
Presented by:
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Workshop on Polyphosphoric Acid (PPA) Modification of Asphalt Binders
Minneapolis, Minnesota
7-8 April 2009
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.
Grading of Asphalt Binders

- Prior to 1970 asphalts were specified as penetration grades.
  - 5/9, 50/60, 60/70, 85/100, 140/160 and >300 pen

- Beginning in 1970, asphalts were specified as viscosity grades.
  - AC-5, AC-10, AC-20, AC-30 and AC-40
Effect of crude Z on Crude A (ref A) asphalt properties.

Note: Pen/Vis relationship:
AC-30 = 2500-2550 poise min 57 dmm.

~1 dmm/75 poise
In the 1990’s State DOT’s began to specify SHRP or Performance Grades of Asphalts. SuperPave™.

- PG 58-28, PG 64-22, PG 70-22, PG 76-22, etc

Though asphalt specifications have been upgraded through time, any of the are previous grading systems are subject to use.
Useful Temperature Interval (UTI) “SuperPave Made Simple”
Useful Temperature Interval

Simply put, the “useful temperature interval” (UTI) of an asphalt is the differential, or spread in °C, between the high temperature grading and the low temperature grading.
Useful Temperature Interval

Perfomance Graded Asphalt Binders

Log of Stiffness vs Temperature (°C)

-60 -30 0 30 60 90 120

SHRP Grade 58-16
SHRP Grade 84-22
SHRP Grade 76-22

Bending Beam Rheology
Dynamic Shear Rheology

98 °C
86 °C
74 °C
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
SUPERPAVE PERFORMANCE GRADES and PG Line

Max PG Temp, °C

Min PG Temp, °C

PG 64-22 (hard)
PG 52-34 (soft)

Puzic 2005
For a given crude, asphalt grade is defined by refinery processing conditions.

Crude ABC PG Line

soft

hard

Puzic 2005
SUPERPAVE PG line is a signature of a crude.

Puzic 2005
True Grade Range vs. Composition

R² = 0.9148
UTI of Performance Grade Asphalts

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Narrow UTI’s of 86 and 89 C° May Require Modification
Phosphoric Acid Modification of Asphalt Binder
Definition – Polyphosphoric Acid

- Inorganic Polymer
- Obtained by Condensation of Monophosphoric Acid or by Hydration of $\text{P}_2\text{O}_5$
- 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 (Hammet) = 6 (ref $\text{H}_2\text{SO}_4 = 12$)
- Highly soluble in organics
- Non oxidant compound
Background

- Dr. Arnold Hoiberg
  - US Patent 2,450,756 – October 5, 1948
- Dr. Stephen Alexander
  - US Patent 3,751,278 – August 7, 1973
Background Contd.

- Gorbaty
- Moran
- Goodrich
- Geviarini
- Reinke
- Puzic
- Planche
- Baumgardner/Burrow
- Et. Al.
Phosphorous Pentoxide and Stable Acids of Phosphorous, $\text{P}_2\text{O}_5$, $\text{H}_3\text{PO}_4$

- Lowered the temperature range of processing air blown asphalt binder from a typical range of 490-500°F to a range of 440 to 450°F (254-260°C to 227-232°C)

- Typical straight air blown properties 212°F (100°C) softening point with 12-15 dmm penetration, Catalytic air blown properties 212°F (100°C) softening point with 35-40 dmm penetration
Definition

- Catalyst – “a substance that initiates a chemical reaction and enables it to proceed under different conditions (as at lower temperature) than otherwise possible”

- Cat. Air Blown: 440 to 450°F (227-232°C)
- Phosphorous Pentoxide, Stable Acids of Phosphorous and Phosphorous Pentasulfide, $P_2O_5$, $H_3PO_4$, $P_2S_5$, plus Organic Amine

- Catalytic Air Blowing Provides Improved Binder Properties (Higher Pen per Softening Point), Amine Added to Catalytically Blown Binder to Promote Adhesion
Condensed Derivatives of Phosphoric Acid (Polyphosphoric Acid, “PPA”) used to modify to non air-blown Paving Grade Asphalt

Provided Increase Viscosity e.g. AC30 Modified to AC40 with little to no effect on Penetration Values (Improved PG or wider Useful Temperature Interval, UTI)
• Effect of PPA Modification is Crude Dependent Based on Asphalt Chemical Composition

• Increases “Useful Temperature Interval” or PG True-grade by Improving Both Upper and Lower PG Limits

• PPA Modification Does Not Oxidize Asphalt or Promote Brittleness

Why are we talking about PPA usage in asphalt field?

Martin 2005
True Grade Range vs. Composition

![Graph showing the relationship between Range (°C) and Psh, with a linear trend line and an R² value of 0.9148. The graph includes data points for both Range vs. Psh and Range vs. A/(A+R).]
# PG76-22 from Saudi Asphalt

<table>
<thead>
<tr>
<th>PG Grade Achieved</th>
<th>76-22</th>
<th>76-22</th>
<th>76-22</th>
<th>76-22</th>
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<tr>
<td>PPA %</td>
<td>0</td>
<td>0.2</td>
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<tr>
<td>Polymer %</td>
<td>4.75%</td>
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<td>BBR S Value</td>
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<tr>
<td>BBR M Value</td>
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<td>85.00%</td>
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## PG Grade Achieved

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<tr>
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<tr>
<td>PPA %</td>
<td>0</td>
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<td>Polymer %</td>
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PG76-16 from CA Valley

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<td>Polymer %</td>
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<td>85.00%</td>
<td>82.50%</td>
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Phosphorous Magnetic Resonance of PPA Modified Asphalt
Polyphosphoric Acid Complex Composition: many chain lengths exist and are proportioned depending on concentration.
Polyphosphoric Acid

$$\text{H}_3\text{PO}_4$$

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<th>#P atoms</th>
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<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
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<td>105%</td>
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<tr>
<td>115%</td>
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<td>23.0</td>
<td>19.3</td>
<td>15.9</td>
<td>12.3</td>
<td>8.21</td>
<td>5.73</td>
<td>3.89</td>
</tr>
</tbody>
</table>

Miknis 2008
NMR Spectra of Polyphosphoric Acids

Ortho | End | Middle

100 % H₃PO₄
110 % H₃PO₄
114 % H₃PO₄
117 % H₃PO₄

Nuclear Magnetic Resonance Method for Analysis of Polyphosphoric Acids
Phosphoric Acids

Ortho            End             Middle

Phosphorous Chemical Shift, ppm

85 % H₃PO₄

105 % H₃PO₄

115 % H₃PO₄

Miknis 2008
Polyphosphoric acid is highly hygroscopic and rapidly absorbs moisture when exposed to air. Besides making accurate weighing of a sample difficult, the absorbed moisture begins the hydrolysis process.

When water is added to the sample, the hydrolysis process is free to proceed to completion. Quantitative data on rate of hydrolysis is scarce. At room temperature the rate is slow. .....*

* http://www.innophos.com/brochures/Plphsphrccdss/page1.asp
105 % PPA in Water

PPA (105 %) in H₂O @

- 0 h
- 5 h
- 32 h
- 96 h
- 144 h

Chemical Shift, ppm

Miknis 2008
1.5 % PPA in Asphalt

% of phosphate end groups

41.1
35.4
19.4
14.6

Miknis 2008
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 is a valuable tool to binder suppliers necessary to provide binders that meet current specifications and provide performance desired.
- It is the Formulators Responsibility to Investigate Performance Characteristics, Good or Bad
Thank You!