

Polyphosphoric Acid What really is it

Review of the PPA workshop April 2009
and recent studies

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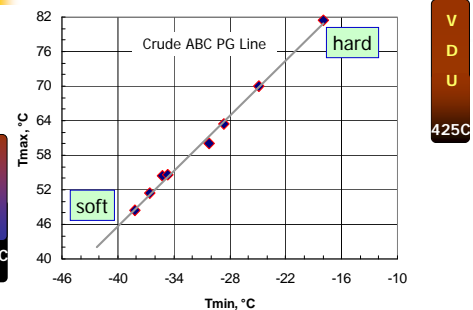
Definition - Asphalt

a high molecular weight, thermoplastic hydrocarbon constituent, found in a large number of petroleum crude oils. Although some asphalts do occur naturally, asphalt as we know it, and as discussed herein, is derived from fractional distillation of petroleum crude oil.

UTI of Performance Grade Asphalts

- A PG 64-22 would have a UTI of 86 C°
- A PG 58-28 also has a UTI of 86 C°
- If we needed a PG 76-22, which has a UTI of 98 C° - how is this accomplished?
- As a "rule of thumb", to achieve a UTI of >92 C°, the asphalt has to be "modified".
- Depending on crude source, some binders with more narrow UTI's of 86 and 89 C° may also require modification

For a given crude, asphalt grade
is defined by refinery processing conditions



Puzic 2005

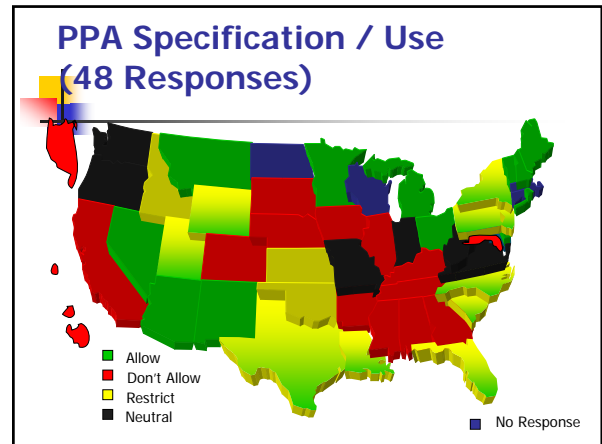
Phosphoric Acid Modification of Asphalt Binder

Definition – Polyphosphoric Acid

- Inorganic Polymer
- Obtained by Condensation of Monophosphoric Acid or by Hydration of P_2O_5
- 0%wt of Free water
- Viscous liquid (25°C) from 840 cP (105%wt) to 60 000 cP (115%wt)
- Crystallisation temperature below 0 to 15°C
- Medium strong acid : Acidity function (Hammett) = 6 (ref H_2SO_4 = 12)
- Highly soluble in organics
- Non oxidant compound

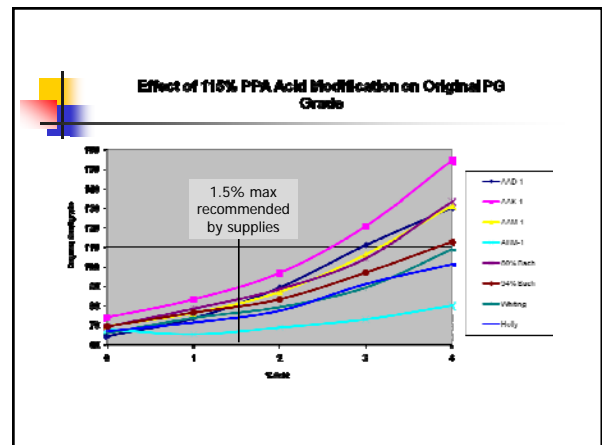
Survey of PPA Use

- Penn DOT Survey 2008
- Ontario Survey 2007



PPA reaction with binder & Polymer

- Review of several studies
 - FHWA
 - Baumgardner
 - Arnold
 - ICL - Dongre



PG76-22 from Saudi Asphalt

PG Grade Achieved	76-22	76-22	76-22	76-22
PPA %	0	0.2	0.4	0.6
Polymer %	4.75%	4.10%	3.75%	3.40%
Brookfield Vis.@ 135	2950	3870	3290	2230
ODSR	1.606	1.532	1.561	1.534
Phase Angle	67.1	64.5	66.2	69.2
Wt. Loss	-0.105	0.21	-0.053	-0.034
RDSR	2.378	2.613	2.569	3.03
PDSR	1198	1126	1422	1276
BBR S Value	125	142	148	143
BBR M Value	0.325	0.335	0.332	0.327
Elastic Recovery	87.50%	86.70%	85.00%	85.00%

PG76-22 from Venezuelan Asp

PG Grade Achieved	76-22	76-22	76-22	76-22
PPA %	0	0.2	0.4	0.6
Polymer %	4.25	3.75	2.9	2.6
Brookfield Vis.@ 135	2350	2030	1510	1360
ODSR	1.557	1.524	1.366	1.42
Phase Angle	68.7	68.6	78.3	79.4
Wt. Loss	0.012	-0.024	0.23	0.008
RDSR	2.472	2.802	2.281	2.58
PDSR	1424	2038	1804	1934
BBR S Value	138	150	163	172
BBR M Value	0.32	0.31	0.311	0.306
Elastic Recovery	80.00%	77.50%	69.00%	64.00%

PG76-16 from CA Valley

PG Grade Achieve	76-16	76-16	76-16	76-10
PPA %	0	0.2	0.4	0.6
Polymer %	5.5	4.4	3.8	3.25
Brookfield Vis.@ 135	2060	1450	1310	1140
ODSR	2.092	1.595	1.414	1.253
Phase Angle	55.8	61.5	67.3	72.2
Wt. Loss	0.11	0.24	0.127	0.049
RDSR	2.327	2.521	2.335	2.296
PDSR	1959	2203	2782	1719
BBR S Value	211	286	291	115
BBR M Value	0.337	0.317	0.312	0.425
Elastic Recovery	85.00%	87.50%	85.00%	82.50%

PPA reaction with binder and Polymers

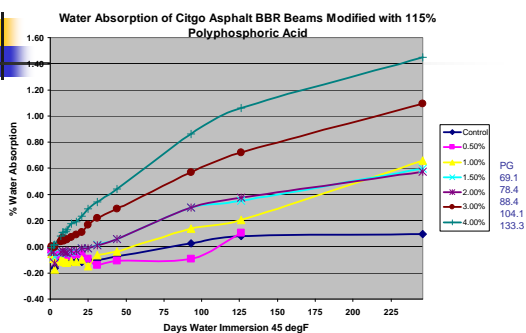
- PPA reaction with binder is binder specific.
 - Stiffening effect varies for different binders.
- PPA appears to improve SBS elastomeric response.

Moisture Sensitivity

- Does adding a hydrophilic material like phosphoric acid impart moisture sensitivity to the binder?

Moisture Sensitivity

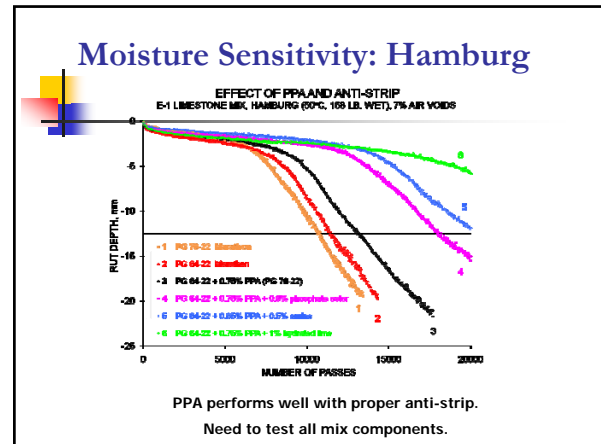
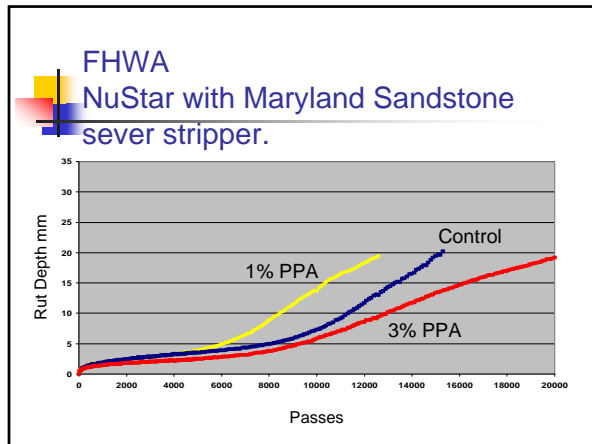
- BBR Beams and DT samples of neat binder were soaked in a 45°F water bath
- Beams were dried with a paper towel and weighed
- For this Asphalt (Citgo) water absorption increases with increasing PPA particularly at levels greater than 1.5%



Hamburg Moisture testing

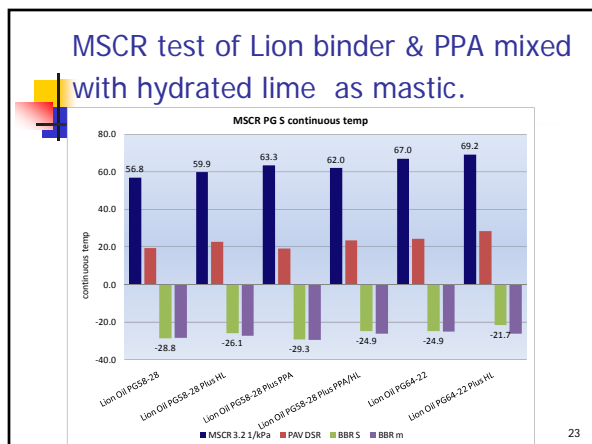
- FHWA Research study
- Mathy study





- ### Conclusions – Hamburg Testing
- Test is only an indication and was with limited asphalt
 - PPA increased moisture sensitivity of the neat binders for one AC
 - Action of amine and phosphate ester anti-strips is aggregate specific- PPA may increase moisture sensitivity with certain Amine's
 - With lime treated aggregates the moisture sensitivity is unaffected or improved by PPA modification
 - Users need to test each asphalt/aggregate/anti-strip combination.

- ### MSCR testing of binder with hydrated lime still in binder
- One binder source Lion Asphalt, 58-28 & 64-22.
 - 1.2% PPA
 - 20% lime by wt 9% by volume.
 - Mix binders with Lime, Lime and PPA
 - Evaluate binder properties with Lime still in the binder

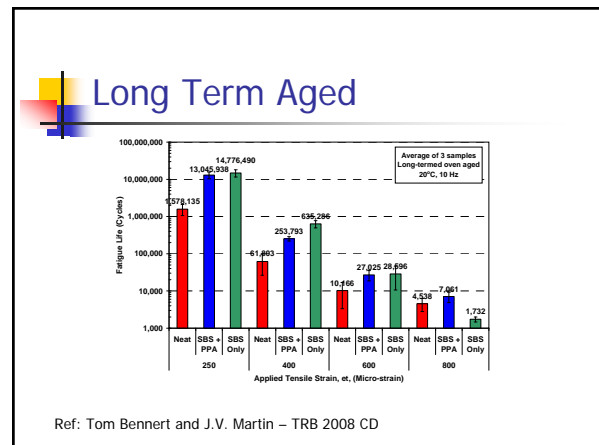
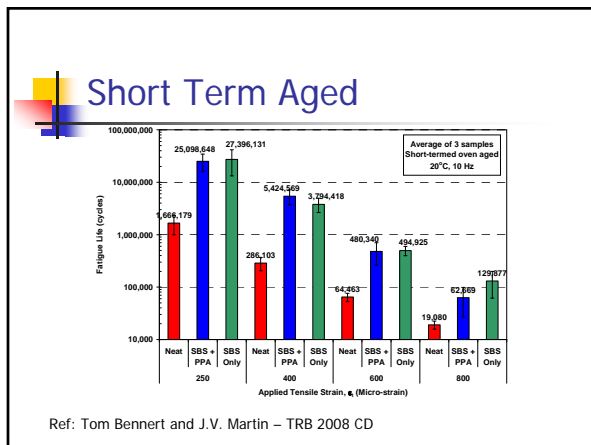


- ### MSCR testing of binder with hydrated lime still in binder
- Lime increased the stiffness of the binder 2 to 3 degrees.
 - PPA increased the stiffness of the binder 6 degrees or one full grade.
 - The combined lime and PPA only increased the grade 5 degrees. This is less than what would be expected from the combined, but only a 1/3 loss.

PPA and Fatigue

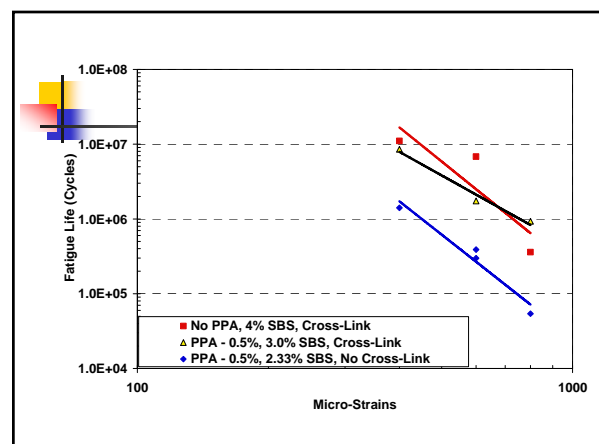
- Review of several studies.

Bending Beam Fatigue

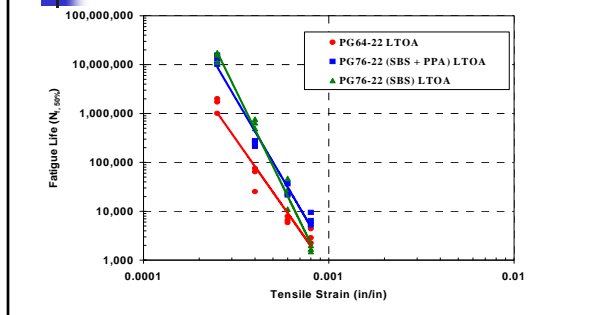



ICL Fatigue Study – polymer reduction

- Selected three blends (New Crude Source)
 - 4.0% SBS D1101 + Sulfur Cross-Linking – No PPA
 - 3.0% SBS D1101 + Sulfur Cross Linking + 0.5% PPA
 - 2.33% SBS D1101 + 0.5% PPA – No Cross Linking



Tom Bennert et al.,



Closing Comment

Common Opinion is that Polyphosphoric Acid Chemically ages or Accelerates Oxidative Aging of Asphalt. Results Reported in Patents Cited Indicate that Polyphosphoric Acid Actually has Anti-Oxidative Characteristics in the Asphalts Studied.

Conclusions

- The Effects of Asphalt Modification with Polyphosphoric Acid is Asphalt and Crude Source Dependent.
- Polyphosphoric Acid works with SBS polymer to improve cross-linking and improve elastomeric response.
- The Effect of PPA on moisture damage is asphalt and aggregate dependant and is treatable with both lime and liquid anti-strips.

Conclusions

- Polyphosphoric Acid is a valuable tool to binder suppliers necessary to provide binders that meet current specifications and provide performance desired.
- PPA use should be limited to one grade bump.
- It is the Formulators Responsibility to Investigate Performance Characteristics, Good or Bad

Thank You!