Asphalt Binders

Mike Anderson, Asphalt Institute
45th Ohio Asphalt Paving Conference
February 5, 2020
Lab Technician Training and Certification

➢ Binders
  • Basic Binder Technician Training
  • National Binder Technician Certification
  • Basic Roofing Technician Training

➢ Emulsions
  • Basic Emulsion Technician Training
  • National Emulsion Technician Certification

For more info and class dates: www.asphaltinstitute.org/education/seminars
Petroleum Asphalt Production

A. Natural Gas Petroleum Sand And Water

B. Field Storage

C. Atmospheric Distillation
   - Gasoline 60-325°F
   - Naptha 300-400°F
   - Kerosene 325-500°F
   - Gas Oils 450-600°F
   - Gas Oils 575-700°F

D. Vacuum Distillation
   - Gas Oils 650-750°F
   - Gas Oils 700-850°F

E. Resid
   - Asphalt Binder
   - Air Blowing
   - Other Processing
• Two distillation towers are common
  ◦ The first tower is operated at atmospheric pressure
  ◦ The second tower is operated with a vacuum
    • The vacuum tower removes additional volatile material

• Asphalt cement is produced from the material collected at the bottom of the second (vacuum distillation) tower
  ◦ Referred to as “residuum” or “resid”
Crude Selection

• Percent of resid or asphalt cement varies according to the crude source
  ◦ May range from 1% to more than 50%

• Some crudes contain a high percentage of wax
  ◦ Wax contents in asphalt cement greater than ~5% are generally considered undesirable
  ◦ Waxy asphalts typically exhibit poor performance
Crude Selection

• As API gravity increases, residuum yield decreases and distillate yield increases
  ◦ Heavy Crude
    • API gravity < 25
  ◦ Sour Crude
    • High sulfur content (>1%)
## Asphalt Content of Selected Crudes

<table>
<thead>
<tr>
<th>Source</th>
<th>Residuum, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boscán, Venezuela</td>
<td>58</td>
</tr>
<tr>
<td>California Valley, Kern River</td>
<td>66</td>
</tr>
<tr>
<td>California Coastal, Hondo</td>
<td>48</td>
</tr>
<tr>
<td>Alaska, North Slope</td>
<td>31</td>
</tr>
<tr>
<td>Arabian, Heavy</td>
<td>27</td>
</tr>
<tr>
<td>Nigeria, Light</td>
<td>1</td>
</tr>
</tbody>
</table>
Chemical Composition – Asphalt

• Complex mixtures containing a large number of different chemical compounds of relatively high molecular weight.
  ◦ Depends on the composition of the original crude oil and on the processes used during refining and blending.
• Asphalt cement is composed primarily of carbon and hydrogen
  ◦ Hence the name “hydrocarbon”

• Sulfur and heavy metals play a significant role in determining physical properties
  ◦ Molecular structuring in asphalt cement is largely due to the presence of sulfur and heavy metals
### Typical Chemical Composition of Asphalt Cement

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>82-88%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>8-11%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0-6%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0-1.5%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0-1%</td>
</tr>
<tr>
<td>Heavy metals</td>
<td>0-1%</td>
</tr>
<tr>
<td>Waxy components</td>
<td>&lt; 5%</td>
</tr>
</tbody>
</table>
Typical Composition of Asphalt Cement

• Asphalt cement molecules range widely in chemical type, size, and polarity

• Polar molecules associate with each other creating an organized structure

• Traditional structure is based upon three broad categories of molecules
  ◦ Asphaltenes, resins, and oils
  ◦ Asphaltenes and resins are highly polar and dispersed in the oily fraction
Chemical Model of Asphalt

• Petroleum Asphalt
  ◦ Collection of polar and non-polar molecules
  ◦ Polar molecules associate strongly to form organized structures through non-polar (continuous) phase
  ◦ As temperature increases, least polar molecules dissociate and asphalt becomes less viscous
    • Reverse happens as temperature decreases
Highly polar resins keep asphaltenes dispersed in the oil fraction
Chemical Separation of Asphalt

• Four Broad Classes of Compounds (ASTM D4124)
  ◦ Asphaltenes
  ◦ Saturates
  ◦ Cyclicks (Naphthene Aromatics)
  ◦ Resins (Polar Aromatics)
Chemical Separation of Asphalt

• Four Broad Classes of Compounds (ASTM D4124)
  ◦ Asphaltenes
    • Black amorphous solids containing carbon, hydrogen, nitrogen, sulfur, and oxygen
    • Trace elements such as nickel and vanadium are also present
    • Highly polar, aromatic materials
    • High molecular weight
    • 5-25% of the weight of asphalt
Chemical Separation of Asphalt

• Four Broad Classes of Compounds (ASTM D4124)
  ◦ Saturates
    • Aliphatic hydrocarbons
    • Waxy and non-waxy saturates
    • 5-20% of the weight of the asphalt
Chemical Separation of Asphalt

• Four Broad Classes of Compounds (ASTM D4124)
  ◦ Cyclicitys (Naphthene Aromatics)
    • Dark, viscous liquids
    • Lowest molecular weight
      ◦ 500-900
    • Major proportion of dispersion medium
    • 45-60% of the weight of the asphalt
Chemical Separation of Asphalt

• Four Broad Classes of Compounds (ASTM D4124)
  ◦ Resins (Polar Aromatics)
    • Dark-colored, solid or semi-solid, very adhesive fractions of relatively high molecular weight
      ◦ MW = 800-2000
    • Dispersing agents (peptizers) for asphaltenes
      ◦ Proportion to asphaltenes may govern rheological behavior
  ◦ 15-25% of the weight of the asphalt
Chemical Changes During Processing

• Vacuum Distillation
  ◦ Selectively removes higher volatility, lower molecular weight hydrocarbons
    • results in a concentration of higher molecular weight (lower volatility) components in asphalt

• Air-Blowing and Oxidation
  ◦ Cyclics converted to resins, which are in turn converted to asphaltenes.
  ◦ As asphaltene content increases, stiffness increases
Chemical Composition

• Oxidation
  ◦ Asphalt molecules react with oxygen
    • New polar sites are formed
      ◦ Increases the tendency to self-assemble
      ◦ Thereby increases the stiffness of the asphalt
    • Can occur at the refinery, during mixing at an asphalt mixture production facility, and/or in service in the pavement
Chemical Composition

• Oxidation
  ◦ Asphalt molecules react with oxygen
  • Asphalts come from different crude sources
    ◦ Have different molecular distributions and different attractive strength connecting the molecules
    ◦ The rate of stiffening can be different
Causes of Change: Oxidation

• Oxygen reacts with asphalt cement
  ◦ Molecular size increases
  ◦ Polarity increases
  ◦ The binder becomes stiffer
  ◦ This reaction is not reversible

• Rate of reaction is highly dependent upon temperature
  ◦ Rule of thumb – reaction rate doubles for every 10°C increase in temperature
Effect of Temperature on Reaction Rate

Rate doubles every 10°C
Rate increases in simple proportion to temperature

Doubling is rarely seen in practice; availability of oxygen slows the rate of reaction.
Chemical Composition – Oxidation

TRB Circular 499

Size exclusion chromatogram of three asphalts
• Different molecular profiles
  ◦ **AAM** (West Texas Intermediate)
    • High amount of large molecules
    • Continuous molecular size
  ◦ **AAG** (California Valley)
    • Low amount of large molecules
    • High amount of small molecules
    • Not continuous (lacking intermediate sized molecules)
  ◦ **AAK** (Boscan)
    • High amount of large molecules
    • Low amount of small molecules
    • Not continuous (lacking intermediate sized molecules)
Chemical Composition – Oxidation

• What happens during oxidation?
  ◦ **AAM** (West Texas Intermediate)
    • Continuous molecular size allows for conversion of smaller molecules to larger (more polar) molecules
    • “normal” increase in stiffness during aging
  ◦ **AAG** (California Valley)
    • High amount of smaller molecules
    • More polar molecules can develop without changing physical properties as significantly
    • Less increase in stiffness during aging
  ◦ **AAK** (Boscan)
    • High amount of larger molecules
    • Already dominated by polar species; increased by oxidation
    • Greater increase in stiffness during aging
Chemical Composition – Oxidation

![Graph showing the change in G*, Pa (60°C, 10 rad/s) for Original, RTFO, and PAV for AAG, AAK, and AAM.]

- **G**, Pa (60°C, 10 rad/s)
- **AAG**, **AAK**, **AAM**
- **Original**, **RTFO**, **PAV**

**Legend:**
- **AAG**
- **AAK**
- **AAM**
Delta Tc
Delta Tc

- Published Oct 2019
- IS-240
- 11 chapters, 64 pages
- Free download as e-Book on AI’s website (under Engineering)
AI Delta Tc Publication

• Download the document from AI website
• www.asphaltinstitute.org
• Click on Engineering
• Click on “Delta Tc – Technical Document”

Asphalt Institute Technical Document:
State-of-the-Knowledge: Use of the Delta Tc Parameter to Characterize Asphalt Binder Behavior
Asphalt Institute Technical Advisory Committee
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ISBN: 978-1-934154-77-9

Download the preliminary PDF
• IS document is a technical “state of the knowledge” document that captures the consensus of the asphalt binder suppliers in the United States on a wide variety of topics related to:
  ◦ Aging/testing
  ◦ Pass/Fail criteria
  ◦ Adoption of ΔTc in a binder purchase specification

• Not intended to provide guidance
• Asphalt Institute does not take a position on the adoption of ΔTc in a binder purchase specification
At the time this document was developed (mid-2019), ten user agencies have or soon will implement $\Delta T_c$ as part of their purchase specification, with two more expecting to do so in the near future.

- Several national level research projects are actively considering $\Delta T_c$ as part of their studies.

AI’s Technical Advisory Committee decided that there was substantial need for a state-of-the-knowledge, engineering report to describe $\Delta T_c$ and its relevance in characterizing the behavior of asphalt materials.
AAPTP 06-01 Research Objectives

• Objectives
  ◦ Develop a practical guide identifying means to prevent and mitigate cracking caused by environmental effects.
  ◦ Develop one or more test procedures that could be used by a pavement manager to determine when preventative maintenance is needed to prevent the development of cracking (specifically block cracking).
TPF-5(153) Research Objectives

• Primary Objective
  ◦ to develop and validate technology that can be used by highway agencies to determine the proper timing of preventive maintenance in order to mitigate damage caused by asphalt aging
• In-service aging leads to oxidation and loss of flexibility at intermediate and low temperatures
  ◦ Block-cracking
  • when environmental (non-load) conditions create thermal stresses that cause strain in the asphalt mixture that exceeds the failure strain
General Concept

- In-service aging leads to oxidation and loss of flexibility at intermediate and low temperatures
  - Preventing or mitigating distress
    - identify a property of the asphalt binder or mixture that sufficiently correlates with its flexibility
    - provide a procedure to monitor when flexibility reaches a state where corrective action is needed
Asphalt Oxidation

Vallerga: Age-Embrittlement

Raveling

Block Cracking
Asphalt Oxidation

• Physical Changes – Ductility
  ◦ Block cracking severity related to ductility at 60°F (15°C) – Kandhal (1977)
    • “Low-Temperature Ductility in Relation to Pavement Performance”, ASTM STP 628, 1977
  ◦ Loss of surface fines as ductility = 10 cm
  ◦ Surface cracking when ductility = 5 cm
  ◦ Serious surface cracking when ductility < 3 cm
Relationship between $\Delta T_c$ and Ductility

\[ y = 7.77e^{-0.27x} \]

\[ R^2 = 0.74 \]
What is Delta Tc ($\Delta T_c$)

- **Delta Tc ($\Delta T_c$)** is a parameter that provides insight into the relaxation properties of an asphalt binder which can contribute to non-load related cracking or other age-related embrittlement distresses in an asphalt pavement.

- It is a calculated value using the results ($S$ and $m$) from the BBR test.

- It is intended to be used on binder that has been short and long-term aged (RTFO plus PAV)

- Can also be used on binder recovered from asphalt pavements
What is Delta Tc (ΔTc)?

• Delta Tc (ΔTc) is the difference between the critical low temperatures of the asphalt binder, determined using the Bending Beam Rheometer (BBR), where the stiffness (S) at 60 seconds of loading time is exactly equal to the specification value of 300 MPa and the m-value (m) at 60 seconds of loading time is exactly equal to the specification value of 0.300.
What Does $\Delta T_c$ Represent?

$\Delta T_c$ represents the relationship between stiffness and relaxation

- As aging occurs, $S$ increases and $m$ decreases
- Similar response at intermediate temperatures for $G^*$ (increases) and $\delta$ (decreases)
- Balance between change in stiffness and proportion of viscous and elastic properties
Determining $\Delta T_c$

• Fourth Step
  ◦ Calculate the value of $\Delta T_c$:

  \[\Delta T_c = T_{c,S} - T_{c,m}\]

• Positive values of $\Delta T_c$ indicate an S-controlled asphalt binder
• Negative values of $\Delta T_c$ indicate an m-controlled asphalt binder
ΔTc is related to the relaxation properties of a binder. What is relaxation and how does binder relaxation properties relate to mixture performance?

- Asphalt exhibits a bit of viscous behavior, even at low temperatures when its behavior is mostly considered elastic.
- Therefore, when thermal stresses build up as a pavement gets colder, the asphalt binder will gradually experience viscous flow and the stresses will greatly reduce.
  - This reduction of stresses over time is what is known as relaxation.
  - In general, as a binder ages, its relaxation properties are diminished.
  - An asphalt pavement that has a binder with good relaxation properties will be less likely to have durability-related cracking than a pavement containing a binder with poor relaxation properties.
$\Delta T_c$ is an Indicator of Oxidative Aging
$\Delta T_c$ is an Indicator of Oxidative Aging

CT RAP (from NCHRP 9-12)

$\Delta T_c$ vs RAP Binder in Blend, %

- PG 52-34
- PG 64-22
$\Delta T_c$ is an Indicator of Oxidative Aging

### AZ RAP (from NCHRP 9-12)

- **PG 52-34**
- **PG 64-22**

![Graph showing the relationship between $\Delta T_c$ and RAP Binder in Blend, %]
Can $\Delta T_c$ be used to predict cracking?

- $\Delta T_c$ is thought to be **directly** related to block cracking.
  - However, fatigue, edge, longitudinal, reflection, and transverse cracking may indirectly be related to $\Delta T_c$ of the binder.
  - These distress types are typically caused by other factors, yet $\Delta T_c$ can play a supporting role in their development.
Steps to Consider Before Implementation

• What are some things that an agency should consider before implementing ΔTc in a purchase specification?
  ◦ A brief summary of these steps is described in the “Considerations for Implementation of ΔTc as a Specification Parameter” section of the document
  ◦ When implementing important specification changes, AI encourages agencies to work together regionally (such as in User-Producer Groups) to facilitate uniform transition for the asphalt industry.
Are agencies using $\Delta T_c$ in their specifications?

• At the time this document was developed, ten agencies in North America had or soon will adopt $\Delta T_c$ as a specification parameter in some manner
  ◦ There is about an even split between agencies using 20- and 40-hour PAV aging protocols
  ◦ Most (but not all) agencies have adopted a minimum limit for $\Delta T_c$ of -5.0°C. The basis for that specification value is the AAPTP research mentioned earlier
PAV Film Thickness

- AAF-1, 20 hrs
- AAF-1, 40 hrs
Summary

• $\Delta T_c$ can be easily calculated using standard BBR test data
  ◦ Depending on lab and practices, 1-2 additional BBR tests at different temperatures may be needed

• $\Delta T_c$ appears to be an indicator of oxidative aging and loss of relaxation properties
  ◦ Related to intermediate, durability cracking even though the tests are performed at low temperatures
  ◦ Greater aging results in lower (more negative) values of $\Delta T_c$
Summary

• Variability of $\Delta T_c$ appears reasonable, as it is a product of BBR testing
  ◦ Consider variability if establishing guidance for use

• Asphalt binders with very negative values of $\Delta T_c$ may be more difficult to test in the BBR
  ◦ RAS binders

• Caution when using $\Delta T_c$ with polymer modified asphalt binders
  ◦ Higher elastic component may make $\Delta T_c$ more negative
Plastics in Asphalt
Background

• The world is generating about 300 million tons of plastic waste per year
• India and China banned the import of plastic waste materials in 2018
• The Plastics Industry Association is trying to find somewhere other than a landfill to place the millions of tons of plastic waste we formerly shipped to Asia.
  ◦ One Target – ASPHALT PAVEMENT
• Thirty global corporations have created the Alliance to End Plastic Waste (AEPW) and have pledged $1 billion with a goal of $1.5 billion over 5 years
Background

- Many different types of plastics
- Most of recycled plastic waste will not melt in asphalt – less than 5% of plastic waste stream
- History of melting plastics in asphalt (wet method) has shown stability and cracking problems
- Recycled plastic can be added wet or dry, but dry is the easy target as more plastic can be disposed of in that manner
- Most research and test projects come from Europe and India, and those results are misrepresented in U.S. marketing efforts
  - Plastic typically added dry while amount touted is calculated as percent binder
  - Little to no performance testing
• Working with NAPA and NCAT
• Conducted research at University of Alabama, NCAT and WRI
• Wet method
  ◦ Blended with asphalt binder
  ◦ Up to 10% by weight of binder
• Dry method
  ◦ Aggregate replacement/mixture modifier
  ◦ Up to 3% of aggregate weight
• NCAT - Wet Method and Dry Method testing – used recycled plastic that will melt in asphalt
  ◦ If Dry Method is used for majority of recycled plastic will not melt and only serve as filler material
Dow Chemical paved 2600 feet of 2 lane road with low density polyethylene plastic (1686 lbs.) to evaluate performance in their facility south of Houston.
Background

• Groundswell of interest generated by recycling plastics industry
• Substantial social media efforts and newspaper/magazine articles
• Congress wants to be “green” – several legislators proposed a “plastics in asphalt” mandate for the next Highway Bill
  ◦ NAPA has been fighting the proposed mandate, pushing for research funding versus a mandate
  ◦ Outlook is positive for no mandate at this time
Plastics in Asphalt

• 2020 TRB Session 1113 (AFK10, ADC60), Jan 13
  ◦ 4 podium presentations; 2 were case studies
Industry Response

• AI HSE Committee discussed plastics in asphalt at recent strategy meeting
  ◦ In conjunction with TAC Chair, agreed that there are many unknowns related to environmental and performance issues
  ◦ Agreed that AI needs to form task force to draft a document that outlines needed research
• NAPA also decided to form a task force to draft position paper
Industry Response

• Makes little sense for both groups to draft similar documents
  ◦ One position paper representing the asphalt industry will carry more weight

• AI and NAPA agreed to form joint task force
  ◦ Will also invite Eurobitume and EAPA to participate

• NAPA Task Force co-chair
  ◦ Ron Sines, CRH Americas Materials

• AI Task Force co-chair
  ◦ Ron Corun, Associated Asphalt
AI/NAPA Joint Task Force on Plastics

• Common message in position paper
  ◦ Not ready for implementation
  ◦ Parallels w/ failed crumb rubber mandate in early 90s.
• Common message in position paper
  ◦ Knowledge gaps and unknowns that require research
    • Performance – especially cracking
    • Binder stability (wet process)
  • Recyclability
    ◦ Environmental dangers of microplastics generated by milling
    ◦ Leaching from RAP storage piles
    ◦ Leaching from pavement
    ◦ Increased / New plant emissions
    ◦ Worker exposure
    ◦ Odor
    ◦ Handling at plant leaching
  • Life Cycle Costs - economics
AI/NAPA Joint Task Force on Plastics

• Initial Task Force meeting via conference call
• Defined task force objective
  ◦ To develop a comprehensive document which outlines the current knowledge related to the use of recycled plastics in asphalt binders and mixtures as well as the knowledge gaps.
  • This document would be part 1 of a marketing package which could be taken to legislators and specifiers to discuss the use of recycled plastics in asphalt mixtures.
  • Spring 2020 is target release date
AI/NAPA Joint Task Force on Plastics

- Overarching theme is to avoid unintended consequences of using waste plastic in asphalt before technology is ready
  - Crumb rubber industry says mandate in late 90s really set them back
AI/NAPA Joint Task Force on Plastics

• Developed an outline to accomplish objective
  ◦ Introduction
  ◦ Background – plastics overview
  ◦ Literature Review – hired Fan Yin of NCAT as consultant
  ◦ Summary of Findings
    • Impacts on Binder Performance
    • Impacts on Mixture Performance
    • Plant Operations
    • Construction
    • Health and Safety
    • Environmental Impacts
  ◦ Questions to be answered (knowledge gaps)
Acknowledgements
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