North East Asphalt User/Producer Group
Portsmouth 20 - 21 October 2004

“Asphalt chemically modified with polyphosphoric acid”

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PhD Chemistry
For the last few years, the use of product based on Polyphosphoric Acid (PPA) as a performance chemical asphalt modifier has strongly increased, especially in North America. Field trials have expanded to Europe and Latino America with additives based on polyphosphoric acid chemistry.

Publications:
- 2004 Journal of Pavement and Road Design (To be published Nov 2004)
- 2004 TRB Hussain Bahia et. al.
- 2002 TRB Ho, et. al.

Patents:
- Air blown: 3 (Lion Oil, Exxon, Shell)
- Chemical modification: 1 (Tosco Lion)
- Polymer modified asphalt: 6 (MTE, Ergon (Innophos), Elf, Exxon, Marathon, Innophos)

Recent presentations on PPA as asphalt modifier:
- RMAUPG 2004 (Sante Fe) - 2004 (Phoenix (AZ))
- Eurobitume 2004 (Vienna (Austria))
- Petersen Asphalt Conference 2004 (Cheyenne (WY))
- 4th International Asphalt Congress 2004 (Cartagena (Colombia))
- NEAUPG (2004 Portsmouth)
summary

- What is polyphosphoric acid (PPA) ?
- How PPA influence the asphalt rheology ?
- How PPA is working (investigation study) ?
- Does PPA work with all asphalt ?
- Is a PPA modified asphalt compatible with aggregates ?
- Could PPA be combined with Polymer ?
- Is a PPA+Polymer modified asphalt compatible with aggregates ?
- Is it a tried and tested technology ?
What is Polyphosphoric acid?

Polyphosphoric acid is an Inorganic polymer, obtained by thermocondensation of Orthophosphoric acid.

$$\text{HO-PO(OH) + HO-PO(OH)} \rightarrow \text{HO-PO(OH) + OH}_2$$

$$\text{HO-PO(OH) + HO-PO(OH)} \rightarrow \text{HO-PO(OH) + OH}_2$$

Main physical chemical characteristics

- 0% wt of Free water
- Viscous liquid (25°C) from 840 cP on up
- Freezing point = below 0 to 15°C
- Medium strong acid: Acidity function (Hammet) = 6 (ref H2SO4 = 12)
- Highly soluble in organics
- Non oxidizing molecules
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Asphalt Characteristics

Asphalt: Two different asphalt are used

<table>
<thead>
<tr>
<th>General description</th>
<th>Saturated (%wt)</th>
<th>Aromatics (%wt)</th>
<th>Resins (%wt)</th>
<th>Asphaltene (n-heptane) (%wt)</th>
<th>PG grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraffinic</td>
<td>4</td>
<td>48%</td>
<td>30%</td>
<td>9,3%</td>
<td>64-22</td>
</tr>
<tr>
<td>Naphtenic</td>
<td>4</td>
<td>38%</td>
<td>32%</td>
<td>17%</td>
<td>67-22</td>
</tr>
</tbody>
</table>
Paraffinic asphalt (PG 64-22)

- Polyphosphoric acid improves the rheological behavior at high temperature compared to the neat binder:
  - complex modulus $G^*$ is increased and phase angle $\delta$ is reduced.
  - large effect from 0 to 1.2% PPA
  - no more effect at content > 1.2%

Typically: + 1 PG grade, with 1% PPA

PPA contributes to more interactions within the asphaltenes network, leading to increased elastic behavior.
Asphalt Rheological behavior - Effect of Polyphosphoric Acid

DSR (1.5 Hz) - Fresh state (no aging)

Naphthenic asphalt (PG 67-22)

• Similar effect as with paraffinic asphalt, but naphthenic asphalt is much more reactive with PPA.

• Polyphosphoric acid improves the rheological behavior at high temperature:
  - complex modulus $G^*$ increases and phase angle $\delta$ is reduced.
  - large effect from 0 to 2% PPA

Typically: +2 PG grade, with 1% PPA

Large range of interactions between asphaltenes -> consolidated network.
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Polyphosphoric acid - asphalt interaction: Model

Asphaltenes Dispersion: *Polyphosphoric acid acts as a ‘defloculant’*

Continuous phase: Maltene (aromatics + saturates)

Asphaltene agglomerate
Asphalteneunit
Resins: Asphaltene solvant

PPA (condensed Polyphosphoric acid)

Asphaltene reactionalsites
[Sheu & Mullins]

\[
\begin{align*}
&\text{OHP} \quad \text{OH} \\
&\text{O} \\
&\text{P} \\
&\text{OH} \\
&\text{O} \\
&\text{R2} \\
&\text{R1} \\
&\text{N} \\
&\text{S} \\
&\text{N} \\
&\text{OH}
\end{align*}
\]

Esterification and acid base neutralisation type reactions

Dispersed phase: deagglomerated asphaltene peptised by Resins layer

Published at Eurobitume 2004, Study done in partnership with LCPC (French Central Laboratory of Road and Bridges)

R1, R2: H or C linked to asphalteneresines molecules
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HIGH TEMPERATURE PERFORMANCE

A = CITGO  
B = BP Canada  
C = TOSCO  
D = Marathon  
E = CHEVRON  
F = Mayan (AC-20)

DSR  
(RTFO)

Usage: 1% by weight

High Temperature PG Grade

Asphalt

PPA improves the High Critical Temperature Tc
One to two grade jump with PPA (cf asphalt spec)
Low Temperature Fracture behavior: PPA modified asphalt

Aging treatment: PAV

Naphthenic Asphalt (PG 67-22)

- PPA modification: 1.2%
- SBS modification: 3%

**Fracture Strength, & Thermal Stress**

- **Thermal stress** curve is shifted towards lower temperatures with PPA modification
- **Tensile strength** of neat asphalt is well improved with PPA (1.2%), similar to SBS (3%) modification
- **Cracking behavior**, according to MP1A, is improved with PPA modification

BBR-DTT: AASHTO-MP1-A

**Thermal stress** of base and 3% SBS

**Tensile Stress of base Citgo**

**Thermal stress of 1.2% PPA**

**Tensile Strength of 1.2% PPA**

**Tensile Strength of 3% SBS**
PPA : CRITICAL CRACKING TEMPERATURE

A = CITGO
B = BP Canada
C = TOSCO
D = Marathon
E = CHEVRON

BBR/DTT (AASHTO MP1A) (PAV)

Usage: 1% by weight

PPA improves the Low Critical Temperature Tc
**PPA : CRITICAL CRACKING TEMPERATURE**

**Usage (weight % vs. asphalt)**

<table>
<thead>
<tr>
<th>Usage</th>
<th>Neat</th>
<th>PPA105%</th>
<th>PPA116%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>-30</td>
<td>-30</td>
<td>-29</td>
</tr>
<tr>
<td>0.5%</td>
<td>-26</td>
<td>-29</td>
<td>-28</td>
</tr>
<tr>
<td>1%</td>
<td>-25</td>
<td>-29</td>
<td>-29</td>
</tr>
<tr>
<td>1.35%</td>
<td>-25</td>
<td>-29</td>
<td>-29</td>
</tr>
</tbody>
</table>

**Asphalt A (Citgo)**

**PPA improves the Low Critical Temperature Tc**
PPA : High Temperature Viscosity

Shell 70/100 PC (France)

PPA reduced the viscosity resulting in reduced application temperature versus a polymer asphalt
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Adhesion-Moisture sensitivity evaluation

- **Boiling Water Test (BRRC Procedure ME65/91)**
  - Procedure defined by The Belgian Road Research Centre (BRRC), correlated with field results
  - Aggregates coated with binder (1.5%) at 160°C and Coated aggregates suspended in boiling water for 10 minutes
  - The boiled sample is attacked by mineral acid. Acid is then consumed by decoated aggregates.
  - Remaining acid is then determined and Stripping Rate is obtained

- **TSR (AASHTO T 283)**
  - Procedure on mixes, at fixed air voids content
  - Compression test: at dry, and water conditioned state
  - Determination of the compression strength ratio.

- **Cantabro**
  - Procedure on mixes, at fixed air voids content
  - Abrasion test on dry, and water conditioned samples
  - Determination of the lost of sample weight after impact into Los Angeles drum

- **Hamburg (+Rutting)**
  - Procedure on mixes, at fixed air void content
  - Rutting measurement under hot water conditions
PPA Improve mix moisture resistance in case of silicious aggregates

Boiling Water Stripping: BRRC test

Asphalt (Citgo)
Usage: 1% by weight

Stripping Rate (%)
0 10 20 30 40 50 60 70 80 90
Porphyry  Limestone  Granite

Naphtenic Asphalt (Venezuelian)

PPA provides improved antistrip properties (except with this Limestone in this asphalt case (which is already very acidic))
PPA improves mix moisture resistance in case of silicious aggregates and limestone.

Boiling Water Stripping: BRRC test

Paraffinic Asphalt (Middle East)

PPA provides improved antistrip properties in case of silicious aggregates.

Moisture sensitivity in case of limestone could be improved depending on the nature of the asphalt and aggregate.
Cantabro test: Moisture sensitivity as well as cohesion are improved with PPA

Basalt aggregates

Mayan asphalt

Cohesion of binder is improved with Innovat modification

Moisture sensitivity is improved due to PPA modification of asphalt

• T=25°C
• Binder rate = 4.5%
• Air Void = 20%
• Average of 3 measures
TPA Improve mix moisture resistance in case of silicious aggregates

**TSR RESULTS : Granite Aggregates (Cisler)**

| Granite Aggregate | A : CITGO 67-22 | B : BP 64-22 |

No need for antistrip additives with granite aggregate
Depending on the nature of the asphalt and the aggregates, antistrip additive could be required in combination with PPA.

**TSR RESULTS: Limestone Aggregates (Medary)**

**In case of Naphtenic**
- Higher moisture sensitivity in presence of PPA is observed
- A compatible antstrip is requested

**In case of Paraffinic**:
- Dry and wet sample tension strength are improved in presence of PPA, but the improvement is higher in dry condition than for the wet one

Consistent results with Boilling Tests observations
Combination of PPA + Compatible antistrip improves TSR

**Limestone** *(Ergon Asphalt)*

Combination of PPA + Compatible antistrip improves TSR

![Graph showing compression strength and TSR for PPA and PPA+ 0.5% Innovalt W](image-url)
Conclusion on Asphalt Modification with PPA

- In case of granite aggregates:
  - PPA improved the cohesion of the mix
  - PPA improved the resistance of mix to moisture

- In case of limestone aggregate
  - For a Naphtenic asphalt (high acidity level) the combination with PPA reduces the resistance to moisture
    - A compatible antistrip may be used to improve resistance to moisture
  - For a Paraffinic asphalt the combination with PPA does not impact the stripping and moisture resistance
Generally speaking the amount needed of PPA is within 0.5 to 1.5%.

PG Grades: generally at least one grade bump in high temperature SHRP number with excellent low temperature properties, and durability. At high PPA contents (>1,2%), a two grade bump is possible (according to asphalt composition).

Adhesion is maintained - or even improved - according to the type of aggregates used.

PPA is easily incorporated into asphalt (viscous liquid), with no large modification of viscosity (135°C) and no storage problem of modified asphalt.

Health Safety and Environment: OK (high temp. stable, no emission, and not classified)

PPA is an economical asphalt modifier.
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Partial Substitution of SBS with PPA at same PG grade

**76-22 PG**

(4% SBS can be substituted with:
2.5% SBS + 0.6% PPA)

**82-22 PG**

(4.5% SBS can be substituted with:
3% SBS + 0.6% PPA)

1% PPA perform as well as 3% SBS
PPA + SBS : Brookfield VISCOSITY @ 135°C

Partial Substitution of SBS with PPA at same PG grade

<table>
<thead>
<tr>
<th>A : Ergon (Venezuela)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B : Lion Oil (Middle East)</td>
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<tr>
<td>SBS : Dexco Vector 2411 (radial)</td>
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</table>

**High temperature viscosity is reduced**
Partial Substitution of SBS with PPA at same PG grade

SBS : Dexco Vector 2411 (radial)

Elastic recovery is maintained

76-22 PG

82-22 PG

Elastic recovery is maintained
Partial substitution of polymer (SBS) with PPA:

- **Maintain the PG grade** *(low Tc / High Tc)*
- **Lower viscosity** *(0.4% PPA and higher)*
- No or little decrease on **elastic recovery**
- **Economical modifying cost**: decrease the amount of modifier
- PPA + SBS (patented)

**Polymer+PPA combination is an economical way to reach performance specifications.**
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PPA+SBS : ASPHALT MODIFICATION

TSR (Ergon asphalt - Granite)

SBS : Dexco Vector 2411 (radial)
EVA : Exxon Polybilt 103C/Polybilt 152

PPA improves TSR with granite (moisture resistance)
PPA + Polymer: Moisture Sensitivity

TSR (Ergon asphalt - Limestone)

PPA doesn’t affect TSR with limestone (moisture resistance)

SBS: Dexco Vector 2411 (radial)

2.6% SBS / 0.6% PPA

Innophos Formerly Rhodia
PPA + SBS: Better rutting+stripping behavior than SBS alone

HAMBURG WHEELTRACKING (Asphalt A – Granite)

[Graph showing the comparison of rut depth with different asphalt compositions: neat, neat + 4.25% SBS (PG76-22), neat + 2.6% SBS + 0.6% PPA (PG76-22).]
Compared to a 100% Polymer modified Mixture, a Polymer/PPA modified mix at the same PG grade shows:

- Equivalent or higher moisture resistance (stripping resistance)
- Equivalent or higher resistance to permanent deformation (rutting)

General conclusion:
Asphalt has to reach several specifications that does not translate in the same amount of modifier.

Polymer/PPA combination is a good way to reach all specifications at the optimized cost.
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I. POSITION STATEMENTS:

The Association of Modified Asphalt Producers (AMAP) supports the responsible use of modification of asphalt materials for improved performance. AMAP believes that through the innovation of material suppliers, new and improved products will be made available that will improve life cycle costs. AMAP does not endorse any specific form of modification.

Acid Modification

After a review of the available information on the use of polyphosphoric acid in the modification of paving grade asphalts, it is the position of AMAP that the correct use of polyphosphoric acid in the appropriate amount can improve the physical properties of bituminous paving grade binders. AMAP endorses appropriate testing on the modified asphalt binder after the addition of any and all additives to determine the final product specification is met. However, incorrect application of the technology, as with many additives, can result in problems associated with construction and/or performance.
INNOVALT™ is used since 97 in North America

I-40 Memphis, TN

- Paved in 1998
- PG 76-22
- Base asphalt PG 64-22
- 2.8% radial SBS
- **0.5% InnovaElt E**
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