Phosphoric Acid
Modification of Asphalt Binders

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Outline

• Problem statement
• Literature review
• Proposed work plan
• Solicit comments
Problem Statement

• Acid modification has been shown to be a low cost way to increase the high temperature stiffness of asphalt binders (per Superpave Binder Specification) but…

• Studies have shown both beneficial and harmful effects of acid modification.

• How should it be used?
• How should it not be used?
• What are the pitfalls to avoid?
Acknowledgements

- Western Association of State Highway and Transportation Officials (WASHTO)
- “Impact of different types of modification on low-temperature tensile strength and $T_{critical}$ of asphalt binders.” Ho, Zanzotto & MacLeod (TRB 1810)
- “Modification with Acid – Advantages and Disadvantages” Bishara, Mahoney Reynolds & King, Kansas DOT Report FHWA-KS-02-2,
- Nebraska DOT Laird Weishahn, private communication
- Western Cooperative Test Group (WCTG)
- Baumgardner Private Communication
- “Polyphosphoric Acid Modified Asphalt” Baumgardner, Masson, Hardee et al. AAPT 2005 Under Review
- “Acid/Base Chemistry for Asphalt Modification” King Bishara & Fager AAPT 2002
- King Private Communication
Findings Regarding PPA Modification

- 2% PPA (85%) increases the high temperature stiffness in the range of 11.4 to 18°C or 2 to 3 PG Grades
- The amount of the increase is binder specific
- Low temperature stiffness or m-value is essentially unchanged
- PPA in optimal amounts (0.3-0.7%) did not contribute to moisture sensitivity or rutting
Purported Negative Effects of Acid Modification

- High temperature improvements were reversed by the reaction between the acid and hydrated lime or amine antistrip
- Nullifies the effect of amine anti-strips
- Cracking of I-80 in Nebraska, 186 cracks/mile with acid, 6 without
- Responsible for road failures in KS, OK and MO?
WASHTO Acid Modification
Study Proposal

• Which works best? Polyphosphoric, orthophosphoric or green acid?
• Can it reduce the effectiveness of lime?
• Is the effect transitory in mixes – does rut resistance disappear?
• Is polymer + acid better than polymer alone?
• Are there long-term mix and pavement performance issues?
• How can an agency identify and monitor the optimum level?
• Binder extraction methods need to be developed in order to recovered binders that reflect their in-place properties.
What is the Chemistry?

- PPA modification gives rise to higher levels of asphaltenes. Venezuelan Asphalt showed an increase from 10.5% to 14.9%

- $^{31}$P NMR showed no phosphorous in the asphaltenes from unmodified binders, but did show it present in PPA modified binders

- Can we use this to identify what is happening?
Work Done So Far - Baumgardner et al:

- AFM Atomic Force Microscopy
- P$^{31}$ NMR
- TLC Thin Layer Chromatography – molecular size
- GPC Gel Permeation Chromatography – molecular weight
- Water extraction of toluene / binder solutions
- SPME on water fractions
- Iatroscan hydrocarbon analyses on binders
- Asphaltene determinations
Work Done So Far – King, Bishara and Fager

- Binder DSR study with acid & imidazolene antistrips
- Investigated pH and emulsification potential
- Mix study of moisture resistance using HWTD and APA
- Findings:
  - Moisture damage may occur if acid is present in high concentrations
  - ASAs significantly reduced moisture damage
  - Wheel tracking tests predict significant moisture damage
  - $T_n$ substantially reduced if acid and amine ASA used in the same mix
Suggested Methodologies and Comments

• Need specifications to control the use/misuse of acids

• Need a good study of field projects using acids.

• Environmental factors need to be further examined:
  – Need Moisture Damage tests that create pore pressure – Hamburg or Pine Rut Tester probably best bets
  – Are PPA modified binders less susceptible to aging and subsequent embrittlement?
  – What is the effect of actinic light?
Phosphoric Acids
A Brief Review

- Made in vast quantities
- Direct reaction of phosphate rock (calcium phosphate or apatite with sulfuric acid
- This yields “Green Acid” typically 25-30% $\text{H}_3\text{PO}_4$ heavily contaminated with impurities like chloride and sulfate – corrosion issues?
- Also made by burning phosphorous to $\text{P}_4\text{O}_{10}$ and subsequent hydration
- Acid has tetrahedral $\text{PO}_4$ groups connected by hydrogen bonds which makes the acid syrupy
Phosphoric Acid Grades Available

- Orthophosphoric Acid (H₃PO₄) as 50%, 75%, 85%, 100%
- Polyphosphoric acids have the general formula Hₙ₊₂PₙO₃ₙ₊₁ for n>1
- Polyphosphoric acids range from pyrophosphoric acid H₄P₂O₇ (n=2) to metaphosphoric acid (large values of n)
- Polyphosphoric Acid sold commercially is a mixture of orthophosphoric acid with pyrophosphoric acid, triphosphoric acid and higher acids and is sold on the basis of its calculated content of H₃PO₄, 115%, e.x.
- Superphosphoric Acid is a similar mixture sold at 105% H₃PO₄
Proposed Work Plan

- Forensic method for determining type and level of phosphate additive
- Durability of acid modification
  - Effect of environment: actinic light, water, etc.
- Address corrosion and handling issues
- Optimization of acid modification
  - Chemical / mechanistic considerations
  - Different Asphalts
  - Physical Properties
Thank you.

Questions?