Introduction to Asphalt Materials, Manufacture, and Modification

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Gaylon Baumgardner
Executive Vice President
Paragon Technical Services, Inc.
My Goals for the Next Hour

- Have you understand the basics of how asphalt is manufactured
- Review the different types of asphalt materials and specifications
- Introduce the topic of asphalt modification (set up other speakers)
- Not be boring and have fun!!!
What is 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.
Where Does Asphalt Come From?
(From a refinery manager’s POV)

Petroleum Refining -
Process by which crude petroleum is distilled to produce a wide variety of transportation motor fuels and petrochemical products leaving behind a bunch of black gooey stuff that we don’t like.

Source: Marshall Shackelford
Where Does Asphalt Come From? (From an asphalt guy’s POV...That would be Us!)

Petroleum Refining - Process by which impurities are removed from crude oil to produce asphalt.

Source: Marshall Shackelford
World Wide Refining

- There are ~650 Refineries World Wide
- About 150 of them are in the United States (there used to be 300+)
- The largest in the world is the Reliance Refining Complex, Jamnigar, India @ 1,240,000 BPD crude capacity
- The largest in the U.S. is Exxon Baytown, TX @ 572,500 BPD
- No refineries in Arizona!

Source: Tom Shetina, HFRM
Actual Refinery

Source: Tom Shetina, HFRM
The Refining Barrel

Distilled WTI Crude

- Gasoline ~ 25%
- Jet & Diesel ~ 21%
- Lube Oil ~ 15%
- Residue ~ 37%

~50%

42 Gallons

The Refining Barrel

Refined WTI Crude

- Gasoline ~ 49%
- Jet & Diesel ~ 37%
- Residue ~ 8%

~90%

Volume Gain ~ 6%

This is what crude oil alone gives you...

...this is what the market demands!

Source: Tom Shetina, HFRM
An Example of Distillation

The Good Stuff!
Fractional Distillation Column

Source: Tom Shetina, HFRM
Asphalt Oxidizer

- **Purpose**
  - Via air blowing, chemically change asphalt to produce harder, less temperature susceptible asphalt
  - Most roofing asphalt comes from this
  - In N. America, a little bit of paving asphalt comes from this

Source: Tom Shetina, HFRM
Refinery Products

- Gasoline - automobile, light truck, small engine fuel
- Diesel - automobile, heavy trucks, trains, heavy equipment
- Jet Fuel - Commercial and military aircraft
- Kerosene - Home heating, charcoal fluid
- Liquified Petroleum Gas (LPG) - Chemical feed, heating, commercial applications
- Fuel Oil - Ships, boilers, furnaces
- Asphalt - Roads, roofing material, sealants
- Carbon Black Oil - Carbon black manufacture, carbon composites, tires
- Lubricating Oil - Engine & machinery lubrication
- Waxes - Candles, industrial sealants
- Petroleum Coke - Coal fired boilers, metals manufacture (anodes, fuel)
- Sulfur - Chemical and fertilizer manufacture
Types of Asphalt

- Paving Asphalt for Building Roads
  - Asphalt Cement
  - Cutback Asphalt
  - Emulsified Asphalt
- Roofing Asphalt
- Specialty Asphalt
Specialty Asphalt Products

- Pruning paint
- Sealants
- Grease component
- Waterproofing membranes
- Clay pigeons
- Electrodes
- Many others...
Roofing Asphalt

- ASTM D312 - built up roofs
- ASTM D449 - dampproofing and waterproofing
- ASTM D225 - asphalt shingles
- ASTM D6380 - organic felt asphalt roll roofing
- many others...
Types of Asphalt for Building Roads

- Asphalt Cement
- Cutback Asphalt
- Emulsified Asphalt
Asphalt Cements for Paving in Arizona

- No refineries here, so...
- Terminal supplied in AZ
  - Paramount
  - Valero
  - Ergon
  - Western Refining
  - HollyFrontier
- Produced to meet paving spec
  - PG specs in Arizona and most other places in US
  - PG variants (aka PG Plus)

Gotta have heat
Cutback Asphalts

- Diminished presence in AZ market and elsewhere
- Rapid Cure (RC)
  - high volatility solvent (e.g., naphtha)
  - chip seals, tack coat
- Medium curing (MC) - ADOT grades
  - moderate volatility (e.g., kerosene)
  - patching mix or prime coat
- Slow Curing (SC)
  - low volatility (diesel or something else)
  - patching mix

Gotta have solvent
Emulsified Asphalt

- Made fluid by suspending droplets in water with and emulsifying agent
  - agent imparts charge to droplets
  - this is way cool!
- Cationic (CRS, CSS, etc.)
  - positive charge on droplets
  - work good with gravels (sort of)
- Anionic (RS, SS, HF, etc.)
  - negative charge on droplets
  - work good with limestone (sort of)
Let’s talk about specifications!
So you want to buy some asphalt...

- Tell me what you want
  - “I want it sticky”
  - “it needs to remain pliable if I chew it 100 times” (Early 1900’s binder grading)
  - “if I heat it to 100 F in an oven in an itty bitty cup, it shall not flow out after one hour ± 5 minutes”
- sell me something that works
You Need a Specification!

- Tells important properties
- Identifies ways to measure important properties
- Important part of a contract between a buyer and seller
Specifications
Where do they come from?

AASHTO
ASTM
DOTs (ADOT for example)
MAG
City of Phoenix, Glendale, Mesa, etc.

Material vs. Construction Specs
Past Asphalt Specifications

“AC” Specification
- AC-5
- AC-10
- AC-20
- AC-30
- AC-40

1970-1990
1960s - AR

“Pen” Specification
- 40 - 50
- 60 - 70
- 85 - 100
- 120 - 150
- 200 - 300

1960s-1970
Summary - 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
- From 1960s, asphalts were specified as “Aged Residue” (AR) grades.
  - AR 1000, AR 2000, AR 4000, AR 8000 and AR 16000
- Beginning in 1970, asphalts were specified as viscosity (AC) grades.
  - AC-5, AC-10, AC-20, AC-30 and AC-40
AC 20

Temperature
- 25°C (77°F)
- 60°C (140°F)
- 135°C (275°F)

Ave. Service Temp.

Hot Summer

Mixing & Compaction

Table 1

Viscosity (Stiffness)
- 40 Pen
- 60 Pen

Table 2

Low

2400

1600

300

210

40 Pen

60 Pen
...and then there was PG
(It’s a new thing! 1993 to present)

- Strategic Highway Research Program
  - 1987-1993
  - $50 million research project by state DOTs
  - primarily at universities
- Product was called Superpave
  - Superior Performing Asphalt Pavements
  - PG binder spec with new tests
  - mix design system
- Adopted throughout all of US by now
PG Tests
Big Picture View of PG Grading

Construction

[RV]

[Rutting]

[DSR]

[Fatigue Cracking]

[BBR]

Low Temp Cracking

No aging

RTFO Short Term Aging

PAV Long Term Aging
SuperPave Grading of Asphalt Binders

- 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.
What are the “PG” Grades All About?

PG 70-10

Means Performance Graded Asphalt Binder
What’s this “PG” All About?

PG 70-10

High pavement temp (°C) to protect against rutting

Low pavement temp (°C) to protect against thermal cracking
Another Way to Look at It

Test asphalt binder at temps this layer feels (high, intermediate, low)

Testing binder to get good performance for this layer at expected pavement temps.
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.
Asphalt Stiffness and Performance Limits

- Elastic
- Visco-Elastic
- Viscous

Performance Range

- Low Temperature Limit
- High Temperature Limit
Useful Temperature Interval

![Graph showing temperature interval with labels: Elastic, Visco-Elastic, Viscous.]

- Useful temperature interval: 74°C to 98°C
- Log of Stiffness on the y-axis
- Temperature (°C) on the x-axis
- SHRP GRADE 58-16, SHRP GRADE 64-22, SHRP GRADE 76-22
- Bending Beam Rheology and Dynamic Shear Rheology
A look ahead question for you... which grade is better?

- A PG 70-10 would have a UTI of 80 °C
- A PG 58-28 also has a UTI of 86 °C
- If we needed a PG 76-16, which has a UTI of 92 °C - how is this accomplished?
- As a “rule of thumb”, to achieve a UTI of >90 °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
Where exactly do you find the PG spec?

  - ADOT Section 1005
  - MAG Section 711
  - ASTM D6373
Summary - SUPERPAVE Performance
Graded (PG) system

- AASHTO M320
- Fundamental properties related to pavement performance
- In-service & construction temperatures
- Short and long term aging
- Key issue is property requirements are constant and the temperature at which these properties must be achieved varies
Does This Seem Familiar?
Takeaways so far

- Asphalt comes from refining of crude oil
  - process is called “fractional distillation”
  - one of many products produced in a petroleum refinery
  - no refineries in Arizona...thus terminal purchases

- There are three types of asphalts
  - paving, roofing, and specialty

- We buy and sell asphalt using a specification
  - “PG” asphalt spec is currently used in the US, including Arizona for paving asphalt (UTI)
Let’s talk about modified asphalt binders!
Why Modified Binders?

- Extend the range of temperatures over which the asphalt binder will perform its intended function
  - rutting
  - cracking
- Longer lasting pavements
- *Cheaper pavements...in the long run!*
Log of Stiffness, Viscosity, etc.

UTI

Modified 1

Modified 2

Unmodified

Temperature (°C)

Log of Stiffness

Temperature

SHRP GRADE 58-16
SHRP GRADE 64-22
SHRP GRADE 76-22
Other Reasons

- Reduce moisture damage in mixes
- Stick chips better and faster
- Reduce pavement thickness
  - maybe/maybe not
- Address construction issues
  - drain off on open graded mixes
  - facilitate compaction
- Synergistic co-modifier effect
- Many other reasons...
History of Modified Asphalts

- 1873 – Whiting patent in US, natural rubber
- 1930’s - Test projects in Europe
- 1950’s - Neoprene Latex in U.S. & Canada
- 1970’s - Wide use of polymers in Europe
- 1980’s – Polymer/rubber binders increase in U.S.
- 1990’s - SHRP PG specs increase demand
- 1990’s - chemical modification enters market
- 2000  - U.S. HMAC market - 15% Modified
- present  - Estimated 25% Modified HMAC

Source: H. King, G. Baumgardner, H. Romagosa
Modifier Selection

Considerations

- Will it have the intended performance effect?
  - effect as stand alone modifier
  - effect as co-modifier
- Can it be specified?
- Does it meet purchase spec?
  - recipe vs performance vs both
- How much does it cost?
  - price volatility, availability, alternatives
- How must it be handled and incorporated?
- Does it stay homogeneous?
- Is it heat stable?
- Does it affect constructability?
- Are there testing considerations?
Types of Modification

- Chemical modification
- Polymers and attendant stuff
- Modification by process (air blowing)
- Construction Enhancers
- Waste Products (e.g., crumb rubber)
- Fillers and Fibers
- Antistripping agents
- Hydrocarbons
- Antioxidants
- Extenders

Process - Air
Extenders - Special Fillers
Chemical - PPA, Amines
Polymers - SBS, GTR etc...
Log Stiffness,

Chemical (PPA) modified

Unmodified

Temperature

Temperature (°C)

Log of Stiffness

Bending Beam Rheology

Dynamic Shear Rheology

SHRP GRADE 58-18
SHRP GRADE 64-22
SHRP GRADE 76-22
Effect of PPA on Performance Grade

![Bar chart showing the effect of PPA on performance grade with data points for PG Crossover Temp, C at various temperatures and grades A, A+1%, B, B+1%, C, C+1%]
Effect of PPA on Rutting Susceptibility

Salt River Aggregate, MAG 3/4-inch

Rut Depth (50 C), mm

C C+1% PPA C+1% PPA + 0.75%lime
PPA Modified Asphalt

Advantages
- Easy to manufacture
- Stays homogeneous and heat stable
- No effect on low temp properties
- Relatively cheap increase in PG
- Stable supply
- Performance history
- Favorable co-modifier with polymers

Disadvantages
- Does not work with all asphalts
- Can be negated by basic highway chemicals
- No elastic effect as with stretchy types of polymers
- Cannot use for anionic emulsion bases
Types of Polymers

- Elastic Type (Elastomers)
  - SB diblock (Dynasol 1205)
  - SBS (Kraton D1184)
  - SBR latex (Ultrapave 1156)
  - Natural latex (Firestone Hartex 104)
  - Waste rubber (CRM WRF-14)

- Plastic Type (Plastimers)
  - Oxidized Polyethylene (Honeywell Titan 7686)
  - EVA (Exxon Polybilt 103)
Polymer Modified Asphalt (Elastic)

- **Advantages**
  - Long performance history
  - Elastic effect
  - Improved cohesion
  - Many specs designed around stretchy polymers (no mysteries)
  - Favorable co-modifier with sulfur and PPA

- **Disadvantages**
  - Can be challenging to manufacture
  - Compatibility can be a problem
  - Tougher to handle
  - Not heat stable
  - Challenge to emulsify
  - Relatively expensive
Construction Enhancers

- **Purpose**
  - reduce mix temperature
  - facilitate compaction

- **Examples**
  - warm mix chemicals (e.g., Evotherm, Rediset)
  - mechanical production (e.g., zeolite, foaming)
  - waxy additives (e.g., Sasobit, Honeywell Titan, EBS, Montan)
Fillers

- **Purpose**
  - fill voids, lower asphalt content

- **Examples**
  - baghouse fines
  - crusher fines
  - lime and cement
  - fly ash
  - carbon black
Fibers

- **Purpose**
  - Increase tensile strength
  - Inhibit draindown

- **Examples**
  - Natural
    - Asbestos, rock wool
  - Manufactured
    - Polypropylene, polyester, fiberglass, cellulose
Antistripping Agents

- **Purpose**
  - reduce moisture damage
  - stick asphalt to aggregate

- Lime and cement
- Amines
- Phosphate esters
- Organo silane
- Some polymers
  - SBR latex
Hydrocarbons

- **Purpose**
  - soften asphalt
  - rejuvenate asphalt
  - stiffen asphalt
- Re-refined engine oil bottoms
- Rejuvenating agents (Raffex, Hydrolene)
- Gilsonite, petroleum pitch, TLA
Extenders

- **Purpose** - reduce asphalt demand
- **Examples**
  - Sulfur (Shell Thiopave)
  - lignin
Oxidants and Antioxidants

- Oxidants
  - Purpose - increase binder stiffness
  - Example - manganese salts (aka Chemcrete, Resperion IntegraBase)

- Antioxidants
  - Purpose - increase durability by decreasing binder aging
  - Example - carbon black, some lead compounds
Waste Materials

- **Purpose** - replace asphalt binder or mix with cheaper waste product
- **Examples**
  - Scrap tires
  - Shingles (pre- and post-consumer)
  - “Glassphalt”
  - “Poticrete”
What is Crumb Rubber Modified Asphalt

- Hold that thought until later!
Popular Urban Legend

Chupacabra?
Popular Urban Legend

- “I got this new stuff... you can use dirt in the mix...don’t have to compact mix...puts the “stickies” back in the asphalt...has better positioned carbonyl groups to favorably shift master curve...blah blah blah...
If it doesn’t make sense, it’s probably not true.

- Judge Judy
Thank You!
Questions?