Why Modify Asphalt?

• Improve Performance
  – Increase the stiffness of asphalt at high temperatures to improve resistance to rutting
  – Allow the use of softer asphalts to improve the resistance to low temperature cracking
  – More Resistance to Moisture Damage
  – Improve Fatigue Resistance (pavement damage from repetitive loads at intermediate temperatures)
Types of Modification

• Modifiers to increase viscosity/stiffness at high temperatures
  – Polymers
  – Crumb Rubber (recycled tire rubber)
  – Chemical Modification
  – Air Blowing/Oxidation

• Modifiers to improve low temperature properties
  – High flash point oils

• Additives to improve resistance to moisture damage
  – Antistripping Agents
Key Components of Asphalt

- **Asphaltenes** (the component which thickens asphalt when fluid)
  - Very large complex materials
  - Typically 10-25% of asphalt.

- **Maltenes** (oily type material - everything but asphaltenes)
  - Resins: like asphaltenes but much smaller
  - Saturates: basically oils - think of motor oil or light greases
  - Polar Aromatics: oils which contain sulfur, oxygen, and/or nitrogen. These oils have “sticky” characteristics.

*Modifiers Designed to Improve High Temperature Properties Is About Helping the Asphaltenes*
Asphalt Composition

<table>
<thead>
<tr>
<th>Country</th>
<th>Saturates</th>
<th>Aromatics</th>
<th>Resins</th>
<th>Asphaltenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>10.2</td>
<td>28.5</td>
<td>48.8</td>
<td>12.5</td>
</tr>
<tr>
<td>Venezuela</td>
<td>6.3</td>
<td>16.8</td>
<td>58.3</td>
<td>18.6</td>
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<tr>
<td>Canada</td>
<td>10.9</td>
<td>23.6</td>
<td>49.7</td>
<td>15.8</td>
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<td>Russia</td>
<td>8.4</td>
<td>38.1</td>
<td>41.3</td>
<td>12.2</td>
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</tbody>
</table>
Modifier Effects: Polymers

- Add large molecules that interact with the asphaltenes
- Asphaltene content does not change
Modifier Effects: Chemical Modification

- Change larger asphaltenes into multiple smaller ones
- Combine larger resins into asphaltenes
- Asphaltene content increases, more smaller asphaltenes

Diagram:
- Asphaltenes
- Resins
- PPA
- Combines asphaltenes to make larger asphaltenes
- Asphaltene content goes up, average asphaltene size goes up
Combining modification technologies can provide optimum performance and formulation costs.
Use of PPA as a Single Modifier for Asphalt Cement
• 30+ Patents. Since 2000: 60+ Publications
  – Concerns: Amine, Lime Anti-Strip
• NCAT Test Track 2000/3 18 Test Sections, 10 M ESAL
  – SBS/PPA; Various aggregates; Amine or lime anti-strip
  – Improved rut depth, 1 fatigue crack, no moisture damage
• MnROAD test track 2007 – excellent performance to date
  – Excellent performance to date
  – Successful PPA Symposium April 2009

PPA usage: 3.5 to 14% of the asphalt pavement in USA.
Estimated 150 to 450 million ton of hot mix over last 7 years.
Polyphosphoric Acid (PPA)

PPA Chemical Attributes
- Different from Orthophosphoric acid
- No Free Water

- 105% and 115% most common
- Increases asphalt stiffness, improves rutting resistance, expands PG range to meet Superpave specs
- Does not affect low-temperature grading
- Modification does NOT involve oxidation and actually slows it down
- Retards binder aging
Polyphosphoric Acid increases the high-temperature grading with no loss of the low-temperature properties.
EFFECT OF PPA AND ANTI-STRIP
E-1 LIMESTONE MIX, HAMBURG (50°C, 158 LB, WET), 7% AIR VOIDS

- 1 PG 70-22 Marathon
- 2 PG 64-22 Marathon
- 3 PG 64-22 + 0.75% PPA (PG 70-22)
- 4 PG 64-22 + 0.75% PPA + 0.5% phosphate ester
- 5 PG 64-22 + 0.85% PPA + 0.5% amine
- 6 PG 64-22 + 0.75% PPA + 1% hydrated lime

PPA performs well with proper anti-strip. Need to test all mix components.
Adhesion to Aggregates

Use of Polyphosphoric Acid results in improved adhesion vs neat asphalt

Texas Boil Test
Lithonia Granite

% Adhesion

Neat Asphalt  
Asphalt + 0.5% Polyphosphoric Acid (105)

Asphalt
Type C1, AC 30  
Type D, AC 30  
Type S  
Type A, 64-22  
Type C2, AC 30  
Type H

Use of Polyphosphoric Acid results in improved adhesion vs neat asphalt
Lab and Field Tests

MnRoad Test Track:
PPA + Lime anti-strip evaluation.
Perfect performance after 6-plus years

Hamburg Lab Specimens

Neat Binder
Binder + 0.5% PPA 115
Under prolonged high-temperature storage, Polyphosphoric Acid results in an asphalt that maintains its PG rating.
Use of PPA as a Co-modifier with Polymers
Proper Dosage

- Typical Range – 0.25 to 1.5%
- Most Common – 0.25 to 1.2%
- Affected by:
  - Specification Requirements
  - Reactivity of Base Asphalt
  - Interaction with Local Aggregates
## Anti-aging Effect of PPA

<table>
<thead>
<tr>
<th>Exposure</th>
<th>Carbonyl Index</th>
<th>Carbonyl Index</th>
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<tbody>
<tr>
<td></td>
<td>PAV (100°C, 300 psi)</td>
<td>Thin Film (700 µm)</td>
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<tr>
<td></td>
<td>PG 64-22 with 1 % PPA</td>
<td>PG 64-22 with 1 % PPA</td>
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<td>0</td>
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Polyphosphoric Acid Delivery System (PADS)
Conclusions

- Long history of successful use. Estimated 150 to 500 Million Tons of pavement currently in place where PPA has been used in the last 7 years
- Cost effective- works by making more and smaller asphaltenes
- As stand-alone modifier, high temp. stiffness, no low temp. effect, no negative impact on aging
- Unique properties obtainable when used as a co-modifier with polymers
- Successfully used with hydrated lime and selected amines. Best practice is to test finished products
- PPA modified binders are storage stable
- Continuing research and development
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