“Use of Polyphosphoric Acid in Asphalt"

Pavement Performance Prediction

WRI/FHA Symposium

Cheyenne, WY

22-24 June 2005
Crude Oil Distillation Cut Points

Distillation Range at Atmospheric Pressure

- Light Straight Run < 160°F
- Gasoline 160 - 250°F
- Naptha 250 - 365°F
- Kerosene 365 - 475°F
- Diesel 475 - 600°F
- Gas Oil # 1 600 - 650°F
- Gas Oil # 2 650 - 700°F
- Gas Oil # 3 700 - 750°F
- Gas Oil # 4 750 - 800°F
- Sticky 800 – 800°F
- Asphalt Residuum > 800°F
Summary

- Effects of Additives on Adhesive Properties
- Interface Interactions Between Asphalt Species and Mineral Surfaces
- Test Methods
- Asphalt Binder Formulations
- Laboratory Mixture Performance in Moisture Sensitivity Tests
- Production Mixture Performance in Moisture Sensitivity Tests
- Conclusions
Effect of Additives on Adhesive Properties

- Discussions of the Adhesive Properties of Asphalt in Combination with Additives
  - Distinguish Between Wet and Dry State
  - Non-Polar Additives Unlikely to have Specific Interaction with Aggregate e.g. Polymers
  - Polar Additives more likely to Interact with Aggregate e.g. Amines, Polyphosphoric Acid
Effect of Additives on Adhesive Properties

- Distinction Between Adhesive and Cohesive Strength
  - Of Most Importance is the “Net Effect” Required to Displace Integrated Components of Asphalt/Aggregate Matrix
  - Typically in Non-Modified Binder Cohesive Strength Lower than Adhesive Strength
  - Addition of Modifiers Influences Net Effect
Force Required to Displace Components of Integrated Asphalt Aggregate Matrix

Force

Percentage Additive

cohesion

adhesion
Effect of Additives on Adhesive Properties

- Relatively Non-Polar Additives e.g. Polymer Modification (SBS)
  - Cohesive Strength Increases While Adhesive Strength Remains Relatively Constant
  - Continues Until Cohesive Strength Becomes Greater than Adhesive Strength
  - Mode of Failure Changes from Cohesive to Adhesive Failure
Effect of Additives on Adhesive Properties

- Polar Additives e.g. Polyphosporic Acid
  - Cohesive Strength Increases, Adhesive Strength Increases with Stronger Asphalt Aggregate Interaction
  - Cohesive Strength Increase Continues Until Greater than Adhesive Strength
  - Mode of Failure Changes from Cohesive to Adhesive Failure
- Effects of Additives on Adhesive Properties
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Adhesion: Interface Interaction Between Asphalt Species Mineral Surface

The polar functions of asphalt have the major contribution to adhesion of the asphalt onto the aggregate surfaces.

Carboxylic acid has the higher affinity for mineral surface as limestone surface is preferred to granite (siliceous).

STRONGEST AFFINITY TO THE SURFACE

LOWEST AFFINITY TO THE SURFACE

LIMESTONE AND GRANITE

Carboxylic acids
Anhydride
dicarboxylics
Sulfoxides
Quinolones types
Ketones

ADHESION: (Plancher et. Al)
A liquid which has strong affinity for a solid will form a film such that the liquid-solid contact is maximized while those which have weaker affinities will collect themselves into beads.

- **Adhesion promoter**
- **Or Chemical modification of existing asphalt species**

By Increasing the polarity of asphalt species (asphaltene), affinity of asphalt for mineral surface may be improved.
Effect of Polyphosphoric Acid Modification on Asphalt Binder Wet-ability Behavior

**YOUNG EQUATION**

\[ \gamma_{(LV)} \cos \alpha = \gamma_{(SV)} - \gamma_{(SL)} \]

The lower the contact angle \( \alpha \) is
• the higher the mineral surface will wetted by the asphalt
• the higher asphalt affinity for the mineral surface will be
• the higher water resistance is expected

By measuring the contact angle we can observe the impact of asphalt modification with Polyphosphoric Acid
Influence of Polyphosphoric Acid Modification on Asphalt – Mineral Affinity (Granite Aggregate)
Influence of Polyphosphoric Acid Modification on Asphalt – Mineral Affinity (Limestone Aggregate)

Asphalt with medium PPA reactivity (PG grade)

PPA improves asphalt affinity to limestone
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Influence of Polyphosphoric Acid Modification on Moisture Resistance of Asphalt Mixtures

- **Boiling Water Test (BRRC Procedure ME65/91)**
  - Procedure defined by The Belgian Road Research Centre (BRRC)
  - Aggregates (14mm) 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 titrated 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.
Belgium Road Research Center
Stripping Rate

Venezuelan (B)
Usage: 1% by weight

Stripping Rate (%)

Porphyry  Limestone  Granite

Stripping Rate (%)

- Neat
- PPA (1%)

Porphyry  Limestone  Granite
## TSR (Lime Treated Gravel)

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<th>Liquid</th>
<th>Dry Strength</th>
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Effects of Additives on Adhesive Properties
Interface Interactions Between Asphalt Species and Mineral Surfaces
Test Methods
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Laboratory Mixture Performance in Moisture Sensitivity Tests
Production Mixture Performance in Moisture Sensitivity Tests
Conclusions
## PG Grade Achieved

<table>
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<tr>
<th>PG Grade Achieved</th>
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<td>Polymer %</td>
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PG76-22 from Venezuelan Asphalt
## PG76-16 from CA Valley

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Moisture Resistance (TSR) Venezuelan Asphalt/Granite Agg.
Moisture Resistance (TSR)
Venezuelan Asphalt/Granite Agg.
W/Lime and Polyamine

![Graph showing Moisture Resistance (TSR) for different asphalt samples with and without additives. The graph displays data for Neat 67-22, Neat 67-22 + E6, SBS 76-22 + E6, SBS/PPA 76-22 + E6, SBS/PPA 76-22 + Lime, SBS/PPA 76-22 + Lime + E6, with Coating (%) and TSR (%) as axes.]
Moisture Resistance (TSR) Saudi Asphalt/Limestone Agg.
Belgium Road Research Center

Stripping Rate

Polyphosphoric Acid Modification Plus Polyamine Anti-strip

- Neat
- Neat + 0.5% 200P
- Neat + 1.2% PPA
- Neat + 2% PPA
- Neat + 1.2% PPA + 0.5% 200P
- Neat + 2% PPA + 0.5% 200P
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Moisture Resistance (TSR) Production
Asphalt/Limestone Mixture

![Bar chart showing Moisture Resistance (TSR) Production for different asphalt and additive combinations.](chart.png)
Moisture Resistance (TSR) Production
Asphalt/Limestone Mixture

![Graph showing Moisture Resistance (TSR) Production for different asphalt and additives.]
Conclusions

- PPA Influences the Rheological Properties of Asphalt Binders

- PPA improves asphalt affinity to mineral surfaces (To a less extent with Limestone than with Granite)

- PPA improves asphalt adhesion onto aggregates
  - In case of granite aggregates
    - Without influence of the asphalt nature
  - In case of limestone aggregates
    - With influence of asphalt nature

- Adequate formulation will provide performance:
  - Appropriate Loadings and Combinations with Other Modifiers
  - Appropriate anti-strip Additives
  - Appropriate formulation with the reactive anti-strip or aggregate.
Acknowledgements

- Jean-Valery Martin – Innophos, Inc.
- Bob Kluttz – Kraton Polymers
- Willem Vonk – Kraton Polymers
- Andy Menapace – Paragon Technical Services, Inc.
- Mike Hemsley – Paragon Technical Services, Inc.