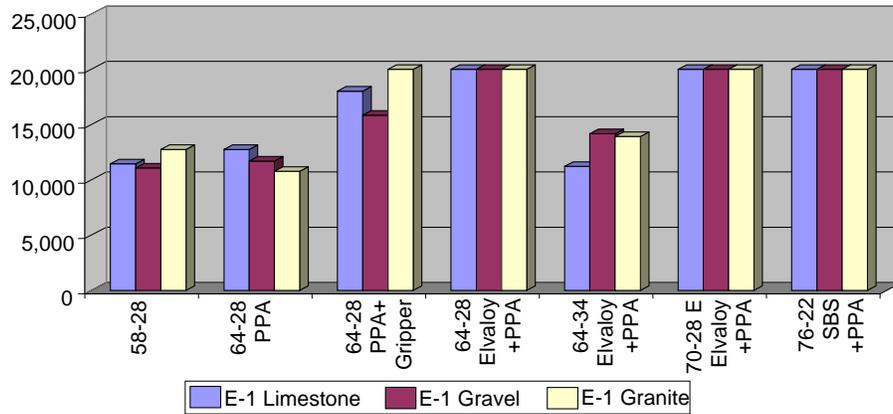


FIGURE 7 Rut passes to 12.5-mm limestone, gravel, and granite E-1 ESAL mixes in the Hamburg wheel tracking test, 50°C, submerged samples.

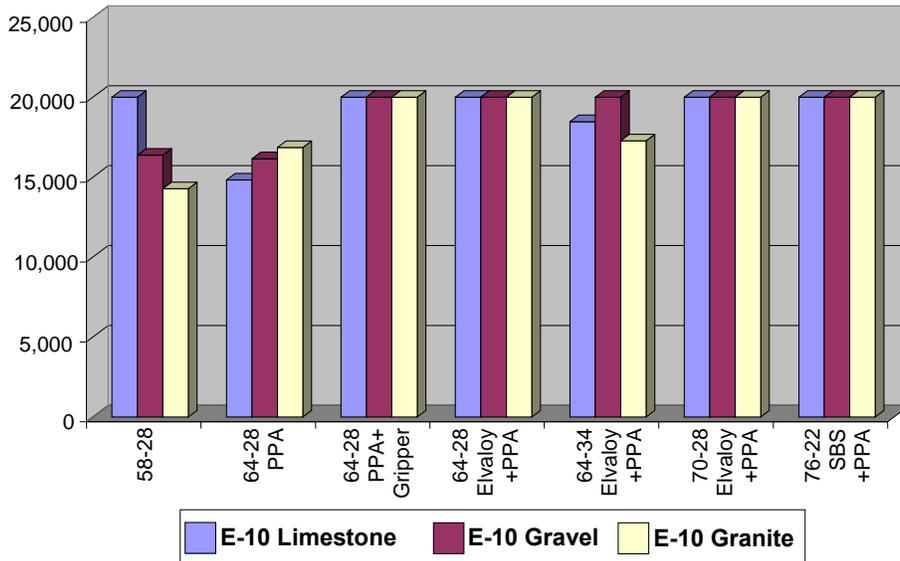


FIGURE 8 Rut passes to 12.5-mm limestone, gravel, and granite E-10 ESAL mixes in the Hamburg wheel tracking test, 50°C, submerged samples.

Moisture Sensitivity Testing of PPA-Modified Binders Using an Aggregate Highly Susceptible to Stripping

A moisture sensitivity study was undertaken at MTE on behalf of ICL Performance Products, a manufacturer and supplier of PPA. A single PG 64-22 control asphalt from the Marathon Detroit refinery was chosen as was an aggregate blend from a Minnesota quarry that has a history of moisture sensitivity issues. Several binders based on this control asphalt were tested for Hamburg wheel tracking moisture sensitivity and TSR as per AASHTO T283. The binder blends tested are shown in [Table 3](#).

The Hamburg Wheel Tracking results at 50°C submerged are shown in [Figure 9](#). The results in Figure 9 show a progressive improvement in mix moisture sensitivity performance progressing from the poorest performer, the PG 64-22 control binder. As mentioned previously the aggregate used in this study has a history of being moisture sensitive and was chosen specifically for this investigation based on this quality. The PG 70-22 manufactured with PPA produced only a minor improvement in performance over the control binder. The addition of each phosphate ester antistriper to the PG 64-22 further improved the binder performance to the point where the mix would have acceptable moisture resistance properties. The addition of phosphate ester antistrippers to the PG 70-22 PPA binder further improved performance with phosphate ester #1 showing a much better improvement over #2. Finally the addition of hydrated lime to the PG 70-22 PPA-modified binder had the best performance, while the addition of hydrated lime to the PG 64-22 control yielded performance results comparable to the PG 70-22 PPA blend plus phosphate ester #1. It is worth noting at this point that despite research showing a reaction between PPA modified binders and hydrated lime (1, 5) the addition of hydrated lime to the mixes produced with the PG 70-22 showed no detrimental effects related to mixture moisture sensitivity.

In a companion study some of the same binders from [Table 5](#) were tested for TSR according to AASHTO T 283 using the same Fabian aggregate. These results are shown in [Figure 10](#). The control PG 64-22 had a very low TSR value of 53.9% and the addition of hydrated lime improved the TSR to a barely passing 70.9%. The PG 70-22 PPA binder also failed the TSR test, with only a moderate improvement over the PG 64-22. The addition of hydrated lime to the PG 70-22 improved the TSR to a passing, although not spectacular, result of 74.3%. The last set of data in Figure 10 is based on a PG 70-22 straight run binder produced by Marathon that also showed improvement with the addition of hydrated lime.

TABLE 5 ICL Binder Blends

Blend	Blend Formulation	Mix Additives
PG 64-22 control	No additive	
PG 64-22 + antistriper	0.5% phosphate ester #1	
PG 64-22 + antistriper	0.5% phosphate ester #2	
PG 70-22 PPA	PG 64-22 + 0.75% PPA	
PG 64-22	No additive	1% hydrated lime in mix
PG 70-22 PPA	0.5% phosphate ester #1	
PG 70-22 PPA	0.5% phosphate ester #2	
PG 70-22 PPA	0.75% PPA	1% hydrated lime in mix

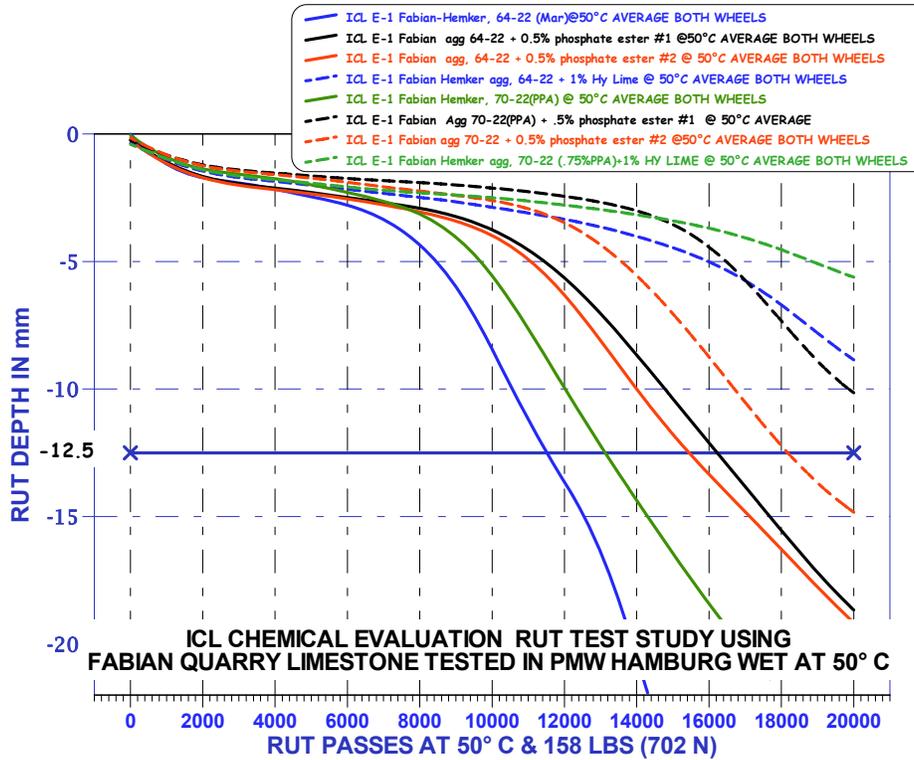


FIGURE 9 Hamburg wheel tracking test, 50°C, submerged samples for ICL mixes with Fabian Hemker aggregate (a known stripper).

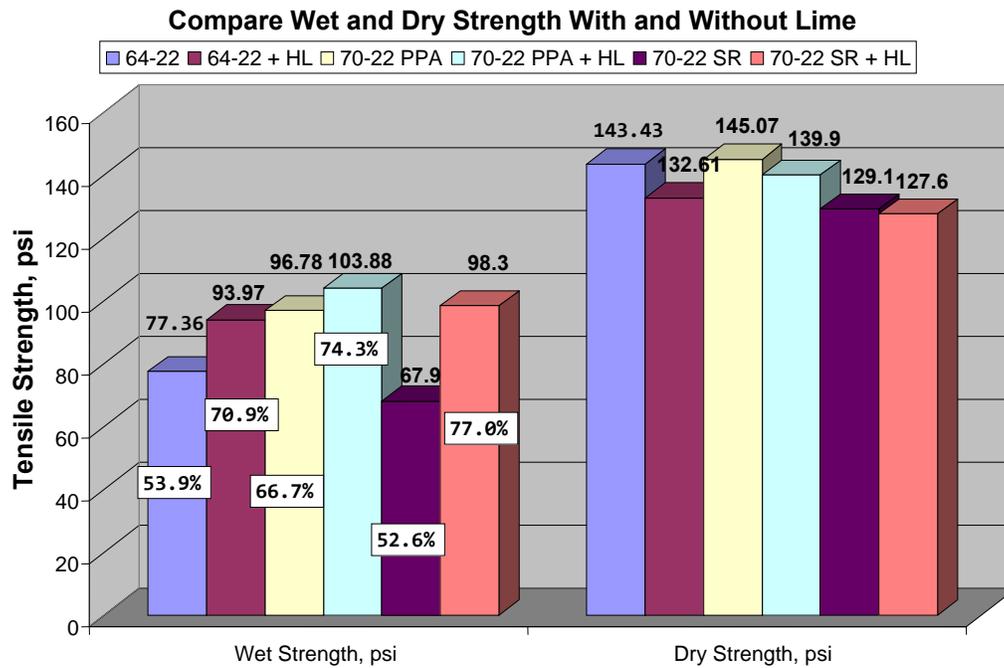


FIGURE 10 T-283 tensile strength and TSR results for ICL mixes with Fabian Hemker aggregate (a known stripper).

Concerns have been raised about the potential for neutralization of some acid functionality in PPA-modified binders due to the use of limestone aggregates and the use of hydrated lime in mixtures. Studies where these mineral materials have been blended with PPA modified binders (1, 2) show that such partial neutralization can occur; however such model investigations are not the same as recovering binder from well-graded bituminous mixtures. To investigate this potential issue, binders were extracted from several of the PG 70-22 PPA-modified binder mixes reported in Figures 9 and 10. Figure 11 summarizes the DSR stiffness of the recovered binder data from several of the Hamburg and TSR test specimens. The original DSR and RTFO stiffness values of the PG 70-22 are shown. In all cases the stiffness of the binders recovered from the TSR and Hamburg test specimens with and without hydrated lime is greater than the RTFO stiffness of the PG 70-22 binder. The lowest recovered stiffness value is for the binder recovered from the unsoaked hydrated lime TSR specimen. The soaked hydrated lime TSR specimens had values well above the 2.2 kPa RTFO stiffness value.

Figure 12 is a comparison of the onset of stripping in the Hamburg wheel tracking test for several Fabian aggregate mixes produced with PG 64-22 and PG 70-22 PPA binders. The neat PG 64-22 and PG 70-22 binders have nearly identical values as do the neat binders used with mixes containing hydrated lime. The phosphate esters improve the stripping onset point for both the PG 64-22 and the PG 70-22 binders relative to the untreated neat binders. Finally the use of amine additive, Redicote E-6 performed as well as phosphate ester #1 and nearly as well as phosphate ester #2 even with the PPA modified binder. Figure 13 shows additional stripping onset data for the PG 70-22 PPA binder and also PG 70-22 binders produced with 2% SBS, 1% Elvaloy-plus 0.3% PPA, and 1% SBS-plus 0.3% PPA and another set of data for all of those binders mixed with the Fabian aggregate plus 1% hydrated lime. It is interesting that with this particular aggregate the PG 70-22 PPA control mix performed nearly as well as the 2% SBS and the 1% SBS + PPA binders prior to the addition of 1% hydrated lime to the mix. The 1% Elvaloy + PPA binder exhibited comparable performance for stripping onset with and without hydrated lime.

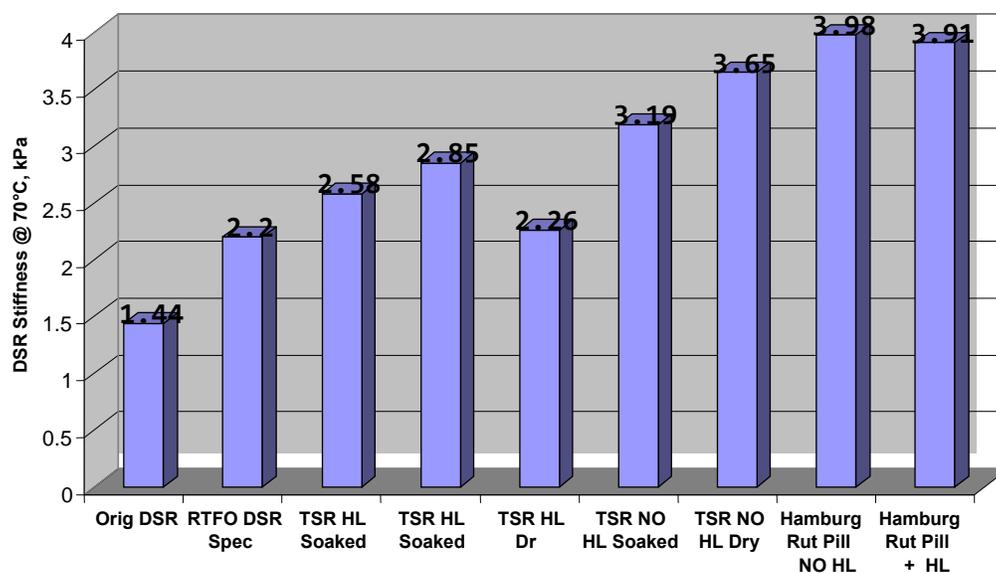


FIGURE 11 DSR stiffness results of binders recovered from TSR and Hamburg specimens of ICL mixes.

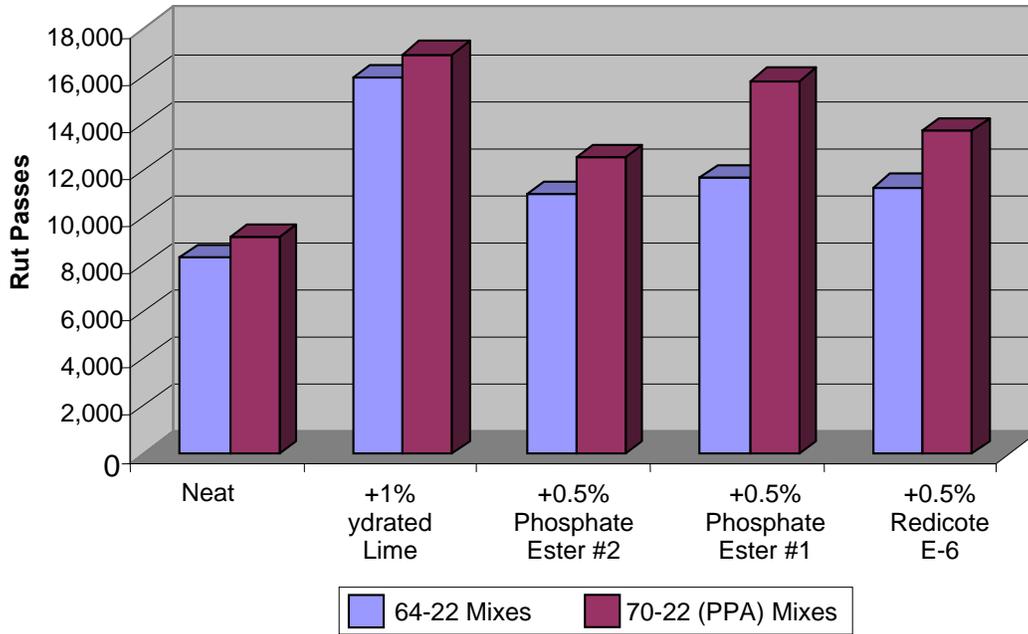


FIGURE 12 Onset of stripping values for hydrated lime, phosphate ester, and redicote E-6 mixes with Fabian Hemker aggregate.

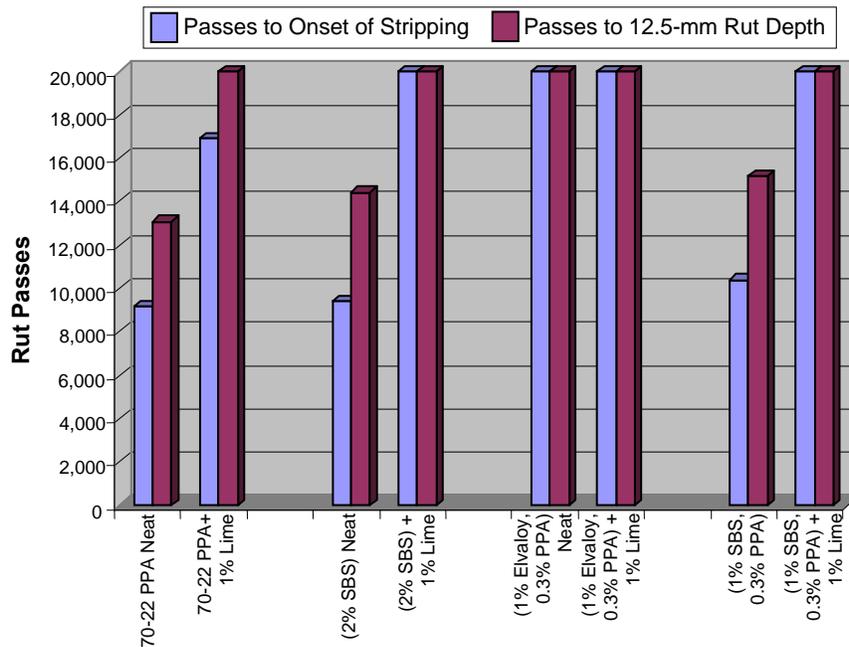


FIGURE 13 DSR onset of stripping and rut passes to 12.5-mm rut depth for ICL mixes produced with PG 70-22 PPA only, 70-22 SBS only, 70-22 Elvaloy + PPA, and 70-22 SBS + PPA.

Evaluation of Permanent Deformation Characteristics of Mixtures Produced with PPA-Modified Binders

In addition to the moisture sensitivity results shown in Figures 6 through 10, dry Hamburg testing of the same mixes was performed. This testing was conducted over a range of temperatures, but only the results at 64°C are presented in this paper. Figure 14 is a direct comparison to the results shown in Figure 6 with the exception that Figure 6 is the submerged Hamburg test results at 50°C and Figure 14 is the data for the 64°C dry tests. Both plots show rutting data at 10,000 wheel passes, but the rut depth scale for the 64°C tests is noticeably higher than that of the 50°C plot. In relative terms however, the dry rutting results for the E-1 mixes are generally more similar to the results for the E-10 mixes than are the results of the E-1 and E-10 mixes tested wet. The main exception is the results of the dry PG 58-28 mixes, which exhibit more rutting because those mixes are being tested above the upper grade temperature of the binder. For all of the mixes, except for the highly polymer modified PG 70-28 and PG 76-22, the E-1 granite mix appears to be the most sensitive to rutting at 64°C.

Granite aggregate is the least absorptive of the three aggregates and also has the highest effective binder content, which probably plays a role in the rutting behavior of this aggregate with the PG 64 grade binders. The three PG 64-28 grade binders had similar rutting results at 10,000 wheel passes for each of the aggregate types and blends, although overall the PG 64-28P (polymer blend) had less rutting than the two PPA-only blends. Whereas the PG 64-28 PPA plus antistrip had much better submerged Hamburg results compared to the PG 64-28 PPA-only

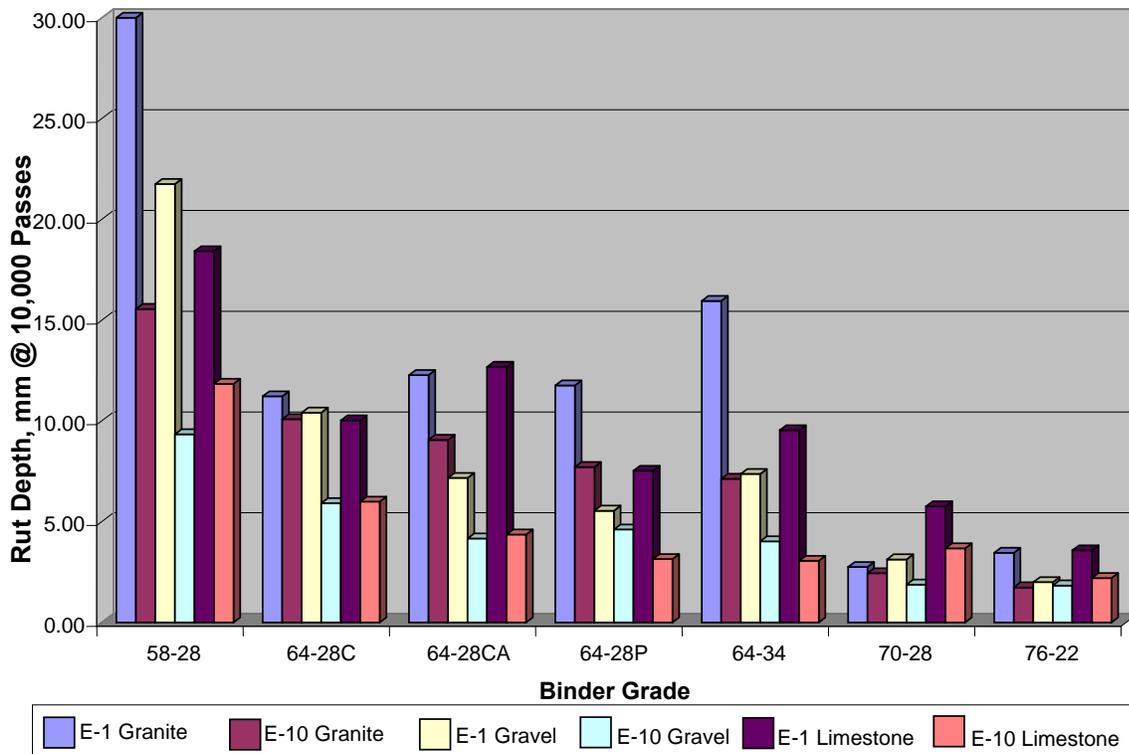


FIGURE 14 Dry Hamburg results at 64°C and 10,000 wheel passes for granite, gravel, and limestone aggregates for seven binders.

mixes, the performance between those two binders in the dry test is similar. Figures 15 and 16 are a closer look at the wet and dry Hamburg performance of the PG 64-28 PPA plus antistrip (Figure 15) and PG 64-28 PPA (Figure 16). The advantage of the phosphate ester antistrip is apparent in the submerged Hamburg performance for all binders including the PG 70-28 and PG 76-22. These figures show that the impact of the antistrip on the rutting behavior dry at 64°C is not as marked as the impact on the submerged test performance at 50°C.

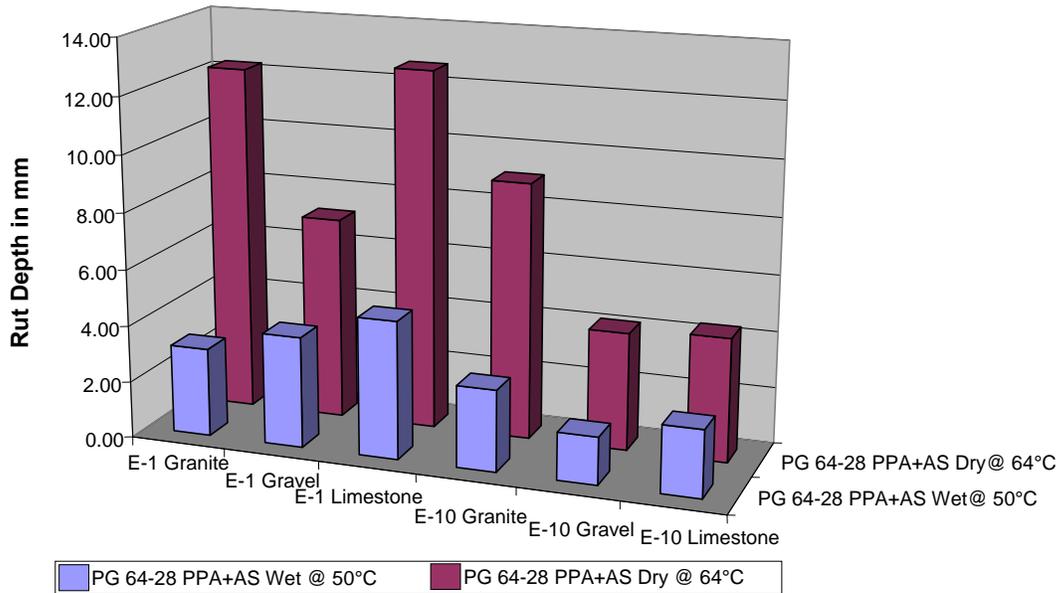


FIGURE 15 Compare rut depth at 10,000 wheel passes for PG 64-28 PPA-plus phosphate ester antistrip wet and dry Hamburg wheel tracking tests.

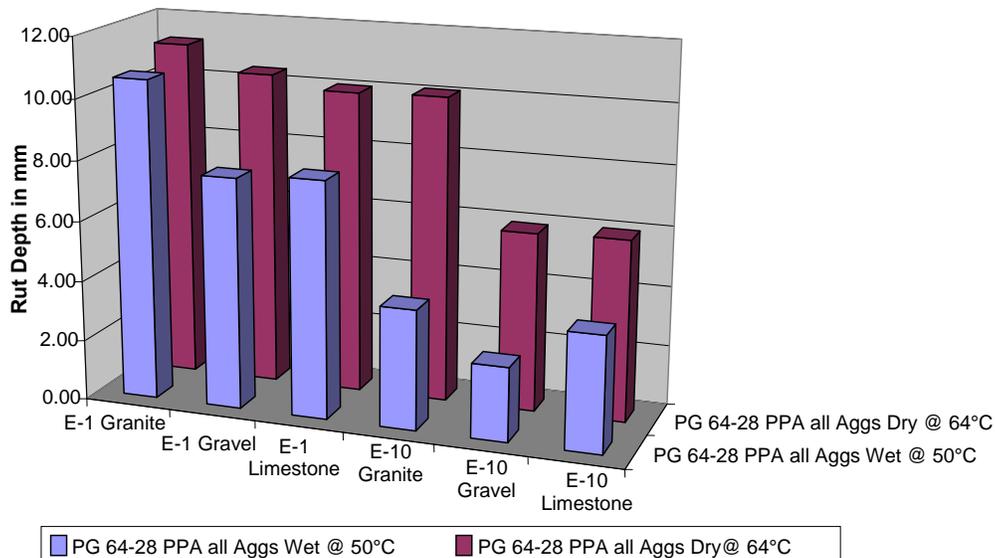


FIGURE 16 Compare rut depth at 10,000 wheel passes for PG 64-28 PPA wet and dry Hamburg wheel tracking tests.

CONCLUSIONS AND DISCUSSION

Interactions of PPA containing binders with aggregates appear to be complex and varied. There have been numerous studies (1,2,5) investigating blends of amines, hydrated lime, aggregate fines, and other alkaline chemicals and their ability to neutralize the stiffness increases resulting from the addition of PPA with asphalt. There is no doubt that processes detailed in these studies will result in a reduction in the stiffness increase due to the addition of PPA. The information reported in this paper has been intended to illuminate what actually happens when PPA modified binders are blended with typical aggregates and when the resulting paving mixtures are tested.

The results of blending PPA modified binders with aggregates of different chemical composition and then testing the liquid asphalt after aggregate settlement has, to the knowledge of the authors, not been reported in the literature previously. This work has raised questions as to the mechanism of interaction of PPA modified binders with aggregates. Previous work¹⁰ has shown that even when less than 100% of phosphorus in the binder is recovered through solvent extraction the recovered binder stiffness is in line with expectations. Recovered binder stiffness data shown in Figure 14, from a limestone aggregate, also demonstrates that there was not a loss of stiffness for PPA modified binder. Recovered phosphorus content was not determined for those samples, primarily because foregoing work (10) had shown that 100% phosphorus recovery is not obtainable via solvent extraction of mixtures. At present the authors are not aware of a mechanism to explain the aggregate/binder behavior summarized in Figure 5. There is nothing in any previous work to suggest that phosphorus content in the binder is directly related to binder stiffness and therefore the data summarized in Figure 5 suggests that both acid functionality and phosphorus have bonded to the aggregate when it settled out of the bulk aggregate and liquid blend thus resulting in the reduced binder stiffness values measured. It is unlikely that the PPA modifier or fractions of asphalt reacted with PPA settled out of the asphalt based on unpublished research conducted at MTE. This research has shown that binders modified with PPA do not separate when maintained at 163°C. Blends with concentrations up to 2.5% were tested at four intervals over a period of 12 days for separation using the standard “cigar tube” technique employed for polymer modified binders (ASTM D7173). Percent phosphorus was checked for upper and lower portions of the tubes and also the bottom 6 mm of the tubes and no changes in phosphorus concentrations were found. Further investigation into the mechanism by which the resident phosphorus concentration and the DSR stiffness of the supernatant asphalt binder decreased in the presence of aggregate is suggested.

The moisture sensitivity and Hamburg wheel tracker testing leads to several conclusions:

1. For the single, highly moisture sensitive aggregate investigated, hydrated lime improved the moisture sensitivity of all mixes regardless of the use of PPA in the binder. This improvement is measurable by submerged specimen Hamburg wheel tracker testing at 50°C and by conventional AASHTO T 283 TSR testing.
2. Phosphate ester antistrips in the studies reported always improved the submerged Hamburg performance regardless of the presence of PPA in the mix and regardless of the aggregate type being investigated.
3. For the moisture sensitive aggregate investigated for ICL, only the Elvaloy + PPA mix performed as well with and without hydrated lime. The SBS and SBS + PPA mixes required the addition of hydrated lime to achieve superior submerged Hamburg performance.

4. The PG 64-28P produced with polymer and PPA (Figure 6) showed better submerged Hamburg performance with all aggregate types than just the PG 64-28 produced with PPA modification alone. The submerged Hamburg results for PG 64-28P were better than those for PG 64-28 produced with PPA modification plus phosphate ester antistripping for all aggregates and mix types except for the E-1 granite mix.

5. Within the context of this study the three PG 64-28 binders exhibited similar dry Hamburg rutting performance when tested at 64°C with all aggregate types and mix levels being investigated (Figure 9). The PG 64-28P exhibited slightly better rutting performance than those mixes produced using only PPA modification.

6. PPA modification alone is not equivalent to polymer modification in terms of resistance to moisture sensitivity and rutting.

7. The use of PPA in conjunction with polymer modification can enhance mixture performance, especially when used in conjunction with a coarser aggregate structure

ACKNOWLEDGMENTS

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NOTE

This paper was also presented at the Association of Asphalt Paving Technologists Symposium on Polyphosphoric Acid Modification and is included in *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 79, 2010. AAPT gave permission to include it in this document.

Binder Modification with Combination of Polyphosphoric Acid and Styrene-Butadiene-Styrene

National Center for Asphalt Technology Test Track Experience

DON WATSON

National Center for Asphalt Technology

JOHN A. D'ANGELO

Federal Highway Administration

The NCAT maintains a 1.7-mi-long oval test track just outside Auburn, Alabama. The initial construction in 2000 was to provide a uniform perpetual foundation on which materials and mix designs for the asphalts layers to be unique to each section. There are 46 200-ft-long test sections incorporated into the track. The sections were to be trafficked for 2 years with 10 million load applications.

The 2000 NCAT test track cycle was primarily an evaluation of different Superpave mixes and aggregate types to evaluate rut resistance. Various types of aggregates were used in the mix designs, including limestone, slag, gravel, granite, and marble schist. This was not a binder experiment, so only one binder source and two grades, a PG 67-22 and a PG 76-22, were used. The binder source was from Venezuelan crude. This binder was modified with 3.5% SBS, 0.25% PPA, and 0.05% amine antistripping. The PPA-modified PG 76-22 binder was used on 18 sections of the 2000 test track.

The 2003 NCAT test track cycle allowed for more variety in the types of experiments than the 2000 track. In 2003 the track sponsors elected to leave 18 of the existing sections for extended trafficking. Of these sections nine contained the PPA SBS PG 76-22. An additional nine test sections had a thin mill and fill using the PPA SBS PG 76-22. The 2003 binder was from the same source and had the same formulation as the binder used in the 2000 cycle.

The loading at the track is done using tractors pulling triple trailers with typical axle loads of 20,000 lbs. There are three triple tractor-trailer vehicles and one standard tractor-trailer with the standard 34,000-lb dual axles. This configuration allows for the application of 10 million ESALs in a 2-year time period.

The performance at the track over the two loading cycles has shown excellent performance and no indication that the PPA SBS-modified asphalt has caused any distress. During the first loading cycle the maximum rutting in any of the PPA sections was less than 5 mm. For the sections that were left in place for the second loading cycle up to the 20 million ESALs, the maximum rutting was less than 6 mm total. There was no indication that the limestone aggregate or amine antistripping neutralized the PPA in the binder. Several sections also had hydrated lime in the mixture and again there was no indication that it affected the binder.

Except for the actual structural design evaluation sections, where fatigue cracking was designed to happen, there was almost no fatigue cracking at the track. There was some longitudinal top-down cracking that did occur in the polymer-modified test sections at the track, but only one was a combination PPA SBS-modified section. This was the coarse-graded gravel mix with low binder content.

The NCAT track does experience significant rainfall. All the mixes used at the track were tested to evaluate the potential for moisture damage and either liquid amine antistripping, hydrated lime, or both were used in all the mixes. There has been no indication of moisture damage on any of the PPA SBS-modified test sections even in cases where these sections have been in place for more than 6 years.

Overall the performance of the PPA SBS-modified binder at the NCAT test track has been excellent. There is no indication that the PPA has been neutralized by limestone, amines or hydrated lime. Moisture damage has not been a problem. The sections with PPA have all performed very well with little rutting and almost no fatigue.

Modified Asphalt Cement Use in Arkansas

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Arkansas has a long history using polymer-modified asphalt binder. As far back as 1981 Arkansas was using SBR, SBS, and SB polymers in asphalt at 3%. In 1995, the Superpave binder specification was adopted for use. The typical grades for use were PG 64-22, PG 70-22, and PG 76-22. The PG 70-22 could require modification to meet grade and the PG 76-22 would typically require modification to meet grade.

Arkansas has an extensive Interstate system that includes I-40 and I-30, for east and west routes, and I-55 for north and south. Spurs such as I-540 and I-530 are also part of the system. Much of the Arkansas system was constructed in the late 1960s or early 1970s and has had over 40% truck traffic on much of the system. By the late 1990s much of the system was nearing the end of its service life.

A plan was initiated in 1999 to reconstruct most of the existing Interstate system over 5 years from 2000 to 2005. The plan included rubblizing 276 mi of portland cement concrete (PCC) and covering with full-depth hot-mix asphalt (HMA) and polymer asphalt concrete (AC). Mill and inlay would be done on 64 mi using polymer AC and 40 mi would be reconstruction of PCC. This plan included 340 mi of new surfacing, all of which would have polymer-modified binder PG 76-22. The total program cost was \$950 million and was completed by the end of 2005.

The typical section for the rubblized concrete was 4.75 in. of base course, 3 in. of intermediate course, and 4 in. of surface mix. The binder in each layer was polymer-modified. The reconstruction program placed 7.2 million tons of HMA on the 370 mi of Interstate. This amounts to 320,000 tons of PG 76-22 used in the construction. A major portion of the PG 76-22 placed was an SBS-PPA combination.

The performance of the system to date has been excellent. In 1999 37% of the system had a poor international roughness index (IRI) of greater than 170 in./mi and 33% had a mediocre IRI rating of 120 to 170 in./mi. As of 2006, after completion on the rehabilitation program, more than 73% of the Arkansas Interstate system is in good condition with an IRI less than 95 in./mi. The Arkansas pavement management system projects the 2016 condition rating to be 53% in good condition if no additional work is done. There have been only very minor distresses on individual projects not related to the binder. Overall the PPA SBS-modified PG 76-22 has performed exceedingly well for more than 10 years with no distress attributed to the binder.

Polyphosphoric Acid–Modified Asphalt Cement

Ontario Perspective

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Different techniques, such as air blowing and polymer modification, have been developed to modify AC to improve the high-temperature characteristics. Among these methods, chemical modification using PPA (an inorganic polymer modifier), although not new, has gained popularity in recent years partly because it is an economical way of modifying AC.

While this technology has provided an economic edge over the other methods used to increase the high-temperature properties, the potential problems associated with the use of such method may offset the benefits it offers. User agencies like the Ontario Ministry of Transport (MTO) are left in a position to protect their interests and to decide how best to manage the use of PPA to ensure that jurisdictions are not building less than optimum quality pavements.

ACTION PLAN

A six-step plan was developed to help the ministry address the concerns with the goal of balancing the benefits with the risks:

1. Conduct environmental scan;
2. Identify issues, concerns, and benefits;
3. Consult with industry;
4. Develop a risk management plan;
5. Specify revision and implementation; and
6. Monitor and review options.

ENVIRONMENTAL SCAN

An extensive review was conducted on available information to determine the extent of the problem and to learn what other jurisdictions were doing to address the concerns. This was done so as to assist us in answering the fundamental question of do we need to take any actions or alternatively determine if our concern warrants any actions.

Information reviewed showed that DOTs experienced pavement failures due to PPA and questionable performance was raised by some reports. Numbers of DOTs were banning the use of PPA. An MTO survey through AASHTO in 2006 showed that 18 states (or 58% of states surveyed) did not allow the use of acid-modified binders. This confirmed the survey results obtained a year earlier by the Nebraska DOT. There were four DOTs (13%) with conditions attached to PPA use, whereas nine others (29%) allowed its use.

Locally, Ontario experienced a number (some 20 contracts in 2004) of unexplained poor performances such as rutting, flushing, instability, and cracking that might be linked to acid-

modified PG AC. An estimate was made that 50% of our annual mix tonnage was potentially impacted by PPA with lime and ASA (antistrip additives).

Comments from questions to suppliers on concerns of restricting use and the negative impacts on use of acid-modified PG AC in ministry contracts confirmed most of the issues reported. It was revealed that 1% of PPA can increase the high temperature by 9°C and lower the low temperature by 1°C. Eleven out of 13 suppliers did not supply acid-modified AC in Ontario, with some strongly opposed to its use.

The review showed that overall some form of restriction was needed to limit the use of PPA, and options ranging from a total ban to conditional use had been implemented by other DOTs.

IDENTIFYING ISSUES/CONCERNS/BENEFITS

The use of PPA in modifying asphalt is known to have negative effects on the asphalt pavement performance, causing rutting and premature cracking. The acid in the AC can degrade in terms of reducing the high-temperature grade and hence can increase the potential of rutting. This is particularly so when combining with other components such as some liquid antistripping additives, hydrated lime, and limestone aggregates. However, it has been also reported that it works at certain low dosages in increasing the high-temperature grade or as a catalyst to enhance polymer modification with no negative side effects.

Premature aging of the AC is of particular concern because the acid increases the level of asphaltenes in the asphalt that simulates the aging process under natural service environment; this is considered to have accelerated the aging leading to premature cracking of pavements. Statements from five papers below have raised the concern of using acid in modifying AC.

1. The paper by Giavarini et al. (1) raises the following concerns:
 - "...the increase of the asphaltene/resin ratio of the modified residue produces changes in the network structure. This alters the properties of the residue to either a 'gellike' behaviour or a destabilized product which, under certain conditions, may flocculate" (p. 498).
 - "...the polycondensed aromatic structures act as reducing agents for the (HPO₃)_n, they being oxidized to more aromatic and substituted structures. Because of the oxidation process some resins will be separated as asphaltenes as well as some saturates and aromatics will constitute part of the resins" (p. 499).
2. The paper by Ajdeh et al. (2) raises the following similar concern: "...aging affects the creep and recovery properties of the chemically modified binders very significantly. There is a concern that the changes were too high because they are higher than what is commonly seen for binders" (p. 63).
3. Dongré and Bouldin (3) again raise a similar concern: "...we found that upon storage the phosphate reacted as a strong oxidizing agent and degraded the polymer and most likely the asphalt" (4) (www.petersenasphaltconference.org).
4. Miknis (4) raises the following concern: "...over time the number of phosphorous atoms in the middle and end groups decreased, indicating a preference of polyphosphoric acid to revert back to the orthophosphate (i.e., H₃PO₄ – form) in the presence of asphalt" (www.petersenasphaltconference.org).

5. Ho et al. (5) raise the following concern: "...It is apparent that after polyphosphoric acid was neutralized by lime the formation of asphaltenes was reversed. At the same time, the physical characteristics as manifested by both the high-temperature and low-temperature properties started to reverse. ...alkaline materials, such as lime or amine-type antistripping agents, were able to undo the changes caused by acid modification" (p. 168).

The concerns and benefits are summarized below:

1. Concerns: PPA can neutralize or reverse the effects of ASA, especially the amine-based additives, and increase moisture damage. Thus any benefits may be negated on some of the aggregates. As phosphate ester ASA do not perform well with some Ontario siliceous aggregates that require ASA, none are permitted for use in Ontario. Hence, all Ontario liquid ASA are amine based. Gain in high-temperature grade may be reversed with added lime/amine ASA, resulting in pavement rutting. PPA can increase the viscosity of the AC by accelerating oxidation of the resin, reducing durability, and cracking resistance. Overall, 1% or more PPA can adversely impact hot mix performance.

2. Benefits: PPA can modify AC to improve high-temperature performance while there is minimum effect on low-temperature grading. Stiffening of AC could be beneficial for lower pavement lifts. It can also enhance moisture resistance. It is a more economical method to modify AC than using polymers. (However, this could give a cost advantage to modification using the acid-modified process as compared to those using more expensive materials, thus creating an uneven playing field for contract bidding.) A low dosage can be used effectively as a catalyst.

INDUSTRY CONSULTATION

A task group (TG) was formed to assist the ministry in developing options to address the issue of the use of PPA-modified AC. The TG consists of ministry and industry representatives from various stakeholders and suppliers.

The goal was to develop a plan of action to address the issue by reducing the risks of the owner on the use acid-modified AC without stifling the technology. Therefore, the goal was to risk manage the potential problems associated with inappropriate dosages used in the modification of asphalt in conjunction with other components.

The main focus of the TG was twofold: (a) what pavement distresses that PPA may cause in the long term, i.e., premature aging leading to cracking, grade reversion causing rutting, and nullification of the ASA effect leading to stripping, and (b) how agencies can mitigate the negative effects and restrict the use of PPA by means of specifications, protocols, or contract administration. The issue of available test methods for testing for acceptance was identified.

The issues and concerns mentioned above formed a framework for the TG discussion and to develop an action plan and solutions.

DEVELOP RISK MANAGEMENT PLAN

The approach was to look at issues and concerns such as those mentioned above that are most likely to pose risks when PPA is used to modify AC. Without sufficient knowledge to fully define what the exact level of risk associated with the dosage of acid in asphalt to be used is, we had to come to some consensus that could allow the use of acid but at a lower risk to the user agencies.

The backdrops were that acid modification of asphalt was an important enough issue that a number of state DOTs had taken action on it and some went as far as banning the use of such processes.

SPECIFICATION REVISION AND IMPLEMENTATION

Subsequent to a number of intensive TG meetings, ministry and industry came to the consensus that a number of checks and balances had to be built into our specifications and designated source manual (DSM) to manage the risks. The actions taken were divided into short-, medium-, or long-term plans:

Short Term

1. To include in the Non Standard Special Provision (NSSP):
 - a. The three grades of PG ACs (70-28, 70-34, 64-34) shall not be acid modified. These three grades of ACs are most often used with heavy-duty highway mixes like SMA (containing high percentage of limestone filler) and Friction Course (FC-2, especially dolomitic sandstone with hydrated lime). Acid-modified AC is defined as any AC that contains an acid dosage that is greater than 0.5% (permitting its use as a catalyst at this dosage).
 - b. MTO will audit ACs supplied to contracts.
 - c. Other grades of ACs for lighter traffic roads shall not contain acid greater than 1% for the purpose of increasing the high-temperature limit of the ACs.
2. To require contractors to work with suppliers to ensure that PG AC meeting the grade per contract requirements when liquid antistripping additive is added at the suppliers' depots.
3. To modify the DSM protocol requiring suppliers to declare in their quality control plan submission for the DSM that if their PG ACs contain acid, range of dosages, and compatibility with antistripping additives. Suppliers shall inform MTO of any changes made to their supplies on an ongoing basis.
4. To identify testing facilities that are available and cost estimates to run tests to check the presence of acid in PG ACs in paving contract samples.

Medium and Long Term

1. To continue compiling a list of contract information, especially the ACs and monitor and evaluate contracts with suspicious premature failures to determine if failures were related to acid modification.
2. To identify contracts, obtain samples and conduct audit testing.

3. To review all findings and policies and revise specifications when more information becomes available.

4. To forward issues that are not within the scope of the TG to MTO–Ontario Road Builders Association Hot-Mix Committee to address (e.g., all ACs shall meet grades at placement, irrespective of any additional mixing with components after leaving the AC suppliers' depots).

MONITORING AND REVIEW OPTIONS

As more information becomes available, including ministry study findings on problem sites, a complete review of options and revision of specs will have to be made.

As for the ministry, contract monitoring is continuing. Recent problem sites are being investigated. While some failures attributed to PPA modified AC are identified on those contracts prior to implementation of the revised specifications and protocol, it is suspected that there are fewer failures since the measures took effect.

Other monitoring work includes following up with the other developments and studies by FHWA, the Asphalt Institute, etc. The Asphalt Institute, FHWA, and other organizations are taking the subject to task and doing studies to understand more about the issue.

CONCLUDING REMARKS

MTO has taken a proactive role in tackling the issue especially since it generated such interest in the asphalt industry. We have been careful in making decisions that may have major impact on the Ontario asphalt industry by conducting our own survey to confirm the magnitude of the problem and consulting with the industry to come to a consensus on how to move forward with risk management of the issue. We believe that we have come up with a workable plan that is meeting our original goals. We have developed an action plan for both the short and medium to long term to address the concerns as we go forward. As well, limiting acid dosages to 0.5% and 1% has been a good compromise based on reliable information. As such, it will reduce the risks of possible failures that might be associated with the use of acid-modified ACs. The industry is fully on board and bought into this approach. Since the implementation of the revised specs, fewer failures are suspected as a result of using acid-modified AC.

The TG put a great deal of effort into arriving at the consensus. The contributions of industry representatives are acknowledged. While we can move forward with this plan with some sense of comfort, we will endeavor to keep up with new developments to further refine our approach to the issue and continue to consult with our industry representatives.

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Field Investigation of Polyphosphoric Acid–Modified Binders at MnROAD

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GERALD REINKE
MTE Services, Inc.

This paper provides details on the 2007 reconstruction of several cells on the Minnesota Road Research Project (MnROAD) low-volume road to support a study investigating the field performance of polyphosphoric acid (PPA)–modified binders. The project is the result of successful partnerships between the Minnesota DOT, private industry, and government agencies (FHWA and the Minnesota Local Road Research Board).

This paper documents the study background, test section construction, instrumentation, and initial laboratory test results of four different asphalt binders. The binder grade was PG 58-34 on all the test cells, which incorporated the following binder materials:

- 0.75% PPA only (Cell 33),
- 0.3% PPA + 1.0% SBS polymer (Cell 34),
- 2.0% SBS polymer only (Cell 35), and
- 0.3% PPA + 1.1% Elvaloy polymer (Cells 77-79; shared with fly ash study).

All of the laboratory tests to date show that the PPA-modified binder materials perform well, at the same level as polymer-modified binders. Rutting, fatigue cracking, and low-temperature cracking performance all appear to be acceptable based on laboratory asphalt binder and mixture testing. Early performance after one year of traffic also shows that the test sections are performing well with minimal rutting or cracking.

INTRODUCTION

MnROAD was constructed by the Minnesota DOT in 1990–1993 as a full-scale accelerated pavement testing facility, with traffic opening in 1994. Located near Albertville, Minnesota (40 mi northwest of St. Paul–Minneapolis), MnROAD is one of the most sophisticated, independently operated pavement test facilities of its type in the world. Its design incorporates thousands of electronic in-ground sensors and an extensive data collection system that provide opportunities to study how traffic loadings and environmental conditions affect pavement materials and performance over time. MnROAD consists of two unique road segments located parallel to I-94:

- A 3.5-mi mainline Interstate roadway carrying live traffic averaging 28,500 vehicles

per day with 12.7% trucks.

- A 2.5-mi closed-loop low-volume road carrying a MnROAD-operated 18-wheel, five-axle, 80,000-lb tractor semi-trailer to simulate the conditions of rural roads.

Over time, many of the test sections (cells) have deteriorated to the point of very little remaining service life. At the same time, some cells have fulfilled their research need and are of little remaining value as a research tool. Finally, several new research opportunities have come along, often with a number of research partners that required new test sections to be constructed. These factors converged at MnROAD in 2007, resulting in the construction of several new HMA cells. One of these studies, namely acid-modified binder, is the subject of this research paper. Additional information on MnROAD can also be found on its website at <http://www.dot.state.mn.us/mnroad/index.html>.

PROJECT BACKGROUND

Acid-Modified Binder Study

PPA has been used for some 30 years to stiffen asphalt for paving applications. Specifically, these additives have improved the pavement performance at high temperatures (i.e., rutting) without adversely affecting the low-temperature properties (i.e., thermal cracking). More recently PPA has been used to stiffen asphalts that may be marginal after the Superpave RTFOT test. This has been particularly so in the case of polymer-modified binders. It was found more cost-effective to add a small amount of acid, which could readily be dispersed in the binder rather than mill in additional quantities of more expensive polymer. It was then found that by adding PPA the amount of polymer could be reduced thereby saving cost for the contractor. The FHWA and their partners have completed several laboratory projects to address the risks and benefits associated with the use of PPA as an asphalt modifier (1–6). These lab studies clearly identified which grades can and cannot be used and the pitfalls associated with the use of PPA with certain antistripping compounds, such as amines and lime as well as asphalt binders from differing sources. The MnROAD study will build upon the findings of extensive laboratory studies and conduct a field trial to assess the performance of PPA mixes over a 5-year period. This study is a joint venture between public agencies and private industry, as shown in [Table 1](#).

Construction of three test cells for studying the performance of asphalt mixtures modified with PPA was completed on the MnROAD low volume road in 2007. The HMA mix designation was SPWEB340C, which indicates a 12.5-mm Superpave mix, Traffic Level 3 (1 to 3 million ESALs), 4.0% design air voids, and PG 58-34 binder. No reclaimed asphalt pavement was allowed in the mix, the quantity of limestone aggregates was limited to 10%, and hydrated lime was added at the drum plant at 1%. A liquid phosphate ester antistripping (Innovalt W) was added to each binder material at 0.5%. The job mix formula is shown in [Figure 1](#). The cells include the following binder materials:

- 0.75% PPA only (Cell 33),
- 0.3% PPA + 1.0% SBS polymer (Cell 34),
- 2.0% SBS polymer only (Cell 35), and
- 0.3% PPA + 1.1% Elvaloy polymer (Cells 77-79; shared with fly ash study).

TABLE 1 Acid Study Partners

Partner	Contribution
Minnesota DOT	Overall project management and administration; design, construction, QA/QC and performance testing; MnROAD operations, performance monitoring, and reporting
FHWA	Asphalt binder and mixture performance testing; Funding for MnROAD instrumentation, monitoring, reporting, and general operations
MTE Services, Inc.	Asphalt blending and transport; asphalt binder and mixture performance testing
Innophos, Inc.	Funding for MnROAD construction; advice and guidance on the proper inclusion of PPA
Marathon Petroleum Company, LLC	Supply of neat PG xx-34 binder
ICL Performance Products LP	PPA supply and funding
DuPont	Support MTE's costs of binder production
Paragon Technical Services, Inc.	Support MTE with PPA + SBS blend
Western Research Institute	Chemical analysis of asphalt binders and mixtures

TEST CELL CONSTRUCTION

Pavement Design

A “typical” pavement design for a low-volume road in Minnesota was chosen for the MnROAD test sections. Being somewhat constrained by existing conditions, the pavement structural and geometrical designs were based on normal low-volume roads in Minnesota. An analysis with MnPAVE, Minnesota DOT’s mechanistic–empirical pavement design procedure, shows that each of the pavement sections has a 5- to 10-year design life.

Cells 33-35 (Acid Study)

The original Cells 33-35 were constructed in 1999 with 4-in. HMA over 12-in. Class 6 (crushed granite) aggregate base over clay subgrade. For the current study the 4-in. HMA was removed and replaced with a new 4-in. HMA layer. The HMA lanes were each 14 ft wide with aggregate shoulders from an existing MnROAD stockpile. The asphalt mixtures on all three cells were designed exactly the same, with the only difference being the asphalt binder material used.

Cells 77-79 (Fly Ash Study)

The fourth asphalt binder (PPA + Elvaloy) in the acid study also served as the wearing course for a fly ash stabilization study. For this study the in-place cells were reclaimed to a depth of 10 in. This reclaimed material was set aside on the shoulders and stockpile area for later use. The underlying aggregate base was subcut to the existing subgrade, and the base material in the middle portion (Cell 78) was removed. Clay borrow material was added across all three cells 5-



MINNESOTA DEPARTMENT OF TRANSPORTATION

BITUMINOUS PLANT MIX DESIGN REPORT
 Minnesota Department of Transportation
 Office of Materials
 1400 Gervais Avenue
 Maplewood, MN 55109
 Phone: (651) 386-5459
 FAX: (651) 386-5580

0-2007-196
 Date: 7/12/2007

THIS MIX DESIGN REPORT IS NOT VALID UNTIL PLANT NO. INDICATED BELOW IS CERTIFIED.

TO BE FILLED IN BY CONTRACTOR		SPEC	2360
ENGINEER	FOR MTRD	SPEC YEAR	2007
PROJECT NUMBER	SP8680-156	MIX TYPE	SPWEB340
		AC GRADE	PER PROPOSAL

THIS MIXTURE HAS BEEN REVIEWED FOR VOLUMETRIC PROPERTIES ONLY, IT DOES NOT ASSURE THAT FIELD PLACEMENT AND COMPACTION REQUIREMENTS HAVE BEEN MET.

PLANT NO. 901204 - 2007 JOB MIX FORMULA

Begin With Test Number	Sieve Size (mm) (in.)	Composite Formula	JMF LIMITS	For Information Only Virgin Formula
SP WE 401	37.5 (1 1/2)			P
-- -- --	25.0 (1)			P
	19.0 (3/4)	100	100 - 100	E
	12.5 (1/2)	85	88 - 100	R
	9.5 (3/8)	84	77 - 90	S
	4.75 (#4)	61	54 - 68	C
	2.36 (#8)	46	40 - 52	E
	0.075 (#200)	2.7	2.0 - 4.7	N
	Spec. Voids	4.0	3.0 - 5.0	T
	Spec. VMA	14.0	13.7	O
	% AC	5.6	5.2	%AC (NEW)
	(TOTAL)			

TM # 2007-083 Indicates a Gyrotory Density of 147.7 (lbs/ft³) at 60 Design Gyration

Use of anti-strip agent required: N

Proportions	Pit	Source of Material	Sp.G
5 %	73006	MARTIN MARIETTA ST CLOUD 3/4" UNWASHED (GRANITE)	2.701
24 %	73006	MARTIN MARIETTA ST. CLOUD CA-50 (GRANITE)	2.719
20 %	73006	MARTIN MARIETTA ST. CLOUD 1/2" CLEAR (GRANITE)	2.711
35 %	73006	MARTIN MARIETTA ST CLOUD WASHED SAND (GRANITE)	2.682
16 %	71002	BARTON ELK RIVER #1 WASHED SAND	2.657
1 %		CALCIUM HYDROXIDE (LIME)	2.300
%			
%			

Mix Aggregate Specific Gravity at the Listed Percentages = 2.697

Remarks MINUS #4 AGG SG AT THE LISTED PERCENTAGES = 2.678

Mix Design Reviewed by:



Mix Design Specialist

cc: Contractor - COMMERCIAL ASPHALT #4
 METRO INSPECTION

FIGURE 1 Acid study HMA mix design.

in. thick. The aggregate or reclaimed base material was put back 8 in. thick, Cell 79 was stabilized with high carbon fly ash, and 4 in. of HMA was paved using the same mix design as for Cells 33-35. The base materials consisted of

- Full-depth reclamation of 50% HMA + 50% Class 4 gravel (nonstabilized),
- Class 6 crushed stone aggregate base (from on-site stockpile), and
- Full-depth reclamation of 50% HMA + 50% Class 3 gravel (stabilized with 14% fly ash).

Cell 78 used the same Class 6 base as in Cells 33-35, so this served as a control section for both the acid and fly ash studies. The pavement lanes were 14 ft wide each, and the shoulders used aggregates from existing stockpiles as well as leftover reclaimed material.

Construction Contract

The project was let on June 8, 2007, and it included construction for the acid and fly ash studies as well as two new test cells in the MnROAD stockpile area for a third study. Three local contractors submitted bids, and Midwest Asphalt Corporation was awarded the contract based on their low bid. The contract start date was July 16, 2007.

Instrumentation

Instrumentation for monitoring unbound material moisture content, temperature, soil pressure, aggregate base displacement, and asphalt strain were installed in the pavement layers during construction (see [Table 2](#)). Sensor arrays were installed within each cell at various predetermined locations (an example is shown in [Figure 2](#)). In each array, sensors were located at specific depths as shown in [Figure 3](#). All instrumentation is connected to a data acquisition system so that the environmental data collection is automated. Data is loaded to the MnROAD database on a daily basis. Dynamic data, pavement response to a moving vehicle load, will be collected manually at certain times throughout the year.

TABLE 2 Instrumentation Installed

Sensor	Description	Manufacturer	Sensor Locations
Thermocouple	Measures temperature of pavement layers at various depths	Omega Type, Texas	One 16-TC tree in each cell
ECH2O probe	Measures volumetric water content, electrical conductivity, and temperature	Decagon ECH2O TE	One eight-EC tree in each cell
Loop detector	Detects truck and activates dynamic gauges	Never-fail inductive loop	One loop in each cell
Soil compression gauge	Measures 2-D displacement (X-Y) at middle of base layer	CTL Potentiometer	One X-Y group in each of Cells 77-79
Dynamic pressure cell	Measures normal stress at base/subgrade interface	Geokon 3500	Three PK sensors in each cell
Asphalt dynamic strain gauge	Measures transverse or longitudinal strain at the bottom of HMA layer	CTL ASG-152	Three longitudinal and three transverse sensors in each cell

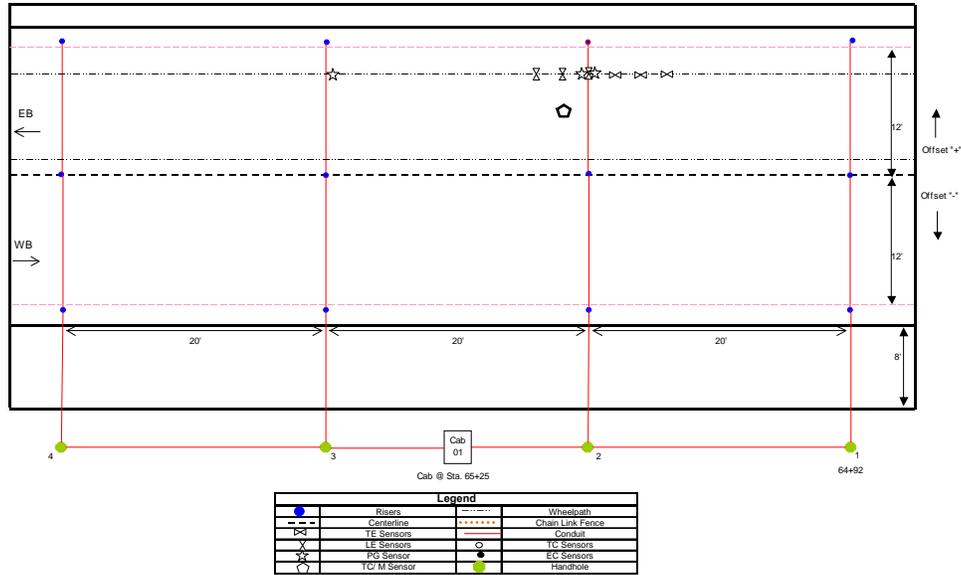


FIGURE 2 Example instrumentation and infrastructure layout, Cell 33.

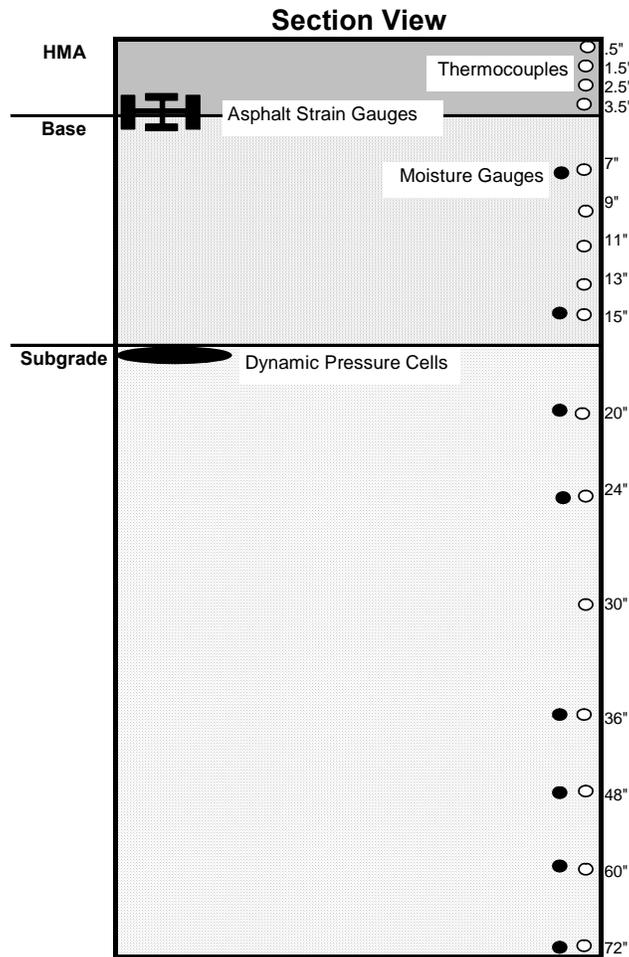


FIGURE 3 Example sensor depth schematic, Cell 33.

Quality Assurance–Quality Control Data

Minnesota DOT treated this project the same as any other construction project in Minnesota, so the typical field inspection was performed during construction. The following tables show the results from quality assurance–quality control (QA/QC) testing. Table 3 shows the average thickness of each cell based on three cores from each cell. Most of the cells were significantly thicker than the 4-in. design thickness. Table 4 shows the HMA gradations, which are all similar due to the identical mix design for each cell. Table 5 contains the volumetric data from each mixture. The PPA + Elvaloy mixture had substantially higher in-place air voids than the other mixtures.

TABLE 3 HMA Core Thicknesses

Cell	Average Thickness, inches
33	4.58
34	4.38
35	4.25
77	5.21
78	4.00
79	4.46

TABLE 4 HMA Aggregate Gradations: Contractor Results

Sieve Size		Cell 33	Cell 34	Cell 35	Cell 77	Cell 79
mm	U.S.					
19	¾ in.	100	100	100	100	100
12.5	½ in.	93	91	92	89	92
9.5	3/8 in.	83	82	83	81	87
4.75	#4	62	62	63	68	65
2.36	#8	49	49	50	46	52
1.18	#16	35	35	35	33	37
0.600	#30	23	23	23	22	24
0.300	#50	13	13	13	13	14
0.150	#100	6	6	7	7	7
0.075	#200	3.9	3.9	4.1	4.0	4.0

TABLE 5 HMA Field Testing Data: Contractor Results

	Test	Cell 33	Cell 34	Cell 35	Cell 77	Cell 79
Loose mix	Ig Oven AC%	5.4	5.5	5.4	5.2	5.3
	%Fine Aggregate Angularity	46	46		46	45
	% Coarse Aggregate Angularity	100/–	100/–	100/–	100/–	100/–
	Gmm	2.478	2.474	2.471	2.484	2.478
	Gmb @ N-design	2.378	2.389	2.379	2.403	2.355
	%Air voids @ N-design	4.0	3.4	3.7	3.3	5.0
	VMA	16.4	16.2	16.5	15.6	17.2
	VFA	75.4	78.8	77.4	78.8	71.1
Field cores	% Max density	94.2	93.5	93.6	92.2	92.1
	% Air voids	5.8	6.5	6.4	7.8	7.9

NOTE: VMA = voids in mineral aggregate (%); VFA = voids filled with aggregate.

FIELD PERFORMANCE

Falling Weight Deflectometer

Falling weight deflectometer (FWD) testing was performed throughout the duration of the project. Data was collected on the subgrade (when available), aggregate base, and HMA pavement layers. The FWD data is stored in the MnROAD database for future analysis by the researchers. [Table 6](#) shows forward-calculated stiffness values for Cells 33-35 based on the method described by Stubstad et al. (7). The data was collected October 3, 2007, shortly after HMA paving, and it shows that the three cells are quite similar in their layer stiffness values.

TABLE 6 FWD Results, Cells 33–35

		Average Stiffness, MPa	Coefficient of Variation
Cell 33	Subgrade	56.4	15.1%
	Base	147.9	15.1%
	HMA	1331.3	13.7%
Cell 34	Subgrade	52.3	11.2%
	Base	137.4	11.2%
	HMA	1250.8	17.7%
Cell 35	Subgrade	58.5	15.2%
	Base	153.6	15.2%
	HMA	1380.3	12.2%

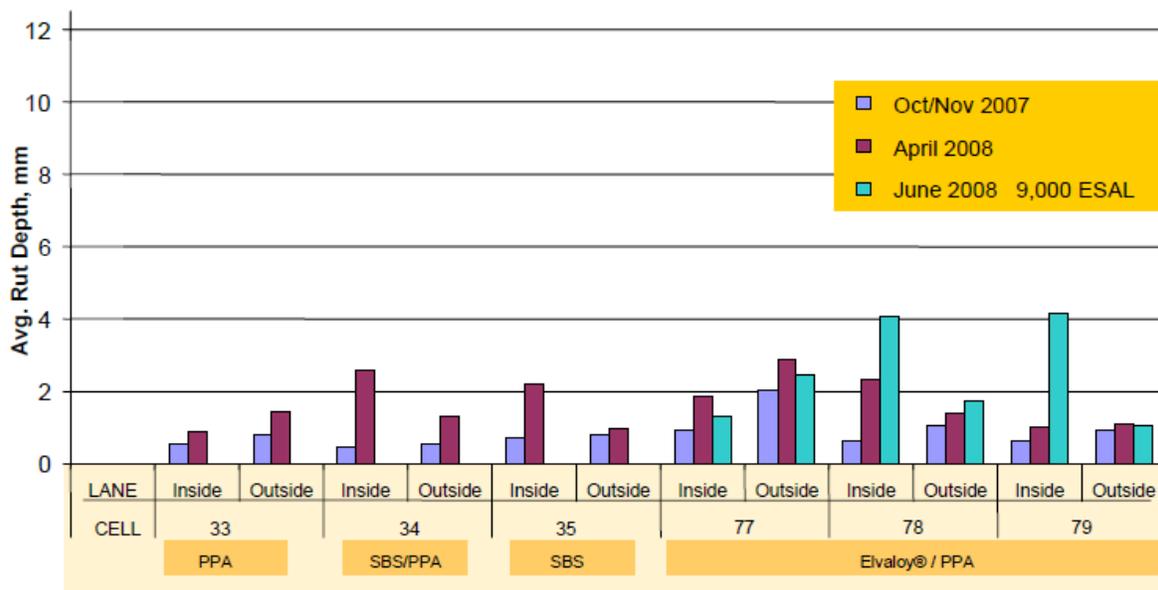


FIGURE 4 Rut depth in PPA test sections.

Rutting

Figure 4 above shows the progression of rut depth over time on each of the test sections. As of June 2008 and after 9,000 ESALs all of the rut depths were below 4 mm. The rut depths are slightly higher on the PPA + Evaloy sections; this is likely due to the aggregate base being 4 in. thinner than the other sections.

Ride Quality

Table 7 shows the initial ride quality measurements of the PPA cells using a Minnesota DOT Pathways van. The cells are all generally in very good condition. Cell 79 has the highest IRI values immediately after construction, which was due in large part to bumps on either end of the cell at the transition to adjacent cells.

The first thermal crack in any of the PPA test sections was noticed in Cell 79 in late January 2009. However, the crack was in an instrumentation area and likely due to inadequate compaction or settlement of the backfill material around the lead wire conduit.

LABORATORY DATA

Asphalt Binder Data

Laboratory testing was performed on both original and extracted binders by MTE Services, Inc. The binders were tested in three conditions: original, short-term aged in the RTFO, and extracted and recovered from field mixtures. The extractions were performed using toluene as a solvent.

TABLE 7 MnROAD Post-Construction Ride Quality Data

Cell	Lane	IRI, m/km	RQI	SR
33	80K	1.31	3.2	4.0
	102K	1.14	3.4	4.0
34	80K	1.40	3.2	4.0
	102K	1.22	3.3	4.0
35	80K	1.56	3.0	4.0
	102K	1.09	3.5	4.0
77	80K	1.55	3.0	4.0
	102K	1.47	3.1	4.0
78	80K	1.36	3.2	4.0
	102K	1.30	3.2	4.0
79	80K	2.05	2.6	4.0
	102K	1.88	2.8	4.0

The next several plots show the results of standard PG grading as well as from MSCR tests.

Figure 5 shows that all four of the original binders were quite similar in stiffness straight out of the tank. However, after RTFO aging, only the SBS binder retained its high-temperature PG grade of 58; the others became PG 64 binders. The binders recovered from field mix showed even more aging, with both the PPA and PPA + SBS binders passing PG 70. One explanation for this behavior is that the plant temperatures during mixing were rather high, increasing the aging of the binders during mix production.

The low-temperature PG grades depicted in Figure 6 tell a slightly different story. All four of the binders show similar performance in the pressure aging vessel (PAV) aged condition, passing a PG-34. The recovered binder also showed similar low PG temperatures, in three of the cases lower than the laboratory-aged material, as one would expect. However, once the recovered binder was PAV aged only two of the binders (PPA + Elvaloy and SBS) retained their -34 grade. The other two binders (PPA and PPA + SBS) stiffened significantly to where they lost a PG grade, becoming -28 binders.

Figures 7 and 8 present the results of MSCR tests. The laboratory-aged binders had significantly lower percent recovery than the recovered binders. This is again likely due to substantial aging during mix production, resulting in much stiffer binders at high temperatures. The PPA binder had the lowest recovery, while the Elvaloy + PPA binder generally had the highest recovery. The nonrecoverable compliance showed similar behavior of the binders, with the PPA binder having the highest J_{nr} and the Elvaloy + PPA binder having the lowest J_{nr} .

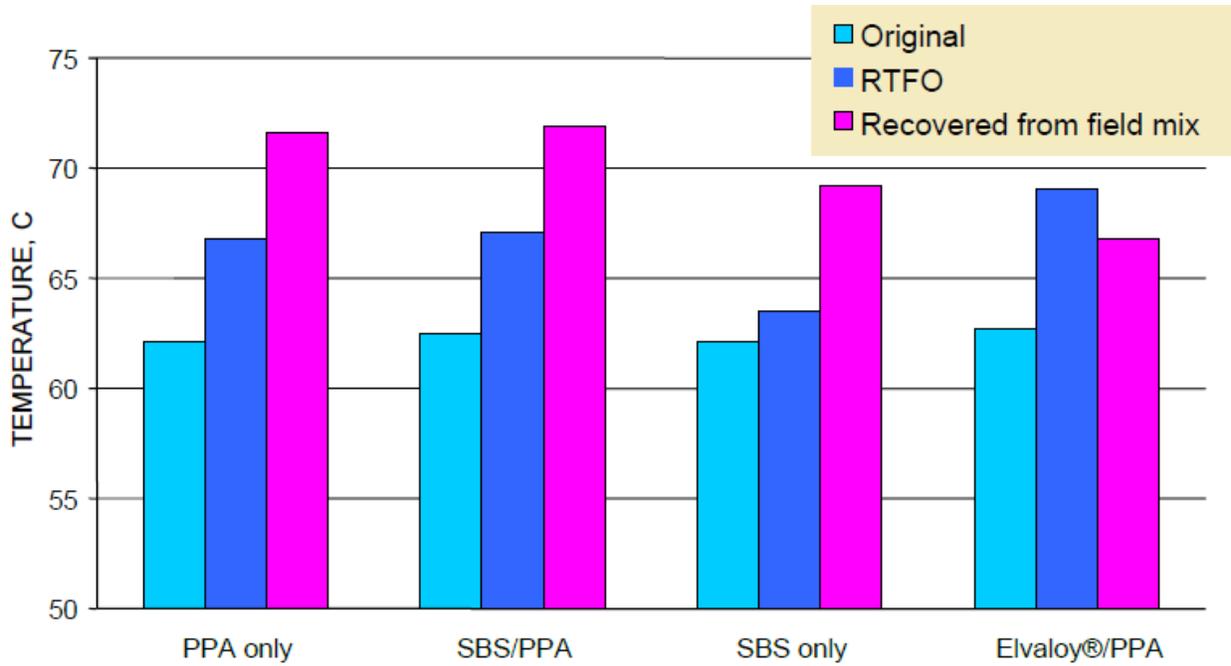


FIGURE 5 High-temperature PG grade.

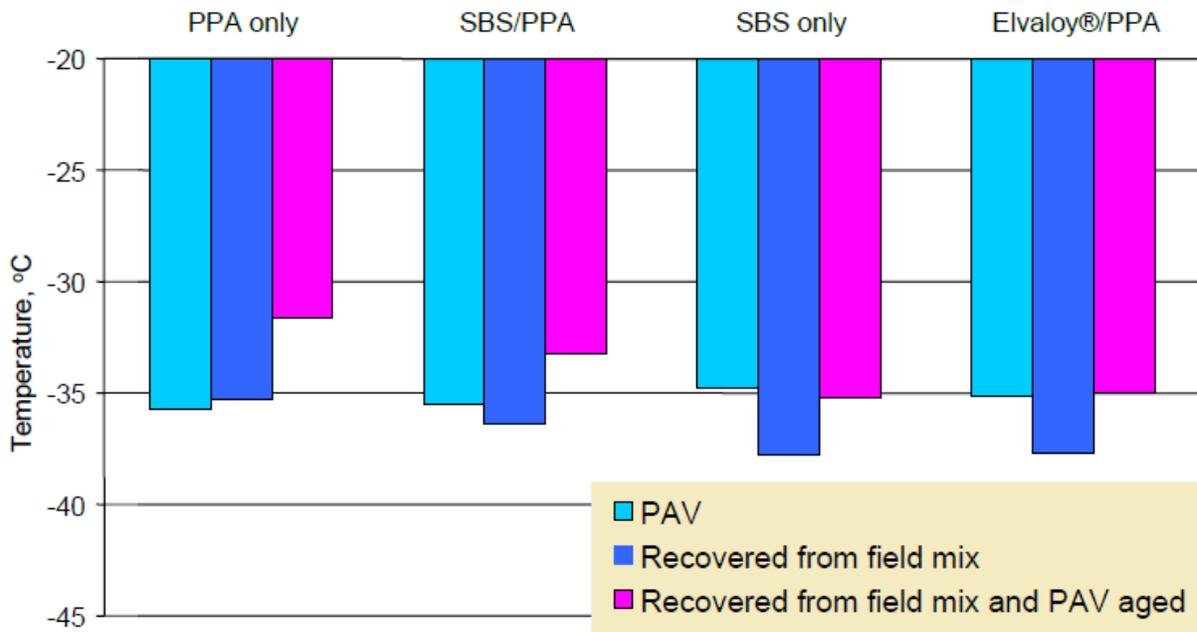


FIGURE 6 Low-temperature PG grade.

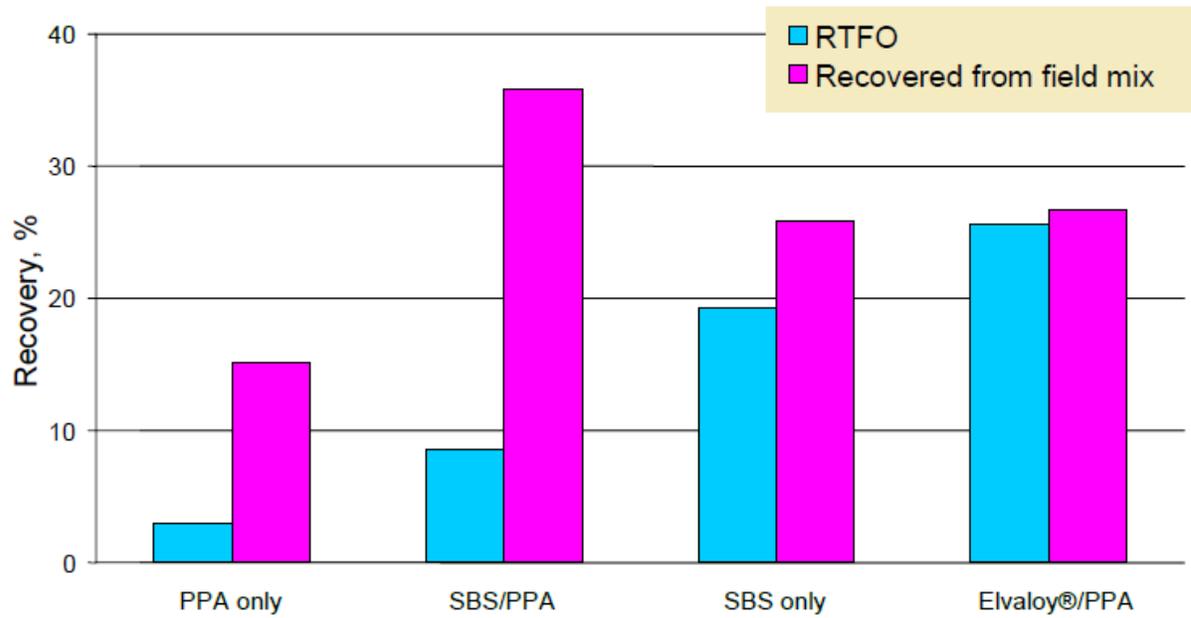


FIGURE 7 MSCR at 58°C, 3.2 kPa.

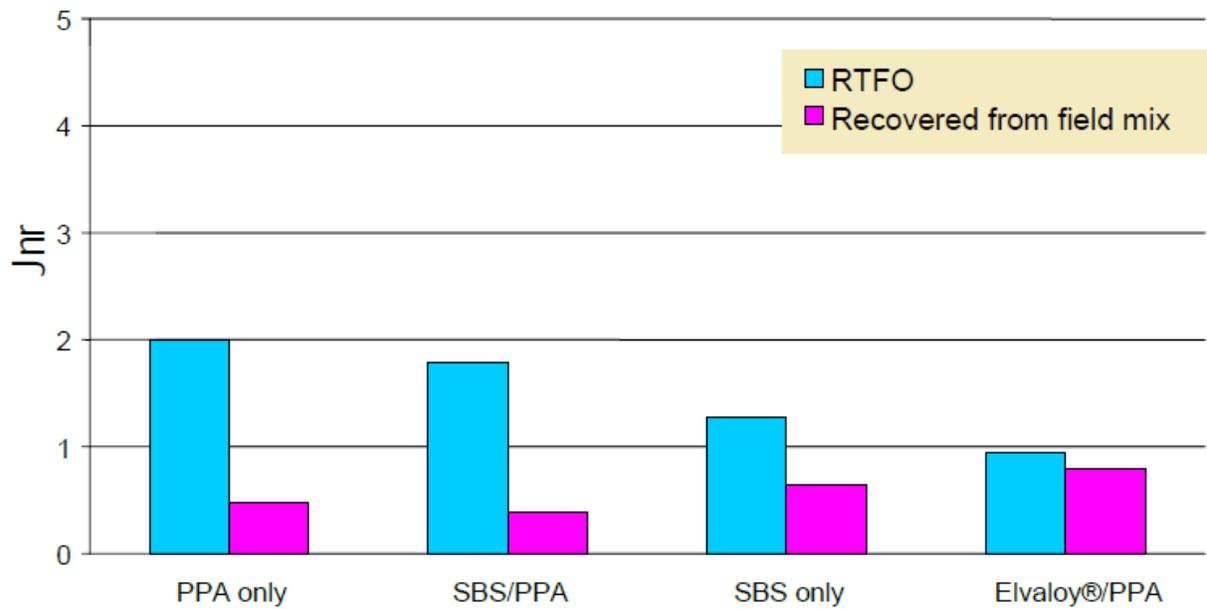


FIGURE 8 Nonrecoverable compliance at 58°C, 3.2 kPa.

Asphalt Mixture Data

The asphalt mixtures were also tested by several groups, and the data is reported below. APA rut tests were performed by the Minnesota DOT. These tests were performed on field cores shortly after construction before opening the road to traffic. The air voids were approximately 7% in all cores. Figure 9 shows that none of the mixes were spectacular in terms of lab rutting performance, while they were not disastrous by any means. The PPA and SBS mixtures had the best rutting performance, while the Elvaloy + PPA mixture performed the worst.

Figure 10 shows similar performance in the wet Hamburg test on field mixtures. There the Elvaloy + PPA mixture again showed the highest rutting while the SBS + PPA mixture performed the best. Given the relatively high level of HMA plant related stiffening of the binders, one should take care not to overinterpret either the APA or Hamburg results. The combination of binder and mixture testing indicates that all of the binders perform quite well, and favorable rutting and moisture sensitivity performance should be expected in the field.

Dynamic modulus (E^*) tests were performed by FHWA on loose mix sampled from the field and compacted in the laboratory. The AASHTO TP62 protocol was generally followed, with slight deviations so that they could also run push-pull fatigue tests. The E^* tests were performed at frequencies of 20, 10, 5, 1, 0.5, and 0.1 Hz and at temperatures of 0°C, 19°C, and 37°C. Figure 11

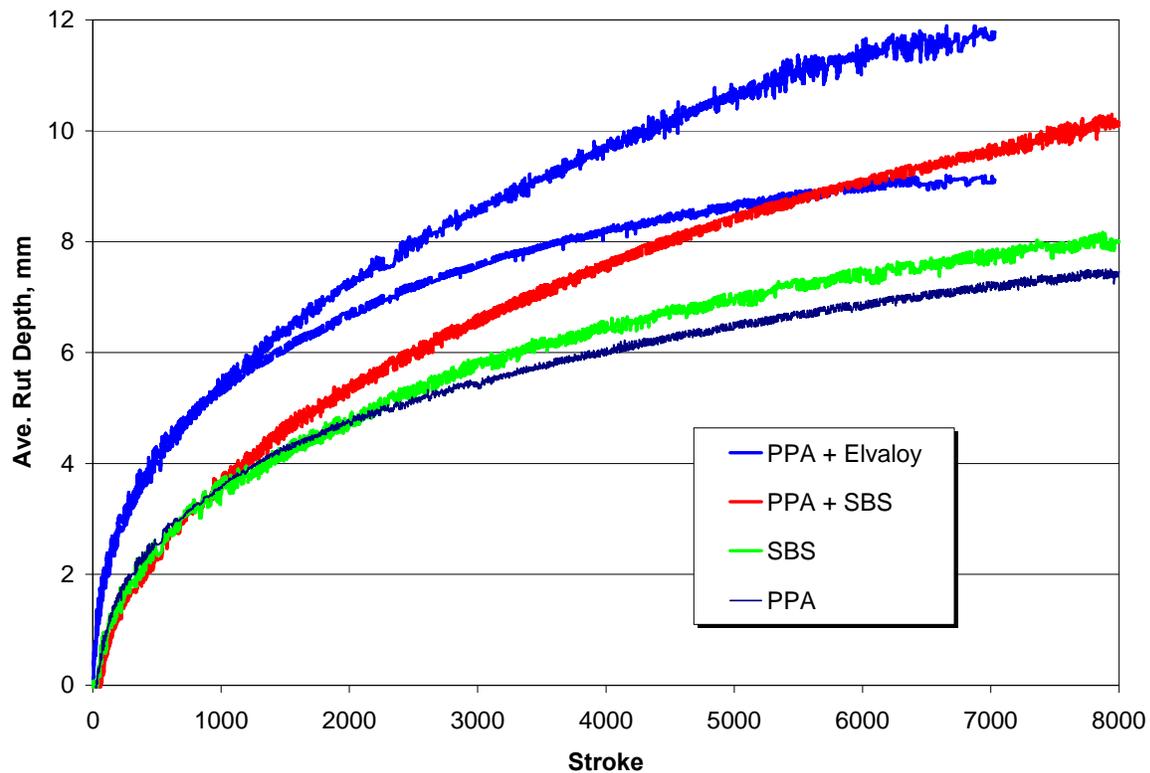


FIGURE 9 Asphalt pavement analyzer rut depths at 58°C, field cores.

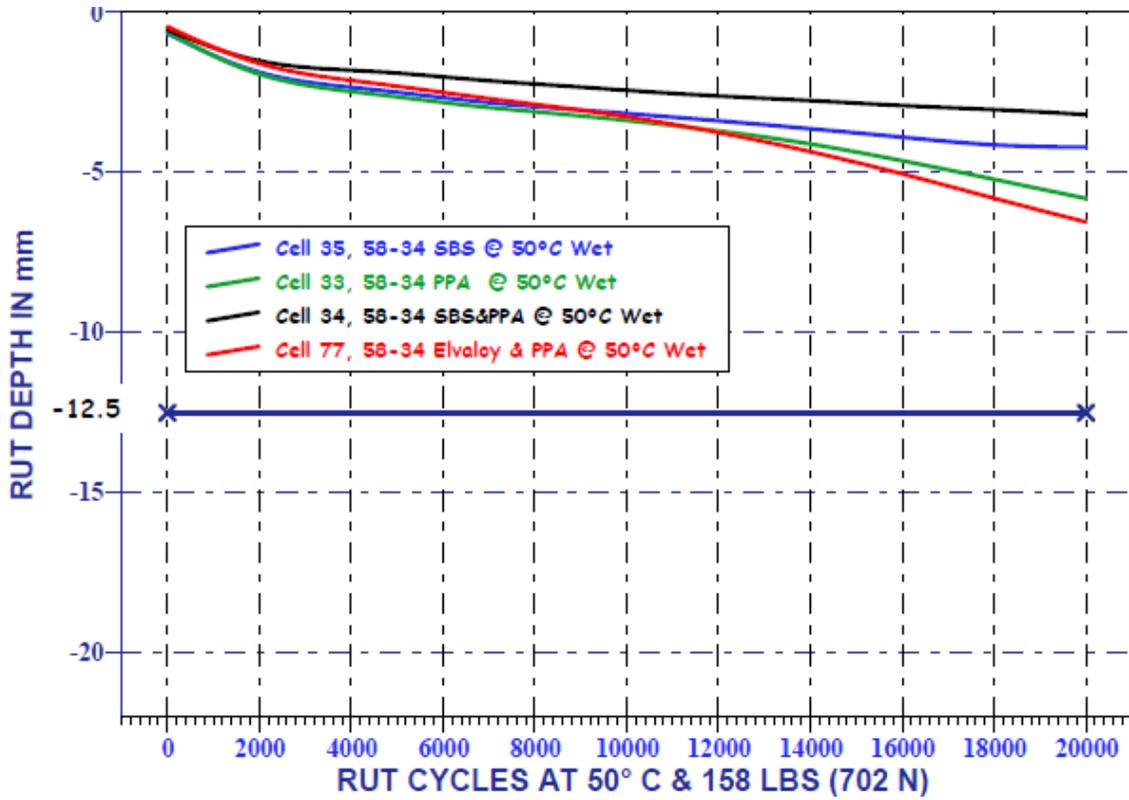


FIGURE 10 Hamburg wet rut test at 50°C, field mix.

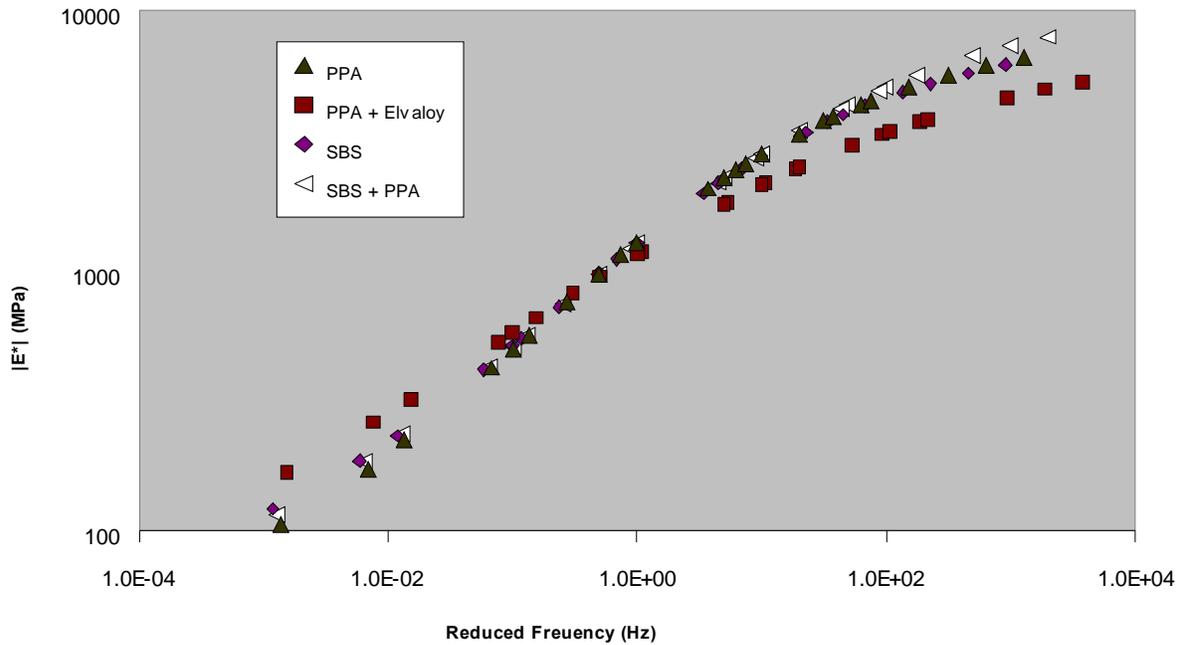


FIGURE 11 Dynamic modulus master curves.

indicates that the Elvaloy + PPA mixture has a higher E^* at low frequencies (high temperatures) and lower E^* at high frequencies (low temperatures) as compared to the other mixtures. This may indicate better rutting resistance at high temperatures and better fatigue resistance at lower temperatures. The SBS + PPA mixture is the stiffest at low temperatures (high frequencies), which may indicate that it is more brittle and prone to fatigue cracking than the other mixtures. The PPA and SBS master curves are almost identical throughout the entire range of frequencies. The mixture data generally agrees with results from binder testing.

SUMMARY

The following statements summarize the performance of the test sections built using PPA-modified binders at MnROAD:

- All of the PPA cells constructed in fall 2007 are performing well, with minimal cracking or rutting distress.
- Field HMA samples showed excellent rutting and stripping performance in Hamburg wheel tracking tests.
- Lab mixtures showed different performance than field mixtures.
- The combination of PPA + polymer generally performed better than either modifier alone.
- The cells will continue to be monitored for field performance for 5 years.

MnROAD staff and their research partners will continue to carry out the research on each of these cells over the next several years. The MnROAD Operations staff will conduct regular pavement performance monitoring, and laboratory tests will continue at periodic intervals.

ACKNOWLEDGMENTS

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NOTE

This report represents the results of research conducted by the authors and does not necessarily represent the view or policy of the Minnesota DOT. This report does not establish a standard or specified technique.

Best Practices for Polyphosphoric Acid Modification of Asphalt

Phosphate Forum of the Americas

Published in Cooperation of the Polyphosphoric Acid Producers in the USA

This paper was prepared by the Polyphosphoric Acid (PPA) Subcommittee of the Phosphate Forum of the Americas (PFA). PFA provides a forum for information exchange on scientific and technical matters relating to inorganic phosphate products. Members of the PPA Subcommittee are ICL Performance Products LP and Innophos, Inc., companies that make purified PPA, which is used as an asphalt binder modifier for asphalt roads.

SUMMARY

PPA has been proven as a successful modifier for asphalt concrete (AC) either by itself or in combination with polymers. On its own, PPA increases the high-temperature performance of AC, as measured by the performance grade (PG) system, with no loss, and sometimes with an improvement, in low-temperature performance. In combination with polymers, PPA has shown its ability to use styrene-butadiene-styrene (SBS) polymers more efficiently, either by providing a product with superior properties at equal polymer loadings, or an equivalent product at lower polymer levels. In many instances, the use of PPA in combination with SBS gives rise to enhanced performance that could not be achieved with either product alone. In combination with ethylene terpolymers such as DuPont's Elvaloy, the use of PPA accelerates the reaction of the Elvaloy, broadens the useful temperature range of the finished product, and improves the elastic response of the binder. In addition, PPA also allows the reaction of Elvaloy and asphalt to proceed at lower temperatures.

This document provides general guidelines for the selection and use of PPA in asphalt modification. Testing is required to demonstrate the performance of each formulation of asphalt, polymer (if any), PPA, antistrip (if any), and aggregate.

Polyphosphoric acid is frequently referred to within the asphalt community as PPA. The typical grades of PPA are 105% and 115%. These grades contain 0% water. DO NOT use phosphoric acids (also called orthophosphoric acid, or purified phosphoric acid, or green acid) which are available in grades of 35% through 93%. These grades contain from 7 wt% to 65 wt% water. The addition of water to an asphalt tank at high temperature, 350°F (177°C) (well above the boiling point of water), will cause the asphalt to foam. (Note: Certain nonasphalt industry segments use the term "PPA" when referring to purified phosphoric acid. Be sure that the PPA used in asphalt is polyphosphoric acid.)

GENERAL CONSIDERATIONS FOR USE OF PPA WITH ASPHALT

There are a number of general considerations for asphalt modified with PPA, asphalt comodified with Elvaloy + PPA, as well as asphalt comodified with SBS + PPA.

Proper Base Asphalt Selection

The low-temperature properties [below approximately 40°F (4°C)] of a PPA-modified asphalt are determined mainly by the base asphalt. The PPA generally provides improvements to the high temperature properties. For example, to meet a PG 64-28 specification, the base asphalt should meet a PG XX-28 specification.

PPA Level Selection

As is true with other asphalt additives, the amount of PPA required will be different for each different base asphalt. The typical range of PPA usage with polymers or alone is from 0.25% up to 1.5% and even higher for some specific applications. The optimum amount is typically determined according to multiple factors:

- Existing specifications (requirement or not of polymer for PG+ specs);
- Reactivity of the base asphalt to PPA;
- Performance of the base asphalt and PPA-modified asphalt with most representative local aggregates (in terms of moisture resistance); and
- Local rules regarding liquid antistripping (mandatory requirement or not).

Antistrip Selection

Additives may be required to meet moisture sensitivity specifications (TSR, Hamburg wheel track tester, etc). When required, the antistrip additive should be determined to be compatible with PPA. A simple DSR test at the stated PG temperature of the binder will quickly determine whether or not addition of the amine antistrip material has caused a reduction in binder stiffness. Antistrip agents that have been found to be compatible with PPA include hydrated lime, phosphate esters such as Gripper X2 or INNOVALT W, and selected amines such as Redicote E-6.

Whatever antistrip additive is used, the performance should be tested and verified. It is recommended that the antistrip of interest be tested with the selected formulation of asphalt, polymer (if any), and PPA. Further, it is strongly recommended that mix tests be conducted on the fully formulated blend of asphalt, polymer (if any), PPA, antistrip, and aggregate.

Experimental Blends Preparation

PPA chemically reacts with asphalt. The reaction time is usually very short. The typical lab sample is prepared by adding the desired amount of PPA to an asphalt sample at 300°F (149°C), or whatever the normal storage temperature of the base asphalt grade is, and stirring for at least 30 min. Normal lab safety procedures and acid personal protective equipment are recommended for handling PPA. Once a target formulation has been developed, lab blends should be evaluated for all specifications and performance criteria.

Use of PPA in an Asphalt Plant

For modification with PPA, the typical operation includes delivering the PPA in bulk trucks or totes, storing the PPA in a dedicated tank, metering the PPA to control addition, and mixing a

small amount of PPA uniformly with a large amount of asphalt. The storage tank, pump, and acid process lines are heated to maintain PPA in a fluent state. The required normal handling temperature for 105% PPA is approximately 100°F (38°C) and for 115% PPA is 200°F (94°C). The product is too viscous to flow efficiently below these respective temperatures. When storing PPA in a bulk tank, it is recommended that a nitrogen blanket be placed over the material. This is a simple and inexpensive process to install and assures that the PPA will not pick up moisture from the atmosphere. The PPA supplier can assist in basic designs for a nitrogen blanketing system. Further, in the handling and storage of PPA, the preferred material of construction is 316 stainless steel to minimize corrosion. The mixing of PPA and asphalt is accomplished by (a) using a mixing tee or in-line static mixer in the process line carrying asphalt to a storage tank, or (b) adding the PPA into the top of a well-agitated asphalt tank. In this case, in order to avoid potential corrosion issues, care should be taken so that the PPA does not splash or directly contact the walls of the carbon steel tank. However, in a tank with asphalt coated sidewalls, there is little danger of any reaction between the carbon steel and the PPA. Once the PPA has been reacted with the asphalt, lab tests have shown that the bulk PPA-modified binder and the head space above the PPA modified binder are not corrosive.

Additional Testing

After the formulation has been developed, additional testing is recommended to validate all performance criteria. These tests may include:

1. Plant trials to determine how large scale batches correlate with lab results;
2. Stability tests to determine how the properties change with storage time;
3. Sensitivity studies to determine how variation in base asphalt properties, storage temperature, etc., affect the properties of the final product; and
4. Correction studies to determine how to correct deficiencies if off-spec product is made.

Modification with PPA only

PPA Level Selection

Typical PPA levels are between 0.5 and 1.2 wt%. With some base asphalts a slightly higher level may produce a value-added result where a marginal increase in %PPA will attain the desired specification. We recommend initial evaluation at 0.4, 0.7, and 1.0 wt% PPA. Results from these tests should provide information for fine tuning the formulation, as noted previously.

Comodification with Elvaloy and PPA

Guidelines for comodification of asphalt with Elvaloy and PPA are discussed in detail on the Dupont website: www.dupont.com/asphalt.

The guidelines include the following:

- Proper base asphalt selection;
- Polymer level selection;

- PPA level selection;
- Experimental blends preparation;
- Additional testing
- Plant operation (equipment and procedures); and
- Patent on comodification of asphalt with Elvaloy and PPA.

Comodification with SBS and PPA

Polymer Level Selection

Typical SBS levels are between 2.5 and 5.0 wt%. The appropriate level depends on the base asphalt and the requirements of the desired specification. The SBS supplier will usually recommend SBS levels for initial testing. Results from these tests should provide information for fine tuning the formulation.

PPA Level Selection

Typical PPA levels for use with SBS are between 0.2 and 1.0 wt%. The appropriate level depends on the base asphalt and the requirements of the desired specification. The addition of PPA may provide a product with superior properties at equal SBS loadings, or an equivalent product at lower SBS levels. Typical reduction of SBS will range from 0.75 to 2.0 wt%, with PPA addition. Typical exchange of SBS to PPA is a ratio of about 3:1.

Experimental Blends Preparation

The SBS and PPA suppliers will usually recommend procedures for lab testing and order of addition (SBS or PPA first). Typical lab samples are prepared by adding the desired amount of SBS to an asphalt sample at 350°F (177°C) to 390°F (199°C) and blending with a high shear mixer for at least 30 min. It is recommended to confirm complete dispersion of both the SBS and PPA in the asphalt. One technique is UV microscope analysis.

Use of SBS and PPA in an Asphalt Plant

The SBS and PPA suppliers will usually recommend procedures for plant operation and order of addition. This includes equipment for handling and blending PPA, handling SBS, milling/mixing SBS into the asphalt, and storing the modified asphalt. It is recommended to confirm complete dispersion of both the SBS and PPA in the asphalt. One technique is UV microscope analysis.

The blending of SBS with asphalt may involve preparation of a concentrate containing SBS and subsequent dilution of the concentrate with base asphalt. There are a number of manufacturers having patents covering specific materials and procedures for modification technology covering the combination of SBS and PPA, as well as the combination with cross-linkers.

The SBS supplier will usually recommend guidelines for storing asphalt modified with SBS (which can usually be extended to comodification with SBS and PPA). The typical storage tank is agitated at all times. The storage temperature for shipping and immediate use is usually between 310 to 350°F (155 to 177°C). For short-term storage (up to 2 weeks) the typical tank

temperature is usually about 275°F (135°C). For long-term storage (longer than 2 weeks) the usual procedure is to remove the heat. Reheating of modified asphalt is usually done gently and reheating above 350°F (177°C) is avoided.

NOTE

Although the information and recommendations set forth herein (hereinafter “information”) are presented in good faith and believed to be correct as of the date hereof, the authors make no representations or warranties as to the completeness or accuracy thereof. Information is supplied upon the condition that the persons receiving same will make their own determination as to its suitability for their purposes prior to use. In no event will the authors be responsible for damages of any nature whatsoever resulting from the use of or reliance upon information or the product to which information refers. Nothing contained herein is to be construed as a recommendation to use any product, process, equipment, or formulation in conflict with any patent, and the authors make no representation or warranty, express or implied, that the use thereof will not infringe any patent. No representations or warranties, either express or implied, or merchantability, fitness for a particular purpose or of any nature are made hereunder with respect to information or the product to which information refers.

Implementation of Polyphosphoric Acid Modification of Asphalt Binders and Related Experience

Case Study

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Holly Asphalt Company

This paper provides a case study demonstrating how a regional asphalt supplier located in Glendale, Arizona, implemented polyphosphoric acid (PPA) as an asphalt modifier. This modification approach was necessitated by a change in asphalt binder selection strategy on the part of the Arizona DOT. The paper outlines why the supplier decided to use PPA, experimentation that validated its use, operational and modification tactics, and identifies projects using PPA-modified asphalt with a performance history of up to 9 years.

INTRODUCTION

Holly Asphalt Company (HAC) is a regional supplier of asphalt products with refineries and asphalt terminals in the Southwestern United States. This paper provides a case study describing how HAC implemented PG asphalt binders modified with PPA. It outlines experiments that were conducted to validate the use of PPA as an asphalt modifier and manufacturing and other practices that have, in the opinion of the author, resulted in a successful modification strategy. Pavement performance of seven projects that utilized PPA-modified binders is described. Typical quality control data of unmodified and PPA-modified binders is included.

BACKGROUND

Arizona DOT implemented performance grade (PG) binders in the mid-1990s and did so using primarily four grades for dense-graded asphalt concrete (AC): PG 64-22, 70-10, 76-10, and 70-16. It is important to note that the majority of these binders indicated an 86°C PG temperature spread and all were manufactured using straight run asphalts, i.e., no modification was required. By 1998, asphalt suppliers in Arizona expressed an interest in reducing the number of binders. Consequently, Arizona DOT maintained use of PG 64-22 and PG 70-10, but in 1999 consolidated PG 76-10 and PG 70-16 into a single grade, PG 76-16. This grade was intended for use in the most demanding pavement applications.

This change meant that approximately 90% of all PG binders in southern Arizona were consolidated into a single grade, PG 76-16. Even more significant, PG 76-16 indicates a wider PG temperature spread, 92°C, and thus, in most instances would require the use of a modified asphalt binder. Adding to the necessity of a modified asphalt binder was the fact that Arizona DOT had previously adopted the use of 110°C pressure aging in its PG specification environment for all binders PG 70-xx and higher. In summary, by specifying PG 76-16, Arizona DOT went from using practically no modified asphalt to using practically all modified asphalt.

This change meant that asphalt suppliers, including HAC, wishing to provide asphalt to Arizona DOT projects would need to develop systems for achieving 92°C PG temperature spreads. Adding to this challenge, this change in binder grades occurred fairly rapidly, within about one calendar year. Projects let for construction in 1999 would require PG 76-16. The end of the 2000 construction season would see the first large-scale use of that performance grade.

The most obvious way to formulate PG 76-16 would have been to use one of the many polymers that were available at the time. Such polymers were typically block copolymers of styrene and butadiene. They typically imparted enhanced binder elasticity or “stretchiness” at intermediate and high pavement temperatures. Although at that time HAC had the ability to make polymer-modified asphalt, it did not have the manufacturing capacity in terms of heat, storage, and personnel to supply a large Arizona DOT project that might require as many as 12 loads of binder in a day, many days on end. Meeting the new Arizona DOT requirements with elastic types of polymers would present a significant operational challenge to HAC.

Likewise, it must be recognized that the use of PG 76-16 would be in a low bid setting. At the time, the prominent supplier of PG asphalt to Arizona DOT projects had the capability of producing PG binders very economically via the use of oxidized asphalt. Clearly there was added cost to using oxidized asphalt, but that cost appeared to be relatively small compared to conventional polymer modification. When it implemented PG binders, Arizona DOT adopted a PG specification strategy that did not incorporate provisions (e.g., elastic recovery) that would require the use of a polymer. As an asphalt modifier, polymers were at an almost insurmountable disadvantage in Arizona.

Therefore, beginning in 1999 HAC began a significant effort to develop a method of producing PG 76-16. The specification criteria for that method were (a) it had to be operationally practical and achievable and (b) economical within the structure of Arizona DOT’s low bid specification environment.

DEVELOPMENT OF A MODIFICATION STRATEGY

One of the first modification strategies that HAC examined was alternative polymers. Although they had largely diminished in use, modifiers such as low density polyethylene and ethylene vinyl acetate were considered. These were abandoned fairly quickly because they met neither of the specification criteria. In general, wetting-out and dispersing solids into asphalt offered the lowest probability of success.

As a consequence, modification of asphalt with liquid modifiers was closely examined. Modifiers that were liquid or semi-liquid at ambient temperatures would solve most of HAC’s operational limitations. Two reports from the FHWA (1, 2) indicated promising results from chemical modification. Although neither of these studies utilized PPA, they did present data suggesting that nontraditional liquid chemicals indicated promise in the asphalt modification arena.

Majidzadeh and Brovold (3) studied the effect of various strong acids on moisture susceptibility of asphalt mixes. Although acids showed some promise in ameliorating moisture damage, the type and quantity was not well established. They identified the stiffening effect of strong acids on asphalt binders.

De Filippis et al. (4) indicated promising results using phosphorus compounds to modify asphalt. Although their work was aimed at reducing binder aging, they concluded that

phosphoric acid produced an effect similar to oxidation with improvements in softening point, viscosity, and penetration index.

Discovery of the paper by De Filippis was significant because it pointed out to the author that PPA exhibited promise as a liquid modifier of asphalt. That led to the discovery of a host of patents in the PPA-modified asphalt arena, the most significant of which was awarded to Alexander in 1972 (5). That patent clearly states that PPA improves the physical property temperature susceptibility of vacuum distilled asphalt binders. Improved temperature susceptibility is an alternative way of indicating an improved PG temperature spread.

The De Filippis paper and Alexander patent seemed very encouraging and led to many industry inquiries on the part of the author of those with knowledge of PPA use. Those inquiries suggested that PPA-modified asphalt was already in sporadic use in the United States and Canada in the late 1990s. Therefore, HAC embarked on a focused effort to explore the use of PPA at its terminal in Glendale, Arizona. In order to use PPA as an asphalt modifier, HAC management believed the following two questions needed to be answered.

1. Would PPA modified asphalt cause detrimental pavement performance?
2. What would be the safest and most efficient way to incorporate PPA into asphalt in a terminal blend setting?

The following section describes HAC's approach in answering these questions.

EFFECT OF PPA ON ASPHALT BINDER AND MIXTURE PROPERTIES

Asphalt Binder Effects

To answer the first question the author conducted several binder experiments exploring the use of PPA as a binder modifier. Figure 1 shows the results of adding 1% PPA (115% H_3PO_4) to three asphalt binders.

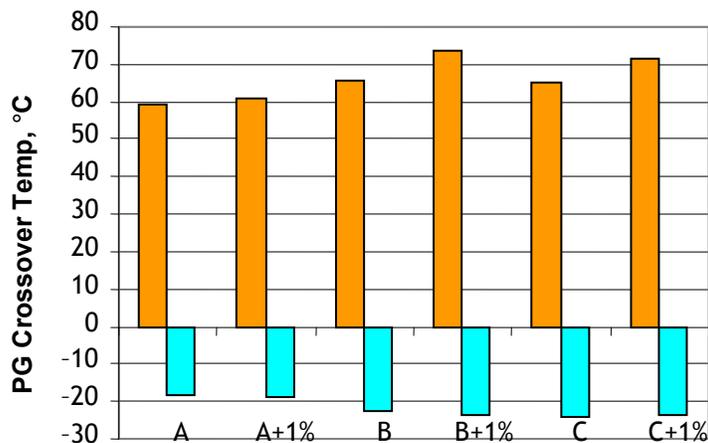


FIGURE 1 Effect of PPA dosage rate on PG temperature spread.

Asphalt A is a binder based on west Texas sour crude oil. Asphalt B is a binder produced primarily from western Canadian crude oils. The base crude for Asphalt C is unknown but was suspected to also be from a blend of Canadian crudes. These binders were chosen because they represented asphalts that were used by or available to HAC at the time. The length of the bars in Figure 1 indicated the crossover temperature, which is the temperature at which the asphalt binder just passes the PG specification. In all three cases, original DSR ($G^*/\sin \delta$) and m-value were the controlling parameters. The most important finding from this data was that not all asphalt binders react to PPA modification. Asphalt A exhibited almost no improvement in PG properties while Asphalts B and C exhibited significant improvements in high-temperature behavior. An important finding was that low-temperature properties in all cases were unaffected.

During the author's inquiries about the use of PPA, there was a prevalent point of view that the high-temperature stiffening effect of PPA was temporary. To test this hypothesis, an experiment was conducted to estimate the stability of high-temperature physical properties as PPA-modified binder is maintained at a storage temperature. Figure 2 shows a portion of this data.

Only data for Asphalt B is presented; however, the same trend was observed for Asphalt C. The unmodified asphalt and PPA-modified asphalt were produced in approximately 4-gal batches. The material was placed in a 5-gal bucket, which in turn was placed in a laboratory bucket heater maintained at 165°C and agitated once per day. This apparatus was thought to simulate tank storage of binders. Periodically a sample was extracted from the bucket and tested for absolute viscosity using procedures outlined in ASTM D2171. The data shows a gradual and roughly equal increase in asphalt viscosity for both the PPA-modified and unmodified binders over a period of 4 weeks. This suggested binder aging with prolonged storage. This experiment showed that the high-temperature properties of the PPA-modified binders did not decay with time. However, it should also be pointed out that this experiment probably did not well simulate

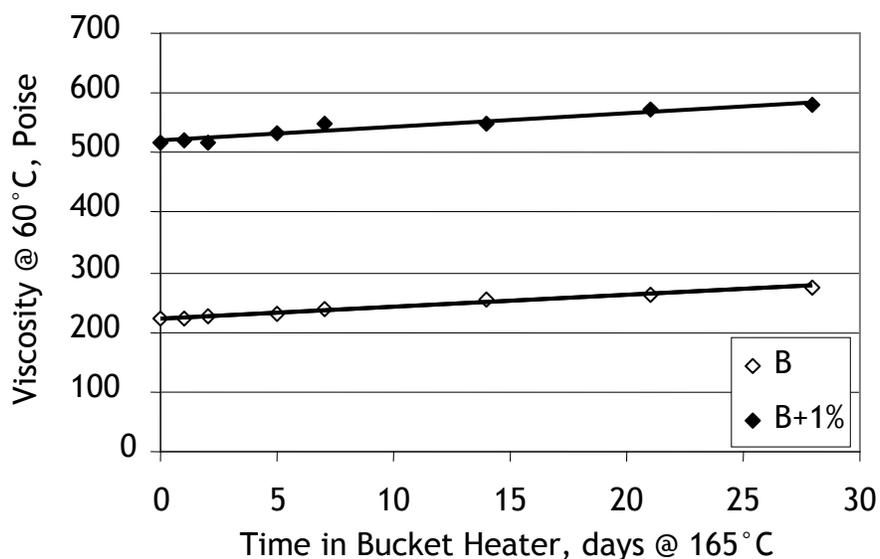


FIGURE 2 Effect of storage time on absolute viscosity.

tank storage because the amount of aging observed in the unmodified binder was excessive compared to actual HAC experience with tank storage at elevated temperatures.

Nevertheless, it appeared as if high-temperature properties of PPA-modified binders did not decay during tank storage.

Asphalt Mixture Effects

Even though Majidzadeh and Brovold suggested that strong acids might actually ameliorate moisture damage, there was concern in the late 1990s over the effect of PPA on moisture sensitivity. To evaluate this effect, aggregate materials were collected from a commercial pit near Bullhead City, Arizona. An Arizona DOT Superpave 19-mm mixture was employed for analysis. This river gravel source had been well known to exhibit moisture damage. In practice, Arizona DOT had largely addressed this problem by requiring the use of an antistripping admixture, either hydrated lime or PCC. Four moisture susceptibility evaluations were conducted using AASHTO T283. [Figure 3](#) shows the results of this evaluation.

The control mix containing unmodified Asphalt C, with no antistripping admixture, exhibited a TSR of about 60%. The addition of PPA, with and without lime, indicated a TSR of about 90%. At least for this aggregate–asphalt combination, it appeared as if PPA actually had a favorable effect on moisture susceptibility. Likewise, there appeared to be no unfavorable interaction between PPA and lime. Therefore, for a well-recognized moisture susceptible mixture in Arizona, PPA did not have a detrimental effect on moisture susceptibility.

Because the primary effect of PPA is to increase the high-temperature stiffness of asphalt binders, a Hamburg rut tester (50°C, 20,000 wet load applications) evaluation was conducted to ensure that modification of a binder with PPA had the intended effect on an asphalt mixture. An asphalt mixture containing Salt River aggregate from a source in Phoenix was employed for evaluate rutting susceptibility. Three mixtures were evaluated. Each met the requirements of the Maricopa Association of Governments (MAG) specifications for a ¾-in. mix. The control was the MAG ¾ mixture with unmodified Asphalt C. Other treatments evaluated were Asphalt C with 1% PPA and Asphalt C with 1% PPA plus 0.75% hydrated lime. The results are shown in [Figure 4](#).

The control mix containing unmodified Asphalt C exhibited the most rutting, about 14 mm. The same mix with Asphalt C modified with 1% PPA, with and without lime exhibited about half the rutting. It should be pointed out that because of the effect of the PPA, the two mixtures exhibiting about half the rutting as the control had a binder that was about twice as stiff as the control. That likely explains the behavior observed in the data shown in [Figure 4](#). The significant findings of the data shown in [Figure 4](#) are that (a) PPA has the intended effect on mixture rutting potential and (b) for this combination of materials PPA has no interaction with hydrated lime used as an antistripping admixture.

Based on these asphalt binder and mixture test results, there appeared to be no reason to abandon PPA as an asphalt modification strategy pursued by HAC. To settle one last issue, Arizona DOT was contacted to determine whether they had or anticipated any institutional barriers to the use of PPA-modified binders. As expected, conversations with Arizona DOT officials reaffirmed their long standing belief that the most important quality of an asphalt binder is that it meet all requirements of the PG specification. In other words, they remained unconcerned over the recipe used to produce PG 76-16.

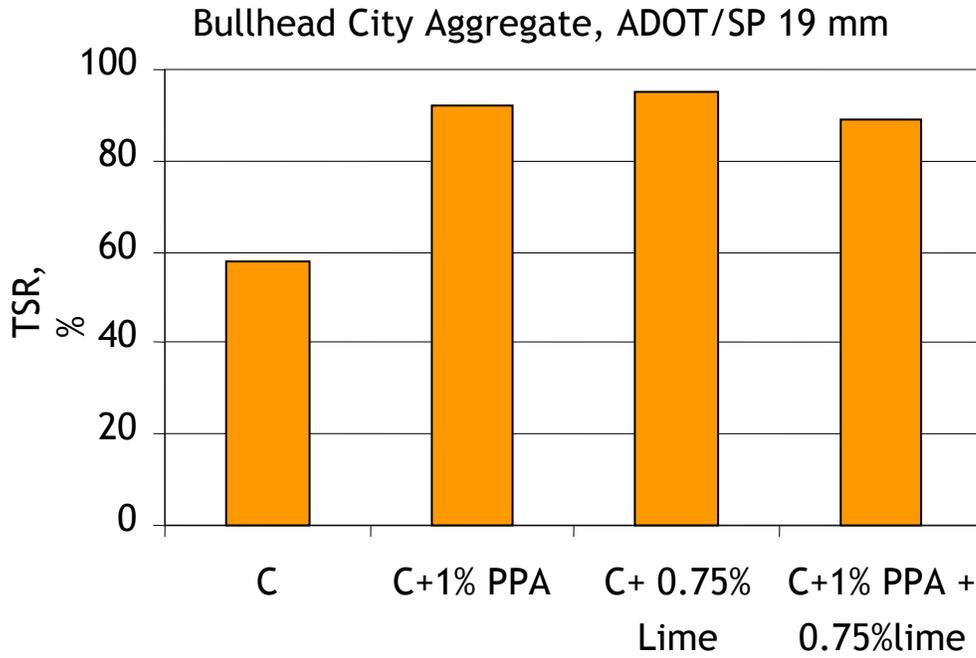


FIGURE 3 TSR of mixtures containing asphalt binders modified with PPA.

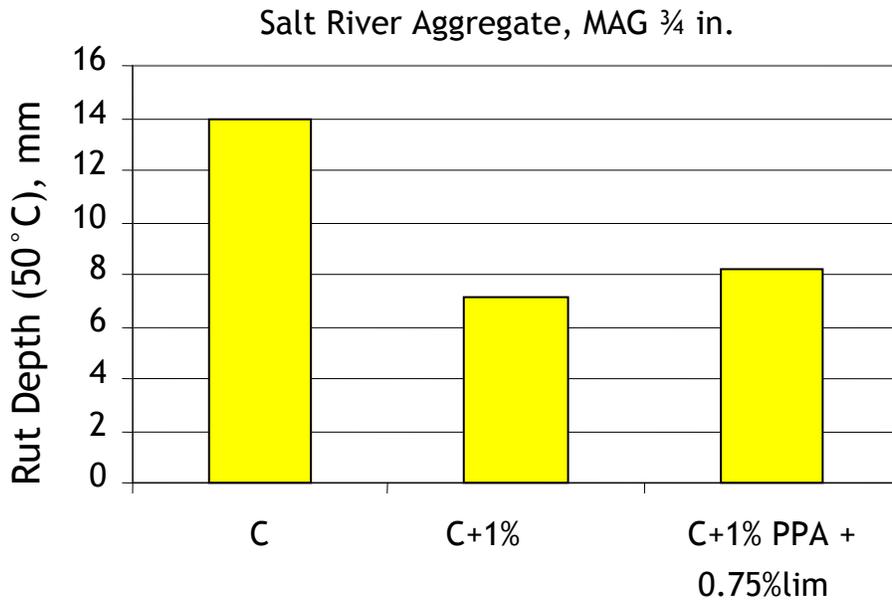


FIGURE 4 Effect of PPA modification on rutting susceptibility.

Therefore, it became necessary to conduct the next step, which would be to explore safe and efficient operational techniques for incorporating PPA into asphalt binders.

OPERATIONAL FACTORS AND MODIFICATION STRATEGY

While the aforementioned experimentation was happening, HAC began exploring operational techniques to incorporate PPA. The need for HAC to develop an in-house PPA system was eliminated in 2000 due to corporate changes. That is, the Holly Corporation formed a joint venture with Koch Materials Company (KMC) called Koch Asphalt Solutions Southwest (KASS), a company that existed from 2000 through 2005. It turned out that by 2000 KMC already had significant experience with PPA-modified asphalt. That experience was applied to the Glendale, Arizona, terminal by creating a state-of-the-art PPA system. Consequently, by the end of 2000, HAC had developed the ability to employ PPA as an asphalt modifier at its Glendale terminal.

The heart of the PPA system is a static mixer that combines PPA with one or more asphalt streams. Key components, including the static mixer, PPA storage tank, and some piping, are fabricated from grade 316 stainless steel to counter the corrosive effects of PPA. A mass flow meter is employed along with a blender to accurately combine the asphalt and PPA. The system used at the Glendale terminal has proved to be safe, effective, and highly accurate.

The positive effect of the KASS joint venture on the use of PPA at the Glendale terminal cannot be overemphasized. Along with a very well-designed PPA system, the KASS joint venture brought institutional controls to PPA modifications that remain in place at present. Examples of this include an inviolable maximum PPA, both without and with polymer modification. These were implemented as 0.75% and 1.00%, respectively. It also included institutional “no fly zones” such as supplying PPA-modified binder as a base for asphalt rubber or asphalt emulsions.

ARIZONA EXPERIENCE WITH PPA MODIFICATION

The Glendale terminal began supplying PPA-modified PG 76-16 starting in 2001. Early experience on Arizona projects was mostly favorable and only minor engineering improvements were made to the Glendale PPA system. Asphalt mixing facility customers and contractors were able to work with PPA-modified PG 76-16. One early observed benefit of PPA-modified PG 76-16 was the reduction in high-temperature viscosity. That is, PG 76 grades made with PPA-modification exhibited a high-temperature viscosity (at 135°C) of about 1,000 Pa·s less than those PG 76-xx grades made with conventional polymer modification.

However, on a national basis beginning in 2002, the efficacy of PPA-modification began to be questioned. A paper by Ho et al. (6) suggested that the effect of PPA was not permanent, was reversed by antistripping agents such as lime or amine agents, and that PPA would be washed away by water while in service. Likewise a paper by King et al. (7) attributed pavement performance problems in Kansas and Oklahoma to the use of PPA in combination with basic antistripping agents such as lime and/or amines.

Concern with PPA modification in the pavement materials engineering community grew throughout 2002 and 2003. By then, the Glendale terminal had supplied seven Arizona DOT projects with PG 76-16 using PPA modification. Due to the national level of concern, in late 2003 the author conducted a survey of the seven DOT projects in Arizona that had been supplied out of the Glendale

terminal and that had used PPA-modified PG 76-16. [Table 1](#) provides descriptive information on these projects.

Despite national concern over PPA modification, which had grown to the extent that some feared immediate and catastrophic failure of PPA-modified pavements, the results of the survey indicated that the Arizona projects were well performing. It must be emphasized however, that even the oldest of the projects had been in service only 3 years. It should also be pointed out that six of the seven asphalt mixtures containing PPA-modified PG 76-16 were covered with a thin, asphalt rubber friction course. The author presented the results of the survey of the PPA-modified Arizona pavements, along with similar projects in New Mexico, at the 2004 Rocky Mountain Asphalt User Producer Group.

Since the initial survey in 2003 of the pavements listed in [Table 1](#), the author has conducted three follow up surveys in 2005, 2009, and 2010. As of the last survey in March 2010, all of the pavements remain in very good to excellent condition. It should be noted that this survey does not constitute a designed field experiment. Obviously, no control sections are included. Yet if the performance of these projects is considered in the context of the concerns expressed nationally in the early 2000s, it is obvious that catastrophic pavement failures using PPA-modified binders have not materialized. [Figures 5](#) through [11](#) show photographs of the projects taken in March 2010 at spot locations that were randomly selected for observation during the original 2003 survey. Similar photos taken in 2003 are not included in this paper, but it should be noted that the 2010 photos show remarkably similar pavement condition to the pavement condition in the 2003 photos.

Features of the SR-68 project bear special mention. This project climbs from the Colorado River up and over a mountain range between Bullhead City and Golden Valley, Arizona. Approximately 10 mi of about 6% grade exist on this project. It was Arizona DOT's first rural design-build project and would normally carry only moderate traffic. However, after the events of September 11, 2001, the federal government closed Hoover Dam to commercial traffic. That meant that all heavy trucks traveling to Las Vegas from points south and east in Arizona were diverted to travel this section SR-68. Arizona DOT has reported that this project on SR-68 received its design level of traffic within 1 year of completion. Another interesting feature of this project is that the hot mix containing the PPA-modified PG 76-16 was produced using the sometimes problematic aggregate source reported in [Figure 4](#) of this study.

TABLE 1 Surveved Projects Using PPA-Modified PG 76-16

Project	Date Complete	Location	Project Type
SR-68 E of Bullhead City	2001	MP 0-14	New construction
I-10 S of Phoenix	2001	MP 160-174	Rehabilitation, mill and fill
US-90 S of Wikieup	2001	MP 129-133	New construction
US-60 in Surprise	2002	MP 210	Geometric improvements to intersection, add capacity
SR-85 in Buckeye	2003	MP 150-152	Geometric improvements to intersection, add capacity
US-60, Thomas Road, 27th Avenue, in Phoenix	2003	—	Geometric improvements to intersection, add capacity*
US-60, Florence Junction	2003	206-212	Geometric improvements to intersection, add capacity

* US-60, Thomas Road project did not utilize asphalt rubber friction course mix.



FIGURE 5 SR-68 near Bullhead City, Arizona, March 2010.



FIGURE 6 I-10 South of Phoenix, Arizona, March 2010.



FIGURE 7 US-90 South of Wikieup, Arizona, March 2010.



FIGURE 8 US-60 near Surprise, Arizona, March 2010.



FIGURE 9 US-85 near Buckeye, Arizona, March 2010



FIGURE 10 Intersection of US-60, Thomas Road, and 27th Avenue in Phoenix, March 2010.



FIGURE 11 US-60 at Florence Junction, Arizona, March 2010.

EFFECT OF PPA MODIFICATION ON ASPHALT QUALITY

With the advent of statistically based quality acceptance programs, it has become critical that contractors receive consistent materials. Lack of material consistency could ultimately affect the contractor profitably. Therefore an important consideration in PPA-modified asphalt concerns the ability of asphalt suppliers to produce it to the same properties day-after-day. To evaluate consistency, Figures 12 and 13 were generated to compare the variability of the HAC Glendale terminal's most common unmodified grade (PG 70-10) with variability of PG 76-16 manufactured with PPA modification. Table 2 shows a summary of this data.

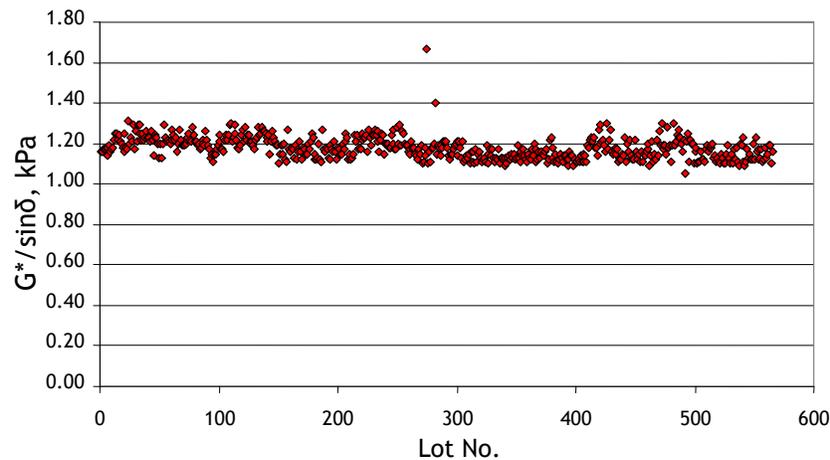


FIGURE 12 Variability of $G^*/\sin \delta$ at 70°C, February 2005 through March 2010 for HAC Glendale Terminal, PG 70-10.

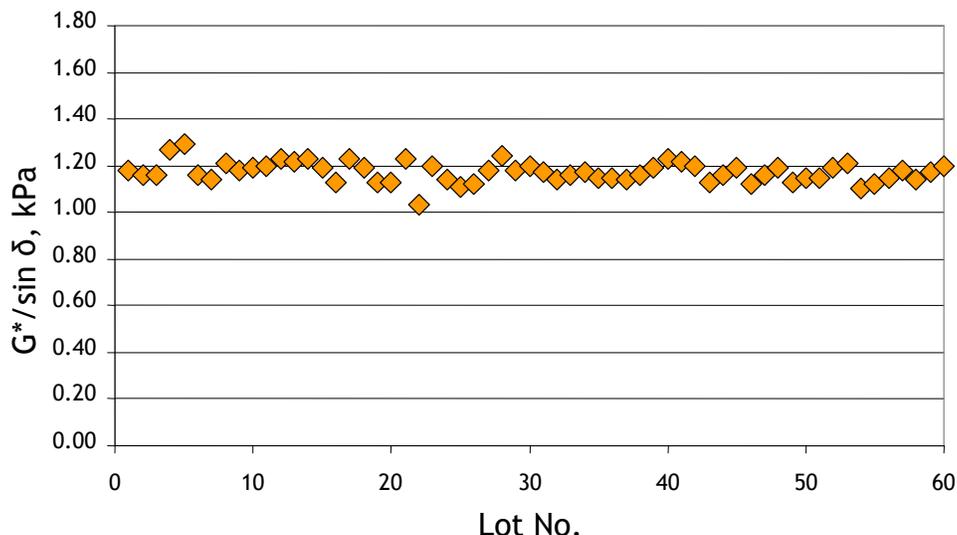


FIGURE 13 Variability of $G^*/\sin \delta$ at 76°C, February 2005 through March 2010 for HAC Glendale Terminal, PG 76-16.

TABLE 2 Summary of Quality Control Data, HAC Glendale Terminal

Grade	$G^*/\sin \delta$, kPa			Binder Tons
	Average	Standard Deviation	N	
PG 70-10	1.178	0.055	565	791,000
PG 76-16	1.174	0.044	60	64,000

HAC's quality control data shown in Figures 12 and 13 and Table 1 indicate that it is possible to manufacture a PPA-modified binder (PG 76-16) to the same level of quality as an unmodified binder (PG 70-10). It should be noted that the two binder grades, PG 70-10 and PG 76-16, are both blends of two or more other asphalts. They are manufactured using the same blend system. Therefore, it is reasonable that they exhibit similar variability. Most importantly, the PPA-modified PG 76-16 that is furnished to end use customers is highly consistent.

CONCLUSIONS

PPA-modified asphalt was implemented by HAC at its Glendale, Arizona, terminal 10 years ago to fulfill new and challenging specification demands of the Arizona DOT. Laboratory experimentation conducted by HAC indicated that PPA-modified binders would perform adequately using Arizona materials and conditions. There has been now over 9 years of performance history of PPA-modified PG 76-16 produced at that facility. Contrary to initial concerns expressed by some in the pavement materials engineering community, PPA-modified binders have performed acceptably in a wide variety of pavements throughout Arizona. Seven of the oldest projects containing PPA-modified PG 76-16 have been closely monitored and in all cases have performed well. Quality, as defined by variability, of asphalt binders produced using

PPA at the HAC Glendale terminal is at least as good as that of unmodified binders, a feature that should assist contractors operating within statistically based quality acceptance specification environments.

Holly Asphalt Company was able to successfully implement a new technology, in this case, PPA-modified PG 76-16. In the author's opinion, this implementation was successful for the following reasons.

1. PPA is a well conceived asphalt modifier; its performance characteristics in binders and mixtures were accurately estimated using existing, known, and trustworthy methods of materials characterization.

2. Implementation of any new technology such as PPA modification requires open and frank communication with engineers from specifying agencies. If one provides those engineers with good information, they will make good decisions regarding the use of new technology. Arizona DOT trusted their testing and traditional specification philosophy and accepted the use of PPA-modified asphalt, even in the face of much pavement performance hyperbole in the early 2000s.

3. Successful implementation of new products such as PPA modification requires discipline. Institutional no fly zones, such as sensible PPA dosage limits, need to be developed and followed. These rules of operation need to be easily understood, rational, and clearly communicated to manufacturing personnel.

4. A well-designed and operated manufacturing system was a key feature of the HAC Glendale terminal's success in implementing PPA-modified PG 76-16.

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NOTE

This paper was also presented at the Association of Asphalt Paving Technologists Symposium on Polyphosphoric Acid Modification and is included in *Proceedings of the Association of Asphalt Paving Technologists*, Vol. 79, 2010. AAPT gave permission to include it in this document.

Wisconsin Approach to Binder Modification

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Wisconsin is a user of the Superpave system—both the performance-related binder specifications and the mixture design system. Wisconsin does use SHRP + specifications as an added precaution on heavy traffic high-volume pavements. In general there has not been an added concern with the use of polyphosphoric acid (PPA) as an asphalt binder additive.

Wisconsin does have concerns with stiffer binder materials in relation to potential for increased thermal cracking. For high-traffic areas stiffer mixes could be more difficult to compact reducing durability. Aggregate and moisture interaction is a concern in Wisconsin. Though these are concerns in Wisconsin, they are not new and not specifically directed at PPA.

The Wisconsin Department of Transportation's (DOT's) primary approach to addressing these issues has been the use of warranty contracting. On many higher-volume roads, performance warranty contracts have been used. This requires contractors to take corrective action if unacceptable pavement develops too early in a pavement life. By doing this the DOT transfers the responsibility of possible distress from binder materials that have been modified by PPA to the contractor.

To date PPA has not been noted as a cause for a pavement failure. The primary issues in the state are slippage of individual pavement lifts, poor longitudinal joints, and segregation. These issues have not been related back to PPA, so at this time no restrictions are in place for the use of the material and none are currently planned.

Louisiana Approach to Binder Modification

CHRIS ABADIE

Louisiana Department of Transportation and Development

JOHN A. D'ANGELO

Federal Highway Administration

Louisiana has made extensive use of polymer-modified asphalt on their roadway system. They currently use the Superpave PG grading system with SHRP + tests of elastic recovery and forced ductility. The typical mixtures used in the state are produced from a wide variety of aggregates from limestone to granites. There is extensive use of liquid antistrips on DOT projects with polymer-modified binders and polyphosphoric acid (PPA). To date they have not noted any pavement distress related to the use of PPA.

The conclusion for the presentation:

- Louisiana specifies PG 76-22 with elastic recovery and force ductility and plans to change from the old + spec to MSCR soon.
- Louisiana's binder suppliers provide material with a wide range of asphaltenes.
- If PPA or any other additive is shown to reduce cost and meet the performance specification, then it will be allowed.
- Louisiana will continue to participate in performance testing and chemical testing of asphalts to verify that performance is maintained and to establish a fingerprint for forensic analysis and research.
- We must all work together to ensure the value, quality, and safety of our asphalt pavements.

APPENDIX A

Workshop on Polyphosphoric Acid Modification of Asphalt Binders
Agenda

April 7 and 8, 2009
Minneapolis, Minnesota

APRIL 7

- 7:00–8:00 a.m.** **Registration Continental Breakfast**
- Introduction**
Phil Blankenship, Moderator
- 8:00–8:30 a.m.** **Welcome**
John Bukowski, FHWA, and Roger Olson, Mn/DOT
- 8:30–9:00 a.m.** **A Department of Transportation (DOT) Survey on Polyphosphoric Acid (PPA) Usage and Issues**
Dean Maurer, Pennsylvania DOT (Retired)
- 9:00–9:30 a.m.** **AI Background Information, Physical Properties, Chemistry, Mechanisms**
Mark Buncher, Asphalt Institute
- 9:30–10:00 a.m.** **Industry Perspective, Usage, Why, How**
Gaylon Baumgardner, Paragon Technical Services
- 10:00–10:30 a.m.** **Break**
- Binders**
- 10:30–11:00 a.m.** **Effect of PPA on Binder Properties:** *John D’Angelo, Consultant*
PPA Only
PPA plus polymers
- 11:00–11:30 a.m.** **Turner-Fairbank Highway Research Center (TFHRC) Study Summary of Results: Binder Testing**
Terry Arnold, FHWA
- 11:30 a.m.–12:00 p.m.** **Analytical Procedures**
Gerald Reinke, MTE Services, Inc.
Detection
Quantitative Recovery
Recovery Issues

12:00–1:00 p.m.	Lunch provided
	Mix <i>Roger Olson, Moderator</i>
1:00–1:30 p.m.	Performance Testing <i>Tom Bennert, Rutgers University</i>
1:30–2:00 p.m.	TFHRC –Moisture Damage Study <i>Terry Arnold, FHWA</i>
2:00–2:30 p.m.	Aggregate Type and Gradation Gerald Reinke, MTE Services, Inc. Includes moisture susceptibility
2:30–3:00 p.m.	Break
	Case Studies
3:30–4:00 p.m.	Field Use of PPA with Lime: NCAT Experience <i>Don Watson, NCAT</i>
4:00–4:30 p.m.	Arkansas Rubblization Program <i>Gerry Westerman, Arkansas DOT (retired)</i>
4:30–5:00 p.m.	Ontario Strategy for Evaluating PPA <i>Kai Tam, Ontario Ministry of Transport (MTO)</i>
5:30–7:00 p.m.	Reception
APRIL 8	
7:00–8:00 a.m.	Registration; Continental Breakfast
	Case Studies (Continued) <i>Moderator Jim Sherocman</i>
8:00–8:30 a.m.	Utah Trials <i>Kevin Vanfrank, Utah DOT</i>
8:30–9:00 a.m.	MnROAD Test Sections <i>Tim Clyne, MnDOT</i>

9:00–10:30 a.m.**Industry Best Practices Document***J-V Martin, Innophos, and Henry Romagosa, ICL Performance Products*

Panel Discussion by Three States with Industry; 5 minute presentation each then discussion of specific questions in open forum:

Louisiana: *Chris Abadie, LADOTD/LTRC***Arizona:** *Dan Simpson, Arizona DOT, and Bob McGennis, Holly Asphalt***Wisconsin:** *Judie Ryan, Wisconsin DOT, and Gerald Reinke, MTE Services, Inc.***10:30 a.m.****Close-Out:** *John D'Angelo, FHWA***11:00 a.m.–3:00 p.m.**

MnROAD Tour

APPENDIX B

Transcript of Polyphosphoric Acid Workshop Discussion *Last Day*

Moderator Jim Scherocman opened the floor for questions and comments following the panel discussion. The panel members were Bob McGennis, Holly Asphalt; Dan Simpson, Arizona DOT; Chris Abadie, Louisiana DOTD/LTRC; Judie Ryan, Wisconsin DOT; Gerald Reinke, MTE Services; and Gaylon Baumgardner, Paragon Technical Services.

Moderator Jim Sherocman: We have time now for discussion and questions to the six panel members. If you are going to ask a question, please take the microphone, identify yourself, and identify which of the six panel people you want to ask your question to. So, the panel is open for questions.

From the Audience: I'll start off. There has been a lot of talk the past day and a half about PPA modification and that it probably should be limited to rather small amounts, maybe one grade bump or even less than that in some cases because of issues. And basically, for the agencies there, your specs allow the acid but what is actually in your specs, do you think, that keep you from having someone trying to do too much acid where there have been so many indications that there could be significant distress issues and failure issues?

Panel Member Chris Abadie: Speaking for Louisiana, I really rely on the moisture susceptibility testing that we do on all of the mixtures, which includes the Lottman and the Hamburg. I believe in this particular case it would catch too much. I'm always concerned that I know I'm not always right and always looking for improvement to that. That is where we stand.

Panel Member Judie Ryan: I would say that in our state, the closest thing we have is really the fact that we are guided by (AASHTO M) 320 and the PG+ specification. However, I think that due to the recent dialog and all the information that is there, I think probably the next place to go is to look at criteria versus just the exclusionary type specification changes. And probably bring (in) more of the arrows going up and to the right by way of other torture testing (in reference to earlier comments during her presentation regarding ensuring positive improvement in pavement performance).

From the Audience: Do any of you all use limestone aggregate and do you have any PPA concerns with the limestone?

Abadie: Yes and no.

Panel Member Gerald Reinke: Wisconsin, or at least southwestern Wisconsin and southeastern Minnesota, is replete with limestone and some of it is not very good quality limestone either for that matter. That was one of our concerns initially when we looked at using acid in conjunction with polymer and by itself. We began running the Lottman test and didn't seem to have any problems there. And we've run Hamburg on many of these mixes over the years. In some cases,

we've seen some difficulties and we've had to adjust using the phosphate ester antistriper. As has been said many times, you need to do some sort of moisture sensitivity testing on these mixes and if you don't, you are probably going to have some problems.

From the Audience: Question for Gaylon or Gerry or both. With warm mix being ever so prevalent... obviously with the warm mix technologies, there are a lot of chemical packages out there that are not readily identified as to what they are. Are there any concerns running some of those projects, pushing to field tests right away with not a lot of lab testing? What concerns are there on that end with some of the different grades and if they are acid modified and reactions with some of the warm mix technologies?

Reinke: We have ourselves done or been involved in two projects that involved polymer with acid in it. One was constructed ourselves and one was constructed at MnROAD last year. And we are using technologies that don't use amine additives and that don't use water. That's what we have gone to to solve that problem. And when we looked at using amine surfactant chemistry, at least in the laboratory, we had issues with that. So just like with the antistrippers, if you are going to use a chemistry that has amines in it, I think you are going to have difficulties. So, you need to choose wisely is what it comes down to.

Panel Member Gaylon Baumgardner: I will just agree with Gerry. One of the issues we were concerned about was also what are the effects of some of the water containing systems in the reaction with amine and PPA? Because we knew there would be binders with PPA in them. But we have done several projects—in fact we just completed one—that have a combination of amine and PPA in warm mix and the performance was as expected. It was basically the typical binder that was sold for that particular state.

From the Audience: Years ago I spent the whole winter pounding out samples and doing antistripping testing for a DOT. One thing we quickly found out when we were experimenting with different liquid antistrippers. Those applications were all constituent dependent: what type of aggregate, what type of crude oil, dosage levels, and so forth. And if you didn't have the right combination, you could get in trouble real quick. We seem to have sorted those out over the last eons and we don't use the things that don't work. Is that situation that I experienced any different with acid? We know there are certain things you shouldn't do just off the bat.

Baumgardner: I may not address that in particular but something very similar which was an issue, long before PPA, dealing with certain states and QPLs (qualified product lists) and certain antistrippers. We shipped a binder (neat binder before Superpave) to the state. The additive we had was on the QPL. They added it and when they tested the binder, it was failing the viscosity spec. That was kind of strange. So, the first thing we did was look at the antistriper agent that we were using. We saw that that was the issue, so we switched from an amine based antistriper to a phosphate ester because of the high acid value in this particular asphalt. What I am trying to say is that what it boils down to is this; you can have the same issues with antistrippers that we see with PPA. It is a formulation thing. That is why we have been stressing that maybe we need to look at the total performance of the system and also look at the binders with the additives rather than just the binders as neat binders. I think that's what you were getting to. It is very similar to the

problem we have had with antistrips; that is why we need to continue to investigate that as we do with liquid antistrip.

From the Audience: You indicated there was a TRB paper that indicated there were some environmental concerns with PPA. I wondered if anyone can elaborate on that and say what the outcome might be.

Panel Member Bob McGennis: There was actually no follow-up study that was done on that. One of the coauthors of the paper cited or did some calculations that there will be several—I think between one and two—tons of free acid that could potentially leach out of the pavement into groundwater. I think during the discussion—I'll attribute it to Gerry—it was pointed out that anyone who has used cationic emulsions knows that hydrochloric acid is one of the constituents of those. And so, if it is a problem, probably it is a bigger problem than we thought. As far as I know, there was no follow-up that was done really to look into that.

From the Audience: I can comment on that. We have been doing a test called Toxicity Characteristic Leaching Procedure, and we touched on that during the Peterson Conference and we shared information. We were above and beyond the typical usage of PPA at 3%. We've got a lot of binder content on the coarse aggregate and are doing the test in water. We have not detected any phosphorous in the leaching water. I think FHWA is going to do some additional work on that matter, and I think there are already some additional work as well on MnROAD. Some of the water has been collected, is that right?

From the Audience: I think what Tim Clyne was saying was that the detection limit for phosphate runoff from the MnROAD Section 78, which was Elvaloy, was less than 20 parts per billion. So there is not phosphate run-off.

Baumgardner: I was at both of the conferences that you were mentioning. In fact, I got up and made a comment at the end of one of the presentations; talking about the hazards of run-off and polyphosphoric acid or phosphoric acid. Remember what I presented yesterday, talking about the hydrolysis of polyphosphoric acid to ortho acid and basically phosphoric acid? Do you drink soft drinks? Coca Cola, Pepsi, Sprite, 7Up, or any of those? Anyone who is drinking one should look at your label. This talk we've had today about "We didn't know what was in there"; one of the ingredients of soft drinks is phosphoric acid. If it is going to be an issue with groundwater... I guarantee you, we probably drink more soft drinks than water. We are all dehydrating ourselves. Phosphoric acid is commonly used as a food preservative. A lot of the frozen foods (contain it). Phosphates and phosphoric acid type materials are in a lot of things that we ingest daily.

From the Audience: I want to start by thanking the organizers. This is an excellent, excellent workshop. I think I respect a lot the idea that we have blind specification. I think what I heard from Gerry and directly from the discussion today, that it looks like we need to be careful about using so blind a specification. Looks like we need to know what's in some of the materials we are producing. My specific question is will the industry and the DOTs be willing to accept an idea where we ask the suppliers just in a way to specify what is in the asphalt that is being shipped if we need to deal with these ingredients?

From the Audience: Just let me add one thing to that—something that is bothering me about that and it builds directly on what has just been said. You talk about mix testing. Well, in the real world, you don't do that. A contractor will start with one asphalt and they'll do all the testing with that. If something happens, they will buy it from somebody else. They are not going to re-test everything. It just doesn't happen. And most times the DOT won't even know it. The supplier is short for some reason so the supplier will buy from someone else and ship it. It still comes from the supplier but it is a different source. So, we just don't know some of these things. I think it builds on what has just been said. Are we going to have to find data on what's actually in there?

Baumgardner: One of the main issues that I have with that as a supplier is, in a free market system, we have competitors. If we have to disclose then all of sudden disclosure. I know for a fact that there are some things we do that our competitors don't. I wish some were in here because we discussed it. We discussed the fact that we look at the performance of our binder versus our competitor's binder at a normal review to make sure that we are doing the job the way we think we need to do it. Many of you have seen presentations from John (D'Angelo) where he has a binder, and he says I don't know what it is but the binder was supplied by Ergon. There are some things we do, additives that we use, not that we don't want the DOTs to know, but that we don't want our competitors to know. In fact, some of them are put in there strictly as performance inhibitors for the mixture. They are designed not just to meet a binder spec. By disclosing that, we are telling the entire world how we accomplish that. You lose the competitive edge with doing that. As long as we could secure the proprietary nature of some of the formulations, that is a possibility. That is what we prefer about the blind specs; the fact that we do not have to disclose everything that we are doing in manufacturing. It is not always just what you add to it, it is how you process it. John (D'Angelo) has a very good presentation where he shows the multistress creep recovery test and looking at the production of the binder to adjust the parameters. As we disclose these things, we actually put a lot of information out. I know it helps the industry, but it also helps the competition.

Abadie: I share the same concerns, as an agency and part of our specifying group. It is very difficult to rely strictly on the test. What you really need is open communication. That was part of my slide and part of my presentation. And what you are talking about is indeed formal open communication about what is going on. That is what I strive for, but knowing all of the other sides and listening to the suppliers and the DOT and ability to test; there are two sides of that and you cannot get there tomorrow. What you are suggesting is a place I will like to get us to where the suppliers fully disclose—on a general basis—what is being supplied and also work with us in research to figure out what they want to change that might affect the performance.

Ryan: I would say also that there might be some medium transition step to go through other than full disclosure as I might understand it. More of a certification that includes values that you are meeting with that particular product; maybe a way to look at going that direction. I do not think there will be many other states—there are many other states here (so) if you want to get a microphone and jump in I think it will be a good comment as well—but I do not think many of the states' highway associations would be opposed to heading that direction.

From the Audience: In the spirit of other states jumping in, Utah DOT is very concerned about quality control issues and the consistency of the material that we get. We understand that we do not control the refinery and that the refinery's diet changes. The terminal that produces the material does not control the material that they receive. We have an informal arrangement with the suppliers of the materials, of binders, if they have to change the formulation by more than half a percent on any particular piece of that. If their flux has to change by a half a percent, if their polymer load has to change by more than half a percent to meet our specifications, if they would at least inform us so that we can do the necessary performance testing on the material because these things may—we don't know that they do—change the performance of the mix.

From the Audience: I made a presentation yesterday, and I am very happy that we are going to talk about state and suppliers issues here. We, as an agency, want to know what is in our road. We have a right to know what is in there. In case of any performance problem, we need to know what is in the road. As far as the proprietary issue, I think... we have a contract obligation with contractor. Contractors, suppliers work through that protocol so that we keep the line of confidentiality in place. That is what we are trying to do; we are trying to ask the suppliers to state what they have in the materials directly to the state rather than to anybody else in the industry. In that case, we can keep their formula secret, their proprietary secret, and we can work through that kind of arrangement without jeopardizing your production secret. I think that is the way to go to have a happy medium.

From the Audience: Just a problem from a supplier point of view, from a formulator point of view, and just to follow up on what was just said. Obviously, it is very logical from an agency point of view to want to know what they put in the road. There is a very fine line to walk here from knowing what type of binder they are using to specifying recipes, because we see that across the United States and Canada. You shall have a minimum of 3% SBS. You shall have a minimum of this much antistripping agent or only this type of antistripping agent and so on. The main point to this is that it gives the agency a comfort feeling that we are doing something to assure that we are putting a good binder in the road, which is not true. A minimum 3% SBS does not translate necessarily into a good quality polymer modified binder. A minimum of 5% antistripping agent does not necessarily work. So this is a very fine line here; do not think that if you are specifying recipes that you are necessarily going to get a better quality binder if you do not have that relation of trust with your supplier and your formulator and you trust them to do all they can to give you a good quality binder. An experienced formulator can circumvent anything and sell you garbage.

Reinke: The comment I have is I wouldn't have a problem—and I am speaking only for myself now because obviously I can't commit the company to this—I would not have a problem with saying yes, there is polymer in here, there is acid in here, there is acid only in here without disclosing the exact formulation. I do not know if the person asking the question is looking for exact formulations or if he was looking for general composition. I think you could achieve the goals that you are talking about with general compositional information and the MSCR test. Between those two things, they are going to tell you the answer to whether or not the binder has the kind of performance characteristics that you are looking for. That still does not translate into the mix performance, which still needs to be accomplished, but general compositional information I don't see as being a big problem.

Scherocman: Before Bob gets up, I have a general question for the group. I thought the whole PG grading system was supposed to be blind to the modifier. Now we seem to have scrapped that whole thought. And when we get to warm mix, we scrap it even further because they are throwing all sorts of things in there at the asphalt plant. So I have a question. What are we doing?

From the Audience: Minnesota along with Wisconsin, Iowa, both Dakotas and Nebraska are part of a Combined State Binder Group. Part of our certification document says that each supplier has to identify each modification technique with a unique identifier. Not necessarily tell us what the formulation is, but it has unique identifier. So, if there is an investigation, if we have problems with it, then we can go back and identify it.

From the Audience: I just wanted to round out that conversation. I am with the Asphalt Institute of Ontario. I stand between the Ministry and the supplier. The point is how the system works in Ontario, just to explain it a little bit more clearly. We had a group that got together with industry to talk through this issue of how we are going to do this. There is a QC (quality control) plan that the supplier has to produce. In the QC plan, it typically says “from this terminal, when I make this grade, I may have PPA added to it and if I do, it is going to be in the range of 0.5% to 1%.” That leaves people the option of not giving away the precise formulation. You are not even saying it is going to be used because in Ontario what comes out of the pipeline the next day could be different and you have to do something different. It gives people the flexibility (they need) but it keeps the ministry informed. If there is a big change, they are supposed to tell them partway through that we are not going to be supplying that grade of whatever it is. It goes from the supplier to the ministry. It is a confidential document, and that’s the way it is treated.

From the Audience: I just want you to know that until 2007 New York State DOT never required PG binder suppliers to tell us anything about if the asphalt is neat or modified; but after 2007, we required every supplier to tell us if it is neat or modified. If it is modified, they have to let us know what they used. Is it polymer or PPA?

McGennis: I guess this kind of gets back to the point Hussain brought up and that John was talking about. In both of the states that I work in, there actually are requirements that we do disclose in a general way. So by specification, this has already been covered. In every state I have worked in or been in I think there is a statement within the specification that says if the source changes that you are to disclose it. What happens in both the states that I work in is at that point the DOT can decide whether or not they need to redo the design. Typically, they will do one-point verification and typically they do the stripping test because they want to check the volumetrics and they want to make sure the asphalt will still stick to the rock. To me that is an issue that is much bigger than PPA. Now I do live in the real world. Do they always disclose that? I don’t know. A lot of times that comes out in the first lot of production where nothing looks like it did during the design. I think this is an issue that is much bigger than even PPA. It happens every day.

Scherocman: John D’Angelo is going to make a final wrap up comment or two.

John D’Angelo: I want to go over what we were really trying to accomplish here in this workshop. One of the primary things was to get actual data on the table so that people can

actually look at it to make a decision on what they want to do with PPA. We have had quite a few presentations about how PPA works with asphalts and how it interacts with other materials other than just the asphalt. Jim asked a question, “I thought this is supposed to be blind.” The binder specification is pretty much blind and it works well. You also have interactions with other components of the asphalt mixture, which are the rocks. The binder spec is a binder spec. You have to go the next step. That is the kind of thing we are trying to bring out in this workshop. You need to look at the whole material as it is going to be used on the road and provide that data.

We are going to put together a TRB circular. Hopefully we will get papers from everybody—I’m going to work on it. We’ll get them published in a book so it is documented and people can go back and reference them. Also, we have been webcasting and recording it and hopefully Purdue will continue to have that available so people can go back and look at it. There were two presentations that didn’t make it due to technical difficulties. We are going to go back and try to re-record those so at least we’ll have the presentations, but not the discussion.

Scherocman: Let’s thank the panel for their efforts and work. And remember, the most important specification is “black side up.”

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