Laboratory Evaluation:
Wax Additives in Warm-Mix Asphalt Binder

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Objective

Evaluate the effect of wax additives on physical properties and characteristics of asphalt binders and their subsequent performance in mixtures.

Can specifications distinguish between beneficial additives versus those that might have a negative impact on the performance of hot mix asphalt (HMA)?
Materials

- **Asphalt** – One (1)
  - Lion Oil PG64-22 Eldorado, AR Refinery (Saudi)
- **Wax Additives** – Nine (9)
  - Non-Paraffin Wax Additives
- **Aggregates**
  - Vulcan Barin Quarry Granite, Columbus, GA (Aggregate used on the NCAT Test Track)
- **Mix Design**
  - 12.5mm Dense Graded SuperPave™ Gyratory
    - ~5.5% Binder
    - ~7.0% Air Voids
Targeted a range of waxes

**Paraffin Wax**
- Size of molecule < C_{45}
- Melting point < 70 °C
  - natural waxes
    - animal (e.g. beeswax)
    - vegetable (e.g. Carnaubawax)
  - modified natural waxes
    - brown coal-derivative
    - mineral oil-derivative

**Non-Paraffin Wax**
- Size of molecule > C_{45}
- Melting point > 70°C
  - partial synthetic waxes
    - acid waxes
    - ester waxes
    - amid waxes
    - alcohol waxes
  - full synthetic waxes
    - Fischer-Tropsch-waxes
    - polyethylene-waxes
Materials tested

0 Lion Oil PG 64-22
1 Romanta Normal Montan
2 Romanta Asphaltan A
3 Romanta Asphaltan B
4 Licomont BS 100
5 Sasobit
6 Luxco Pitch # 2
7 Alphamin GHP
8 Strohmeyer and Arpe Montan LGE
9 Astra Wax 3816D Microcrystalline

9 - Waxes
Test program

- **Binder**
  - M320 – Table 1 and 2
  - Binder master curves – BBR and DSR
  - BBR tests at different aging conditions (0, 2, 4, 8, 16 and 32 days)
  - MSCR

- **Mixture**
  - Mix BBR tests – 2 temperatures for limited mastercurves
  - Repeated creep tests
  - Fatigue – monotonic tests and repeated load
  - Master curves
Mix stiffness in BBR

- Tested BBR beams at varying ageing
- Analysis extended to use 1000 second data
- Removed early part of test data to avoid effects of non-instantaneous startup
PG grading – AASHTO M320 (3% Wax Modified Binders)
PG grading – AASHTO M320
(1% Wax Modified Binders)

![Graph showing PG grading results for different binders and modified binders. The x-axis represents different PG grades (450, 447, 425, 407), and the y-axis shows values ranging from -28.0 to 86.0. The graph includes data for Lion Oil PG64-22* + Licomont BS 100 (PG64-22), Sasobit (PG64-20), and Astra Wax 3816 D (PG64-16), with values for Original DSR, RTFO DSR, PAV DSR, BBR S-value, and BBR m-value.]
Binder – 0 day tests

**RHEOLOGY ANALYSIS** in Abatech RHEA Software

**RHEOLOGY OBSERVATIONS**

- 6 (Luxco Pitch # 2) – has lower $G^*$ mastercurve
- Significant difference in $G^*$ at lower end of frequency range
- $\delta$ with various binders show some type of network at low frequencies, more significant in 2 (Romanta Asphaltan A), 3 (Romanta Asphaltan B), 4 (Licomont BS 100), 5 (Sasobit) and 7 (Alphamin GHP)
- Judging from $\delta$ (*at low temp/high freq.*)
  - 6 (Luxco Pitch # 2) appears to have best relaxation properties
  - 9 (Astra Wax 3816D Microcrystalline) has worse relaxation properties
Master curve $E^*$, $T_{ref} = 25^\circ C$
Master curve $E^*$, $T_{\text{ref}} = 25^\circ\text{C}$
Binder 0 - 0 days

Sample ID: B0-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

0 Lion Oil PG 64-22

Legend
- Observed Data Points
- Complex Modulus
- Phase Angle
- Computed Discrete Spectrum
  - $g_i, 1/\lambda_i$
  - Fitted Complex Modulus
  - Fitted Phase Angle

Frequency, rad/sec

$G^*, \text{Pa}$

Phase Angle, deg.
Binder 1 – 0 days

Sample ID: B1-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

Legend
- Observed Data Points
- Complex Modulus
- Phase Angle

Computed Discrete Spectrum
- $g_i$, $1/\lambda_i$
- Fitted Complex Modulus
- Fitted Phase Angle

1 Romanta Normal Montan
Binder 2 – 0 days

**Sample ID:** B2-0-DSR BBR

Dynamic Mastercurve $T_{ref} = 25°C$

**Legend**
- **Computed Discrete Spectrum**
  - $g_i, 1/\lambda_i$
- **Observed Data Points**
  - Complex Modulus
  - Phase Angle
- **Fitted**
  - Complex Modulus
  - Phase Angle

**2 Romanta Asphalt A**
Binder 3 – 0 days

Sample ID: b3-0-DSR BBR

Dynamic Mastercurve $T_{ref} = 25^\circ C$

3 Romanta Asphalt B

Legend:
- Observed Data Points
- Complex Modulus
- Phase Angle
- Computed Discrete Spectrum
- Fitted Complex Modulus
- Fitted Phase Angle

Frequency, rad/sec

$G^*$, Pa

Phase Angle, deg.
Binder 4 – 0 days

Sample ID: b4-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

4 Licomont BS 100
Binder 5 – 0 days

Sample ID: b5-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

5 Sasobit

Legend
- Observed Data Points
- Computed Discrete Spectrum
- Complex Modulus
- Phase Angle
- Fitted Complex Modulus
- Fitted Phase Angle
Binder 6 - 0 days

Sample ID: B6-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

6 Luxco Pitch # 2
Binder 7 – 0 days

Sample ID: B7-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

7 Alphamin GHP
Binder 9 – 0 days

Sample ID: b9-0-DSR BBR
Dynamic Mastercurve Tref = 25°C

9 Astra Wax 3816D Microcrystalline
Tests conducted at three temperatures
- 58, 64, 70°C

Jnr evaluated at 3.2 kPa and 4 (1/kPa)

Elastic recovery – v. high for some products at low stress levels

Certain products are more stress dependent that conventional binders
2 – % Recovery 58 to 64C

% recovery MSCR

Jnr 1/kPa

-10

0

10

20

30

40

50

60

70

80

90

100

3.2 kPa

3.2 kPa

3.2 kPa

2 58C

2 64C

2 70C
Recovery – near grade temp

-10 0 10 20 30 40 50 60 70 80 90 100

0 Lion Oil PG 64-22
1 Romanta Normal Montan
2 Romanta Asphaltant A
3 Romanta Asphaltant B
4 Licomont BS 100
5 Sasobit
6 Luxco Pitch # 2
7 Alphamin GHP
8 Strohmeyer and Arpe Montan LGE
9 Astra Wax 3816D Microcrystalline
Jnr at 64°C

- 0 Lion Oil PG 64-22
- 1 Romanta Normal Montan
- 2 Romanta Asphalt A
- 3 Romanta Asphalt B
- 4 Licomont BS 100
- 5 Sasobit
- 6 Luxco Pitch # 2
- 7 Alphamin GHP
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Graph showing Jnr, 1/kPa vs. Stress, kPa for various substances at 64°C.
Jnr – near grade temperature

0  Lion Oil PG 64-22
1  Romanta Normal Montan
2  Romanta Asphaltan A
3  Romanta Asphaltan B
4  Licomont BS 100
5  Sasobit
6  Luxco Pitch # 2
7  Alphamin GHP
8  Strohmeyer and Arpe Montan LGE
9  Astra Wax 3816D Microcrystalline
Jnr versus % recovery

% recovery

Jnr, 1/kPa

Elastic

Non-Elastic
Difference in performance

- Binders grade different in Jnr evaluation
- Can be as much $\frac{1}{2}$ PG grade
- Early products that show network – 2 effected from 5
  - 2 (Romanta Asphaltan A)
  - 3 (Romanta Asphaltan B)
  - 4 (Licomont BS 100)
  - 5 (Sasobit)
  - 7 (Alphamin GHP)
- Suggests importance of Jnr evaluation

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<td>9</td>
<td>0.16</td>
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Aged tests - binder
PG64-22 – aging to 32 days

-18°C

Stiffness, MPa

Time, seconds
Binder BBR S(t) at -12°C

Binder BBR Stiffness, -12°C, t = 60 seconds

Aging Time, days

Stiffness, MPa
Binder BBR S(t) at -18°C

Binder BBR Stiffness, -18°C, t = 60 seconds

- Lion Oil PG 64-22
- Romanta Normal Montan
- Romanta Asphaltan A
- Romanta Asphaltan B
- Licomont BS 100
- Sasobit
- Luxco Pitch # 2
- Alphamin GHP
- Strohmeyer and Arpe Montan LGE
- Astra Wax 3816D Microcrystalline
BBR data

- Aging data showed that the -18°C gave significantly more variability when compared to the -12°C data
Mix test data
Mix BBR Data

- Data processed to produce equal-log scale representation with approximate linear double of scale.
- Several cases exist which colder temperature is less stiff than matching warm temperature data.
Removal of early BBR data

- Data before 8-seconds is removed from analysis in similar manner to binder BBR data
- Shows fitted (polynomial) approach versus direct calculation
- Data before $t=8$ seconds is less reliable

![Graph showing stiffness vs. time with data points]

Data point corresponding to 8 seconds
Sample ID: Mix BBR 91-0 Day 0

Apparent Stiffness Isotherms

Add / Remove Ism:
- ttd  mix bbr 91-0 da
- T -18
- T -12

Legend:
- Observed Data Points
- = Apparent Stiffness

Si(t), MPa

Time, t, sec

0.1  1  10  100  1000  1e4

1e3  1e4
Sample ID: Mix BBR 91-5 Day 0

Apparent Stiffness Isotherms

Legend
- Observed Data Points
  - Apparent Stiffness
Material 5 - Day 16

The graph shows the relationship between stress $S(t)$ (in MPa) and time $t$ (in seconds) for Material 5 on Day 16. The data points represent different samples labeled with codes such as 16-91-5-1-12, 16-91-5-2-12, and 16-91-5-3-12. The graph includes a line of best fit for the samples at -12°C and -18°C, with different markers for each temperature.
Re-tests of Mix Beams

- Testing of beams before and after annealing
- Annealing conducted at 64°C overnight
- 64°C chosen since it represents day at likely high-pavement temperature
1 - PG64-22 - retests

Graph showing stress-strain relationship with temperature variations.
5 - Sasobit - retests

91-5-2 RR

Graph showing stress-strain relationship with time for Sasobit retests at different temperatures.
9 - Astra Wax

Graph showing the decay of a property $S(t)$, MPa, as a function of time $t$, sec, for temperatures -18°C and -12°C, with fitting curves for D-S Fit. Points marked with symbols indicate data at different time intervals.
Results from retesting

- In all cases healing overnight increased the stiffness of the mastercurve.
- Most significantly – it resulted in the BBR stiffness of the -18°C isotherm being greater than the -12°C isotherm – as expected!
- The “healing” is more significant for the -18°C isotherm.
Repeated creep torsion bar

- Tests at two stress levels
  - 34 and 68 kPa
- Temperature = 64°C
- 5 replicates – used results of middle 3
- Analysis of various parameters
Repeated load tests

- Concept used in early 1990’s with cyclic deformation tests
- Based on same concept as used for fatigue analysis
- Very ease to use to limit test time - stop test at say 5% less than max
Jnr Grade vs. Repeated Creep Performance

![Graph showing repeated creep performance with Jnr grade using different models and regression equations.](image)
Jnr at 64°C vs. Repeated Creep

Flow Number (modified)
1/slope
min dy/dx

\[ y = 467.69x^{-0.5795}, \quad R^2 = 0.743 \]
\[ y = 302.97x^{-0.6689}, \quad R^2 = 0.7603 \]
\[ y = 112.64x^{-0.6394}, \quad R^2 = 0.734 \]
Fatigue

- Work conducted by MTE Services, Inc
- Monotonic loading test
- Sand cylinders repeated loading
Monotonic tests

3% Wax Blends

RELATIVE AREA VALUE

AREA UNDER MONOTONIC TEST CURVE AT PEAK VALUE

control, Montan, Asphaltan A, Asphaltan B, Licomont BS 100, Sasobit, Luxco Pitch, Alphamin GHP, Montan LGE, Astra 3816
Monotonic tests

Area under monotonic test curve at peak value vs. area 1% blends.

ADDED SOME 1% Wax Blends

Sand Cylinder Fatigue

Generally all modifiers give poorer performance but difference is very small compared to other materials and typical "noise" in fatigue sets.
Master curves on sand-mix
Merged MasterCurve Paragon Wax Study, 91-0-01, Control, 7·1% AV, -30 to 60·0° #1
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7.1% AV, -30 to 60.0°
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7·1% AV, -30 to 60·0°
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7.1% AV, -30 to 60.0°
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7.1% AV, -30 to 60.0°

$G^*$

$[\text{Pa}]$
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7.1% AV, -30 to 60.0°

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Graph showing G* (rad/s) vs. [rad/s] with curves for different wax studies.
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7·1% AV, -30 to 60·0°

![Graph showing viscoelastic properties of various waxes over a range of temperatures and frequencies.](image_url)
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7.1% AV, -30 to 60.0°
Average Merged MasterCurves Paragon Wax Study, 91-0-01, Control, 7.1% AV, -30 to 60.0°

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G* ($\text{[Pa]}$)

|$\theta$ [rad/s]
Summary – Binder tests

- Significant differences in PG grades with different modifiers
  - All had some loss of performance at low end of specification
- Master curves show different structures in binder – note low strain level
- Jnr – results show that binder is stress sensitive
  - Wax products generally vary more with stress level
  - Have apparently good behavior at low stress levels
  - As stress level increases performance drops
  - The wax materials are a non-elastic modifier
    - Note \( \delta \) can confuse the analysis such as used in some specifications
- Aging of BBR binder beams over extended time shows significant change in properties
  - Data at -12C was more in line with that expected
  - Data at -18C appears to be confounded
Summary – mix tests

- **BBR**
  - Avoid using early part of isotherm
  - Issues with -18C data after extended aging
  - Some damage/healing evident in data
  - Annealing at 64C showed that rankings could be restored to that expected
  - -18C is poorer than -12C data

- **Repeated creep**
  - Data lines up with Jrn results
  - Some suggestions for data analysis

- **Fatigue**
  - Monotonic tests show difference in performance
  - Preliminary – 1% and 3% wax show some different results
  - Repeated loading shows again significant differences – all waxes generally give lower performance but difference is small

- **Master curves**
  - Differences evident in $G^*$ master curves
  - Should be able to look at these combined with BBR master curves
What to do

- More work with 1% wax content
- Some additional analysis of data
  - Maybe combine $G^*$ and $S(t)$ master curves for mix to look at trends – do they match binder?
- DTT with notched specimens
- Develop report
Help ... I’m getting wet III

ANY QUESTIONS??