TechBrief

The Asphalt Pavement Technology Program is an integrated, national effort to improve the long-term performance and cost effectiveness of asphalt pavements. Managed by the Federal Highway Administration through partnerships with State highway agencies, Industry and academia the program's primary goals are to reduce congestion, improve safety, and foster technology innovation. The program was established to develop and implement guidelines, methods, procedures and other tools for use in asphalt pavement materials selection, mixture design, testing, construction and quality control.

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The Use and Performance of Asphalt Binder Modified with Polyphosphoric Acid (PPA)

This Technical Brief provides an overview of the implication of the use of Polyphosphoric Acid as a modifier for asphalt binders and implications in relation to asphalt pavement performance.

Background

The modification of asphalt binder to improve performance properties has grown significantly since the implementation of the Strategic Highway Research Program (SHRP) binder specifications. There has been increased use of polymers, crumb rubber modifier and Polyphosphoric Acid (PPA). There has been 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 anti-strips. There have been anecdotal stories about both failures and successes. The Federal Highway Administration in cooperation with the Transportation Research Board and Minnesota DOT sponsored a workshop as an attempt to bring together the real facts about PPA modified asphalt and 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.

Overview

There is a wide variation in the approach of the highway agencies to the use of PPA as based on a surveys conducted by the Pennsylvania DOT in 2002 and 2008 combined with a survey done by the Ontario Ministry of Transport in 2007 . As of the specific point in time of the surveys 12 states had no restrictions on the use of PPA and 15 states outright banned the use of PPA.

Restrictions had been placed on the use of PPA in 14 agency specifications. These restrictions included only allowing the use of PPA as a co-modifier with polymers or they had established 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. This indicates that there is significant lack of factual information on the use and effect of PPA on asphalt binders by the various highway agencies.

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

What is PPA

Polyphosphoric acid ($H_{n+2}P_nO_{3n+1}$) is a polymer of orthophosphoric acid (H_3PO_4). Polyphosphoric acid offered commercially is a mixture of orthophosphoric acid with pyrophosphoric acid, triphosphoric and higher acids and is sold on the basis of its calculated content of H_3PO_4 as for example 115%. Superphosphoric acid is a similar mixture sold at 105% H_3PO_4. Other grades of phosphoric acid may contain water, but are not typically used in asphalt modification. 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, metals finishing and asphalt modification. This circular will specifically discuss the use of PPA as an asphalt modification.

There have been several patents on the use of Polyphosphoric acid 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 involve the use of PPA with polymer modification. The past experience has shown PPA increases the high temperature stiffness of an asphalt binder with only minor effect on the intermediate and low temperature properties.

How is PPA Used

The Superpave Performance Grade (PG) binder specification is used predominantly in the US. In the PG system the high and low temperature performance range is specified i.e., PG 64-22. The 64 represents the expected high temperature range of the binder and the -22 is the expected low temperature range. The difference between the high and low temperature range of the binder is call the useful temperature interval (UTI). A PG 64-22 would have a UTI of 86°C or 64 – (-22) = 86°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. A specific crude may be refined to make a PG 58-28 or PG 64-22 or PG 70-16, but it cannot be refined into a PG 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 typical shifts in grade that can be done in the refining process are shown in Figure 1.

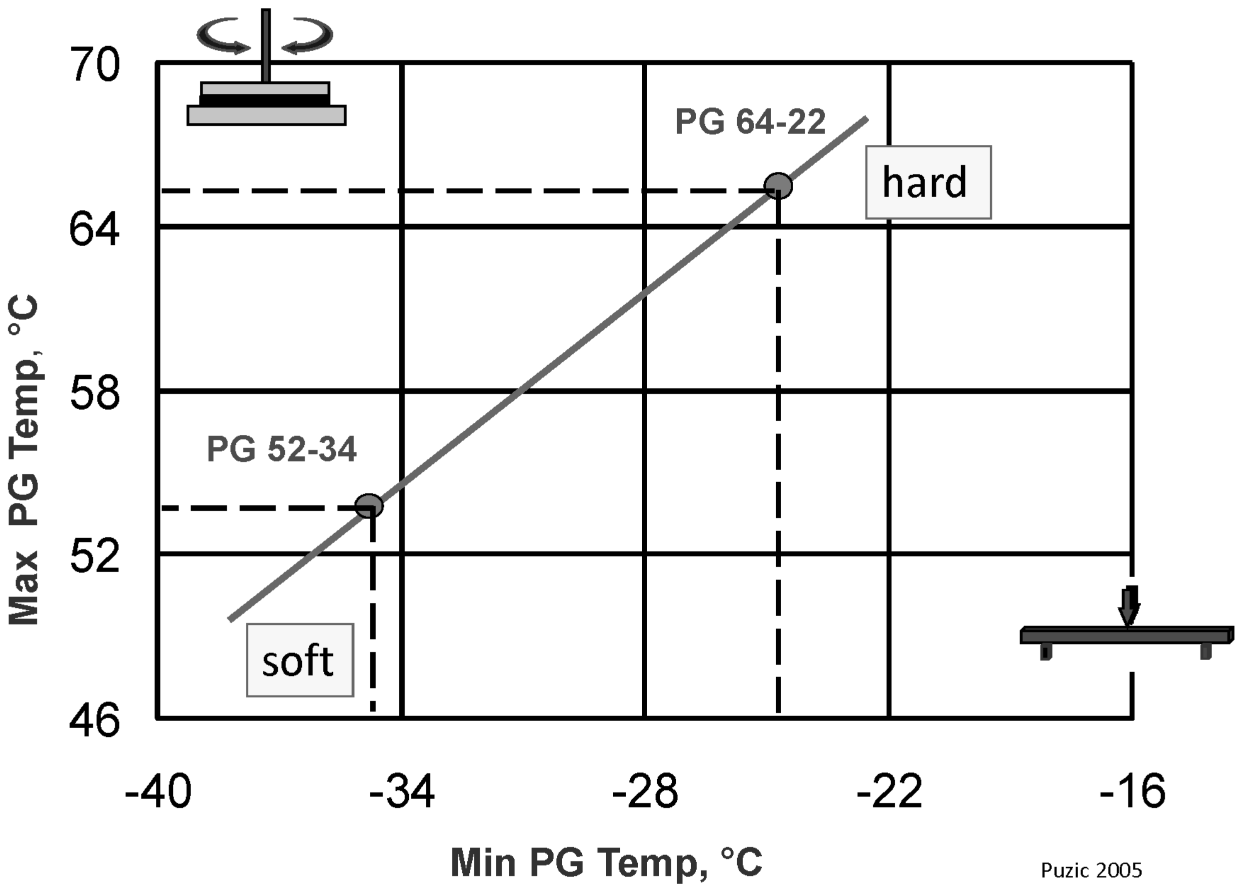

Figure 1. Superpave Performance Grades (PG) and the PG Line

The use of the Superpave binder specification has encouraged agencies to specify stretch grades. These are grades that 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 intermediate temperature properties of some asphalt binders. In cases where adding polymer in percentages greater than about 3% is needed to change a PG 64-22 to a PG 76- there will be a tendency to raise the 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 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.

One question is how much PPA is required to change a binder one high temperature PG grade and does PPA have the same effect on all asphalt binders. To evaluate this 105% PPA was added to 2 very different binders from different crude sources. PPA at 0.5% by wt. 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 2.

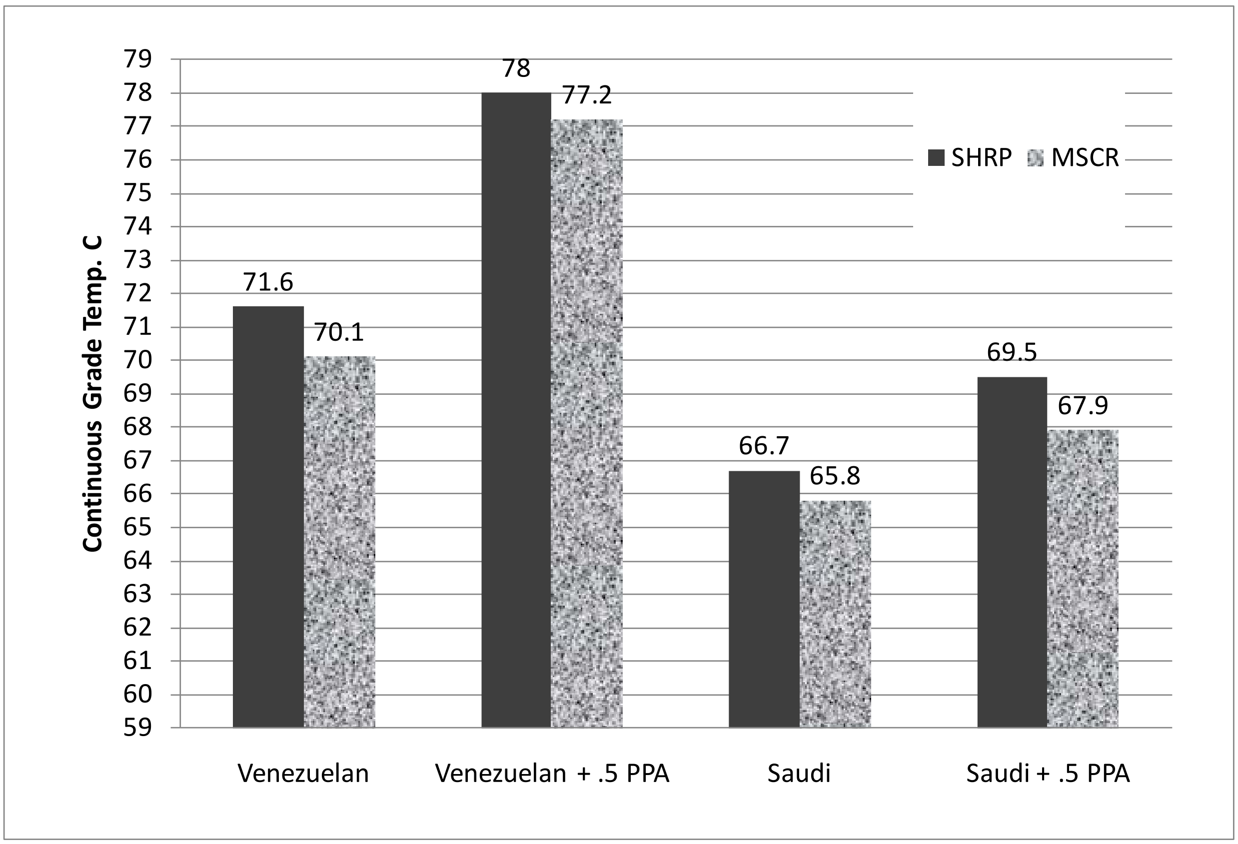

Figure 2: High temperature continuous grades of binders from different crude sources and modified with 0.5% PPA.

The high temperature binder properties were measured using 2 systems, the existing $G^*/\sin\delta$ and the Multi-Stress Creep and Recovery (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 3°C for both the G* and the MSCR grading.

Work by Terry Arnold (FHWA) clearly demonstrated that increase in binder stiffness from the addition of PPA was crude source dependant. 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 applications 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 interaction of PPA and polymer modification was evaluated using the Multi-Stress Creep and Recovery test. The testing demonstrated that there is an interaction between PPA and SBS polymers. The data indicated that the improved high temperature stiffness of the PPA SBS 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 PPA SBS combination. Data is shown in Table 1. The percent recovery for the PPA SBS combination was always greater than just the SBS even though the PPA when tested by itself provides no increase in the percent recovery. In addition to the added stiffening effect, the PPA also acts as a cross-linker, improving the polymer network. This was demonstrated by the evaluation of florescent micrographs of the binder samples along with the improved percent recovery.

Table 1: 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%

Testing for PPA

Once highway agencies realized that PPA may be used as an asphalt modifier their first reactions was can it be measured in the asphalt binder. Gerry Reinke, MTE Services, used an X-Ray fluorescence approach to measure the amount of phosphorous 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. 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. The acid scavenger used is typically 1,2 epoxy butane. If there is acid present in the binder in the form of PPA the 1,2 epoxy butane 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 potential neutralization issues.

PPA and Mix Performance

A study was done at 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 12.5 mm Superpave mix at N_{design} of 100 gyrations. From the study the following conclusions were made.

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 short-term and long-term oven aged samples were statistically equal at a 95% confidence level, shown in Figure 3 Meanwhile, 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 AASHTO R30, showed that both modified asphalts provided very similar modulus values after undergoing long-term oven aging. 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. The beam fatigue data for the LTOA material is shown in Figure 3.

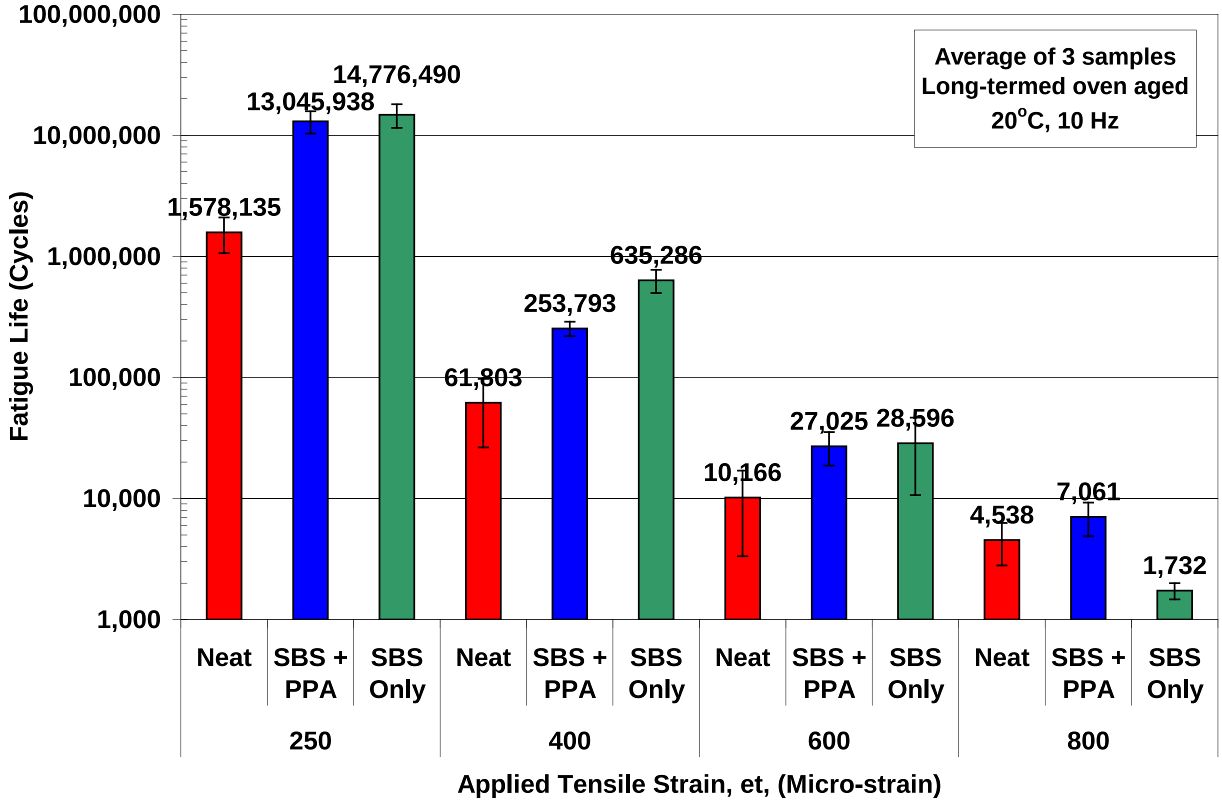

FIGURE 3 – Flexural Beam Fatigue Results for Long Term Oven Aging

Repeated Load Permanent Deformation testing conducted on hot mix asphalt samples showed that both the SBS and SBS+PPA asphalts achieved almost identical resistances to permanent deformation when tested in uniaxial compression.

PPA and Moisture Damage Potential

The potential for increased moisture damage has been a concern when PPA modified binder is used. Terry Arnold evaluated one binder using three different aggregates and with and without lime and liquid antistrips and Gerry Reinke evaluated both neat and polymer modified binders with and without PPA on three different binders.

PPA is a hydrophilic material and easily absorbs water. It was demonstrated that binders modified with higher percentages of PPA above 1% had a tendency to absorb water and loose strength. Beam samples of binder and mastics were made and place in a water bath at 7.2°C for up to a year. Binders 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 binder and mastics.

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 Tensile Strength Ratio as per AASHTO T-283. The binder blends tested are shown in Table 2.

Table 2. ICL Binder Blends

Blend	Blend formulation	Mix additives
PG 64-22 control	No additive	
PG 64-22 + antistrip	0.5% phosphate ester #1	
PG 64-22 + antistrip	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

The Hamburg Wheel Tracking results at 50°C submerged are shown in Figure 4. The results in Figure 4 show a progressive improvement in mix moisture sensitivity performance progressing from the poorest performer the PG 64-22 control binder. The PG 70-22 manufactured with PPA produced only a minor improvement in performance over the control binder. The addition of each phosphate ester anti-strip 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 anti-strips 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. The addition of hydrated lime to the mixes produced with the PG 70-22 showed no detrimental effects related to mixture moisture sensitivity.

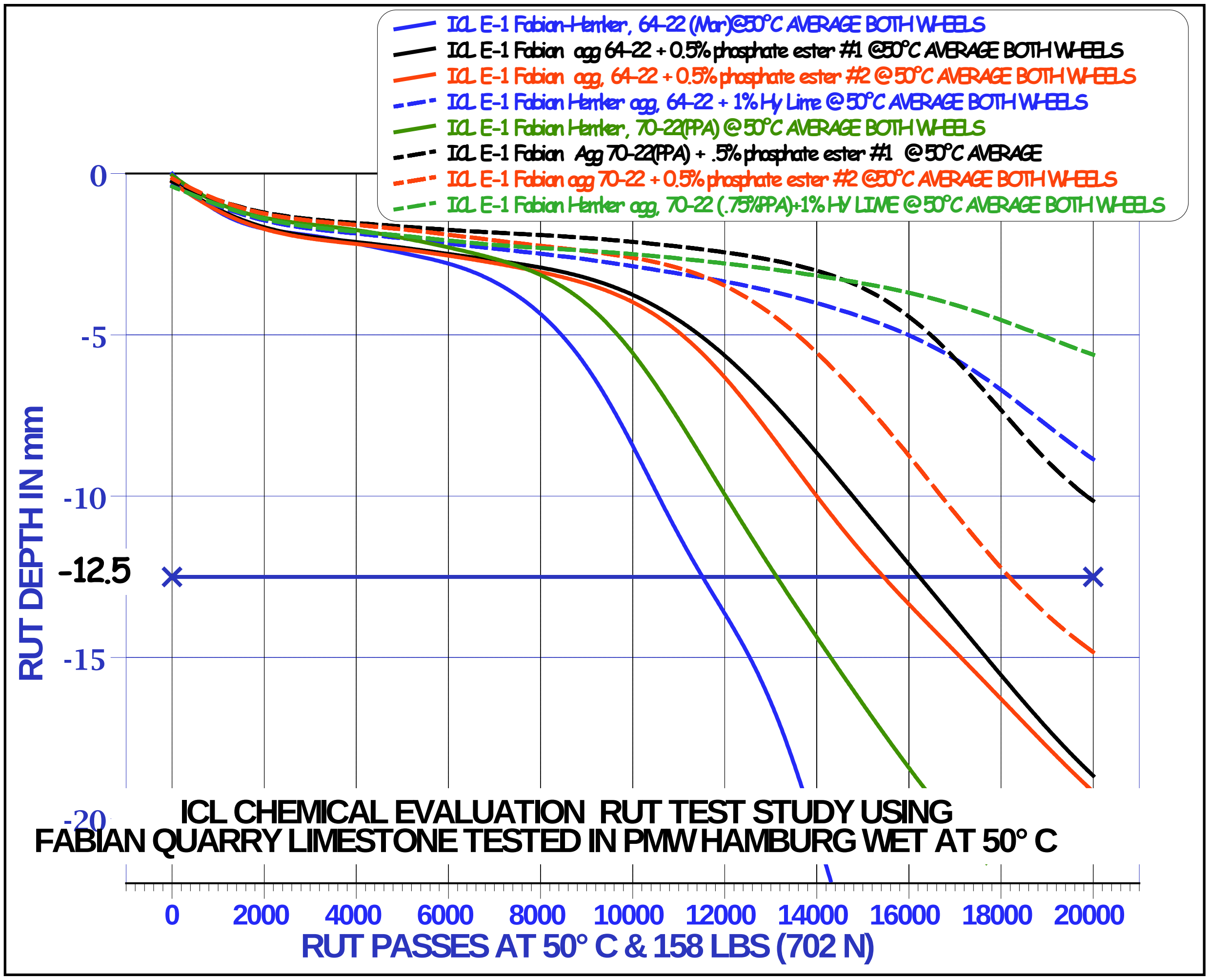

Figure 4. Hamburg Wheel Tracking Test, 50°C, submerged samples for ICL Mixes with Fabian Hemker Aggregate (A Known Stripper)

Tests carried out at the FHWA's Turner-Fairbank Highway Research Center using Hamburg wheel tracking at 50 °C showed that the PPA effect on stripping was asphalt and aggregate dependent. The presence of PPA in doses higher than 1% made stripping worse but not always. The study also found that the effect of amine anti-strips was asphalt and aggregate dependent. Hydrated lime treatment of the aggregate was found to work very well as an anti-stripping agent.

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 additive 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 antistrips. Overall the data indicates PPA may 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.

Field Performance and PPA

Arkansas DOT undertook a major reconstruction plan of their interstate system in 1999. Under the program 380 miles of interstate would be reconstructed over 5 years with 340 miles reconstructed with hot mix asphalt (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 IRI > 170 in/mi and 33% had a moderate rating IRI 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 < 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 antistrip. These sections received 10 million ESAL during the first loading cycle with no indications of poor performance. All rutting for the sections was less than 6mm. There was no evidence of moisture damage. In 2003 a second cycle of the track was constructed where 9 of the existing PPA/SBS sections were left in place and 9 new PPA/SBS sections were constructed. Again after 10 million ESAL's, 20 million for the original sections rutting was less than 9mm on all the sections and there was no fatigue cracking that was attributed to the mixture. After 6 years with over 40 inches a year of rain 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 5 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 antistrip were added to each mix. After 18 months there was less than 3 mm of rutting in any of the sections and no signs of moisture damage. Only one transverse crack had appeared in one section. Performance will continue to be monitored for 5 years.

Utah DOT has done some lab evaluation of PPA modified binders. In mix testing with lower levels of PPA 0.85% max they have identified a potential increase in moisture damage potential in some mixes. Utah has elected to address this with mixture test requirements as opposed to a ban on PPA. Utah requires Hamburg testing for all mixes and feels that will catch any stripping problem and the also require ER for the binder which they feel will guarantee them they have polymers.

The final session of the workshop was a panel discussion lead by 3 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 + binder tests to provide them what they want. Arizona from the desert southwest, Louisiana from the Golf coast and Wisconsin from the upper mid west, all have very different climates.   Each understands the concerns with PPA, but has had success by addressing performance properties as opposed to placing restrictive formulation specification on the suppliers.

Summary of Workshop Findings

The PPA workshop covered extensive laboratory and field evaluations on the use of PPA as a modifier for asphalt binder.

- The stiffening effect of PPA on the binder is crude source dependent with anywhere from 0.5% to over 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 with applications rates of 1.0% to 1.5% or greater for particular asphalt-aggregate combinations.

- Below the level of 1.0% to 1.5% there did not appear to be any increase in moisture damage potential. The lab testing indicates that PPA can work with amine, hydrated lime and phosphate ester anti-strips to mitigate moisture damage potential; however, it is asphalt and aggregate dependent. This was seen in both the Hamburg wheel tracking test and the AASHTO T-283 Tensile Strength Ratio (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.

- Over 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 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 moisture damage evaluation is included, is adequate for PPA dosage rates up to 1.0 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.

Further Information:

- Asphalt Institute Publication IS-220: "*Polyphosphoric Acid Modification of Asphalt*"
- Association of Asphalt Paving Technologists Symposium, *"Polyphosphoric Acid Modification"*, March, 2010

- Transportation Research Circular Number E-C160: *"Polyphosphoric Acid Modification of Asphalt Binders - A Workshop"*, Transportation Research Board, April 7–8, 2009, Minneapolis, Minnesota

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