Current Research in the US to Address Inferior Binders and Cracking

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Sarnia, ON, CAN, June 18, 2019



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#### **Outline**

- WRI An overview
- Context: Asphalt Variability
   The "New Normal"
- The WRI-Fingerprinting Approach to Cope with the New Normal
- Case study: NCHRP 9-60
  - Objectives
  - Approach
  - Examples of Findings
- Summary / Perspectives





#### WRI overview

- US non-profit company 501-C3
  - Affiliate of the U of Wyoming
  - 45+ scientists, engineers & support
- Facilities in Laramie, Wyoming
- Fields of expertise Technologies
  - Energy: oil, coal, biomass processes and products
  - Materials: asphalt and others
  - Environment



- A long history
  - <u>1924</u>: Petroleum lab to study WY high-sulfur crude oil
  - 1983: DOE Laramie Energy Tech Center de-Federalized to become WRI
- Annual sponsored events in July
  - Petersen Asphalt Research Conference <u>56<sup>th</sup> PARC</u>: July 14-17, 2019
  - ISAP 2016 symposium
  - Training on "Asphalt Chemistry & Relations to Properties" in 2015



#### WRI overview - Facilities

#### Bureau of Mines Building - UW Campus



 Asphalt and Petroleum Technologies (APT)

#### Advanced Technology Center - North of Laramie



- Bitumen Partial Upgrading
- Processes
- Coal and Biomass Activities
- Environmental Management



### WRI/APT Activity

#### Main activity: Research, Technology and Development

- Petroleum problematic crude oils and products
- Asphalt for paving and roofing
- Additives / Modifiers / Materials
- Analytical methods/tools
- Analysis, Characterization, Formulation, Forensics
  - Helping companies develop products / processes
- Development of Synergies: to advance the knowledge & toolkit on Petroleum, Asphalt, Coal, Additives and Materials (Carbon fibers...)







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# WesternResearch Context - "360" Industry Changes

#### Drivers: economics, geopolitics, societal, regulatory

- Changes in crude oils and processes
  - Tight oils / heavy oils / cocktails, and others...
  - Blends of various refining bases
- New world of additives and modifiers with different:
  - Functions: modifiers, antistrips, rejuvenators, WM-A, surfactants...
  - Chemistries: polymers, X-linkers, acids, waxes, bio-based, oils...
- Market changes: WMA and Recycling
  - RAP / RAS / REOB / GTR / Plastics / ...
- Specifications changes
  - Superpave and other specs: not truly Perf. related but evolving
  - <u>Other petroleum products</u>: 2020 IMO on Marine fuel (% Sulfur) may release high conversion residues to the asphalt pool?
- LCA/LCI/LCCA
- IARC classification
- REACH regulation (Europe)

#### Adapted from Al-Eurobitume document

#### **Context: Changes in Processes**





#### **Consequences:** Binder Composition & Quality Changes

### Superpave binder specs and quality issues

- PG specs and test methods, designed in the 90's for asphalts from the <u>90's</u>
  - Not for today's binders
  - And even less for tomorrow's binders

## Binder variability and inconsistent quality

Not prevented and not captured by current specs

Binder quality has an impact on pavement

performance





## NCHRP 09-60 NCAT- Agency Survey





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#### **NCHRP 09-60**

#### NCAT- Agency Survey





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### Chemo-Mechanical Fingerprinting to cope with the "New Normal"



WesternResearch The WRI Fingerprinting A		g Approach
		1987 !
	<b>G</b> FP I, II, III & ARC - FHWA-WRI 9	0'-2015
	<ul> <li>The tools</li> <li>Eurovia / WRI cooperation</li> </ul>	2013-
	> The initial "Fingerprint" project	
	WRI – Asphalt Industry Research Consortium #1 (AIRC)	2015-
	> NCHRP 9-60 – WRI-AAT-NCAT-GH	K 2016-
	<ul> <li>&gt; WRI-AIRC #2</li> <li>&gt; Others</li> </ul>	<b>2018-</b> 15



# Understanding Asphalt Composition

#### Asphalt chemical composition

- Complex: 100,000s of molecules
- > Continuum:
  - From Hydrogen-saturated to H-deficient molecules
  - Solubility parameters
- Complex interactions: time, temp., oxidation and additive dependent

Asphalt /	Alkane Soluble Maltenes
Petroleum	Alkane Insoluble/

Aromatic Soluble Asphaltenes

Increasing Aromaticity/Polarity/Heteroatoms and Molecular Weight

The tools



# The tools <u>Understanding Asphalt Composition</u>

#### Using Saturates, Aromatics, Resins, Asphaltene-Determinator SAR-AD<sup>™</sup>



Western Research

#### The tools Understanding Asphalt Composition

#### SAR-AD Fractions: ELSD Area Percent = Weight %



### WesternResearch Understanding Asphalt Composition

 Characterization of waxy materials as a function of solubility + temperature - Waxphaltene Determinator™



## The Tools: Thermal Analysis To measure Tg and Crystallinity



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#### The Tools: The Holistic Approach case of "Old Normal" binders

----(B)

-..(C)

······(D)



DSR- Black Space Diagram

Phase Angle (°)

#### Straight runs asphalts

Different fraction composition but within fairly narrow limits (SAR-AD)

4.5

**SEC-GPC** 

5 Time (min) 5.5

6

6.5

- Fairly similar molecular associations & weight distribution (SEC)
- Fairly similar & simple rheological behavior (DSR)



# The Tools - Structural Model of Asphalt



#### Dependence:

- Crude oil origin
- Refining process
- Temperature
- Aging stage
  - Tank (unaged)
  - Short Term Mixing/Construction
  - Long term Pavement
- Molecular weight / associations and Polymer/additive addition
  - Microscopy, GPC, IR, SAR-AD, AFT

## Colloidal suspension of asphaltenes in a maltene matrix (SARA – SAR-AD)



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## The Tools -Structural Model of PMA's



- Effect of polymer modification on microstructure & properties
   by UV fluorescence microscopy: Multiphase system
  - Polymer swollen with light aromatic oils from maltenes
  - Maltene phase enriched in asphaltenes, impoverished in aromatics
  - Polymer phase inversion between 3 and 6% polymer
  - Jump in consistency (R&B softening point, G\*/sin δ...)



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#### The Tools -Structural Model of PMA's





### The Tools -Structural Model of PMA's



#### Fine dispersion of a crosslinked PMA

- ✓ Homogeneous at micron level
- ✓ Storage stable
- ✓Less evolving during aging

Ref.: Mouillet et al, BLPC 2000, Fuel 2008

#### UV Fluorescence Microscopy



# Microstructure of a cross-linked PMA

3-D Network revealed by N-hexane rinse

W	NesternResearch The WRI Fingerprinting Approach				
		NIT	Partn	ers	
	SHRP		1987 ¦		
	Given FP I, II, III & ARC - FHWA-WRI	90' <b>-</b>	2015 ¦		
	The tools		2013		
	The initial "Fingerprint" project		_0.0		
	<ul> <li>Eurovia / WRI cooperation</li> </ul>				
	WRI – Asphalt Industry Research		2015-		
	Consortium #1 (AIRC)		2040		
	NCHRP 9-60 – WRI-AAT-NCAT-GI	łK	2010-		
	> WRI-AIRC #2		2018-		
	> Others			27	

# WesternResearch EUROVIA 1st Asphalt Fingerprint Study

- Binder Chemical
- Infrared
- Differential Scanning Calorimetry
- SEC/GPC

Binder Mechanical

- US: Superpave DSR, BBR,SCR, LAS, ABCD cracking
- EU: Pen, R&B,

- Mixture tests
- G. Compactor
- Rutting- Wheel tracking
- Trapezoidal fatigue
- TSRST cracking
- Moisture resistance

→ Chemometrics correlations for 14 neat binders

Asphalt composition correlated with mech. properties and some asphalt mix properties – SAR-AD + ExpliFit software
 >Binder impact: fatigue, stiffness modulus, and cracking
 >Aggregate impact: sensitivity to water, compaction, ...
 □ Papers: EE 2016, ISAP 2016, PARC 2017, CTAA 2017













### Approach: Tying Chemical and Rheological Analysis





Asphalt Industry Research Consortium

WRI-AIRC

- Launched by WRI in 2015 (2<sup>nd</sup> iteration in progress)
- Goal: Fingerprint asphalt binders to understand and assess the source variability and impact on properties
- Partners (worldwide)
  - **Q**Road administrations, Road contractors
  - **Additive suppliers, Asphalt suppliers / producers**





Asphalt Industry Research Consortium

#### Worldwide Database of 90+ different asphalt binders (some with field data)

- □ SHRP and ARC asphalts references
- Unmodified straight run, airblown, SDA, and VB blends
- □ Modified with polymers / additives /...RAP...
- Bio-binder



WRI-AIRC



#### "Old Normal" binders



**DSR- Black Space Diagram** 

<sup>32</sup> WRI-AIRC/09-60 data – E&F paper 2019





## Waxy binders (cont'd)



#### **DSR-** Black space diagram



#### AAA-1 AAM-1

#### Waxy binders

- Very diverse fraction composition (SAR-AD) – requires other technique
- High waxy fraction (WD)
- Low molecular associations & high molecular weight distribution (SEC)
- Elastic & complex rheological behavior (DSR)
- **Negative**  $\Delta$ **Tc** (relaxation/ brittleness issue) when high waxy fraction and low aromatics
- Prone to physical hardening

## WRI-AIRC/09-60 data



#### **Airblown binders**



#### **Conversion (Visbroken) residues**



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#### **PMA** binders


WRI – AIRC Highlight

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#### How to estimate PG in less than 90 min

#### PG estimated from SAR-AD & ExpliFit software



**WRI – AIRC Highlight** 



### "New" Rheological Parameter

#### **U** Viscoelastic Temperature Range $(T_{IR} = T_{G'=G''} - T_g)$



WRI – AIRC Highlight

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#### "New" Rheological Parameter



#### WesternResearch

#### WRI – AIRC Highlight "New" Rheological Parameter

**Viscoelastic Temp. Range (T\_{IR} = T\_{G'=G''} - T\_g) and \Delta Tc** 





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WesternResearch The WRI Fingerprinting Approach			
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	> WRI-AIRC #2	2018-	
	> Others	ł	43



### NCHRP 09-60 Project & Objectives

Addressing Impacts of Changes in Asphalt Binder Formulation and Manufacture on Pavement Performance through Changes in Asphalt Binder Specifications

1. Understand the Market Trends and their Consequences

2. Improve the Understanding of Various Damage Mechanisms and Factors Affecting their Severity

> 3. Propose Revised Specifications to Address Current Challenges (premature cracking and raveling)



4. Develop Formulation Guidelines for Suppliers to Meet Proposed Specifications & Expected Performance



### Approach: Tying Chemical and Rheological and Field Analysis



#### 1. Understand the Market Trends and their Consequences

#### Classical Binders – straight runs, modified and compatible blends

### Unconventional (sometimes problematic) Binders

- > Some high  $\Delta T_c$  "out of balance" / incompatible blends
- ✓ Waxy binders
- Airblown, oxidized blends
- Hard SDA / Soft blends
- ✓ Conversion residue (IMO 2020)
- Modified binders
  - Polymers: SBS, SBR, Terpolymer, EVA
  - Additives REOB, PPA, Wax, Biomass
  - Bio-binder
- ✓ High RAP / RAS
- Incompatible crudes (Fracking / Heavy)?



#### 1. Understand the Market Trends and their Consequences

#### Binder with Corresponding Field Sections

- Highway 655, Ontario, Canada MTO (7 sections)
- Rochester, MN (4 sections)
- US 93, AZ (4 sections)
- I 295 SB, Portland, ME
- Route 1, Presque Isle, ME
- Foute 11, Wallagrass, ME
- Foute 12, Westmorland, NH
- > SH 195, Florence, TX



### MTO ON-Hwy 655 2003 Sections

Almost same ranking between Transverse Cracking, Total Cracking, and (Total – Transverse) Cracking



Ranking	Section ID	Trans.	Section ID	Total	Tota-Trans.
1	1	0.3	1	34.9	34.6
2	5	4.3	5	103.4	99.1
3	2	38.2	2	130.9	92.7
4	6	42.5	6	209.3	166.8
5	3	51.4	3	295.1	243.7
6	7	60.2	7	427.6	367.4
7	4	139.7	4	587.2	447.5

- O9-60 Project compares field sections differentiated by binder type, with consistent climate, traffic, mix properties, pavement structure, subgrade materials, construction quality ...
- ➢ Problematic binders (incompatible binders with very low ∆Tc) would perform badly for all kinds of cracking.
- Internal restraint damage will compromise the integrity of the mixture and lead to mixture generally prone to all sorts of cracking.



#### MTO ON-Hwy 655 Sections #1&4





### MTO ON-Hwy 655 Sections #1&4





#### MTO ON-Hwy 655 Sections #1&4



# WesternResearch MTO ON-Hwy 655 Sections #10-15



2. Improve the Understanding of Various Damage Mechanisms and Factors Affecting their Severity

#### Internal Restraint Mechanism Hypothesis

#### External Mix Restraint

#### in red or gray directions

Spheres Packed to Maximum Density

Thermal Cooling With Restraint: Cooling creates tensile stress in direction of restraint:

First yield at aggregate contact points in dimension of restraint

Other Factors

- Long-Term Aging Potential
- Physical Hardening
- Healing Potential

 Confirmed by FEA & Sliver test
 White Paper, Interim report + AAPT 2019 paper

Internal Mastic Restraint

within the aggregate structure

"Internal Restraint": A hypothesis

for mixture damage when cooling

Assumption: Binder/Mastic shrinks

faster than aggregate skeleton

Spheres Packed to Maximum Density

without restraint.

Damage Zone:

within damage zone

**Binder in tension: First Yield** 

Adhesive or Cohesive Failure

# WesternResearch 09-60 Binder Database Mapping

### BBR-Low PG Ranking of 31 Binders after PAV<u>20H</u>-Aging

Unmodified, Polymer-modified, ReOB-modified, SDA,





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### **BBR-**ΔT<sub>c</sub> Ranking of 31 Binders after PAV<u>20H</u>-Aging

Unmodified, Polymer-modified, ReOB-modified, SDA,

PPA-modified, Biophalt, Oxidized, Airblown, Visbroken.



### **BBR-**ΔT<sub>c</sub> Ranking of 31 Binders after PAV<u>40H</u>-Aging

Unmodified, Polymer-modified, ReOB-modified, SDA,

PPA-modified, Biophalt, Oxidized, Airblown, Visbroken.



### **BBR-**ΔT<sub>c</sub> Ranking of 31 Binders after PAV<u>40H</u>+PH<u>72H</u>

Unmodified, Polymer-modified, ReOB-modified, SDA,

PPA-modified, Biophalt, Oxidized, Airblown, Visbroken.



PH72H: 72 hr conditioning at PG+10C

### **ΔTc Correlations after PAV<u>20H</u> and PAV<u>40H</u>-Aging**

- Unmodified, Polymer-modified, ReOB-modified, SDA,
- PPA-modified, Biophalt, Oxidized, Airblown, Visbroken



#### **ΔTc Correlations after PAV<u>20H</u> and PAV<u>40H</u>+PH<u>72H</u>.**

Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Visbroken



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### 09-60 – Effect of PAV aging on Chemistry

#### **C=O+S=O** Correlations after PAV<u>20H</u> and PAV<u>40H</u>-Aging.

Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Visbroken





### **G-R and ΔTc Correlations after PAV**20H-Aging

Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Visbroken



### **□** G-R and **∆**Tc Correlations after PAV<u>40H</u>-Aging

Unmodified, Polymer-modified, ReOB-modified, SDA, PPA-modified, Biophalt, Oxidized, Airblown, Visbroken

![](_page_60_Figure_4.jpeg)

![](_page_61_Picture_0.jpeg)

PMA's microstructure: homogeneous or heterogeneous at micron level – captured by Fluorescence Microscopy

□ Homogenous PMA's often display low △Tc – why?

![](_page_61_Figure_4.jpeg)

- **U** Multi-phase structure: polymer rich phase and asphaltene rich phase with different  $\Delta$ Tc's (under investigation)
- Influence of the base binder, the polymer (type, MW and content) and their interactions (compatibility, swelling, reactions...)
- IR microscopy for a more quantitative understanding

![](_page_62_Picture_0.jpeg)

### **PMA's - Microstructure and** *A***Tc**

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![](_page_62_Figure_2.jpeg)

- ☆ ∆Tc for 18 PMA's (SBS's incl. crosslinked) at 3 aging levels (O, RTFO, PAV20)
- Data mined from Durrieu et al, Lapalu et al, Mouillet et al, Planche et al, 2004-2008

![](_page_63_Picture_0.jpeg)

# PMA's - Microstructure .... and base asphalt and ∆Tc

![](_page_63_Figure_2.jpeg)

- 2 base asphalts: Bc blue = classical (commercial) Bo red = oxidizable (lab)
- ☆ ∆Tc for 18 PMA's (SBS's incl. crosslinked) at 3 aging levels (O, RTFO, PAV20)
- Data mined from Durrieu et al, Lapalu et al, Mouillet et al, Planche et al, 2004-2008

![](_page_64_Picture_0.jpeg)

### **Black Space Analysis of BBR Data**

![](_page_64_Figure_2.jpeg)

![](_page_65_Picture_0.jpeg)

### **Black Space Analysis of BBR Data**

![](_page_65_Figure_2.jpeg)

![](_page_66_Picture_0.jpeg)

#### In Progress !

### **Binder guidelines**

# Unconventional PG Binders

- Many possibilities
  - Blends of fracking / heavy crudes
  - Airblown, oxidized blends
  - High RAP / RAS
  - Hard SDA / soft base blends
  - Visbroken residues (IMO 2020)
  - Waxy binders / REOB blends
  - Modified binders
    - Polymers: EVA, SBS, Terpolymers
    - Additives: PPA, wax, biomass...

#### □ Sensitive to aging/cracking

- "Out of balance" composition inhomogeneous blends
- Rheologically complex
- □ But: All can be made <u>suitable</u> too!

#### **Complex structure & rheology**

![](_page_66_Figure_19.jpeg)

# Summary 9-60

- Wide variety of asphalt origins = wide variety of properties
- Rheological parameters appear to rank the bulk of binders against cracking... but not enough (relevant?) for all cases
  - In depth analysis of their meaning is needed and ongoing
  - LVE rheology parameters do not generally capture failure for PMA's with complex morphology. Need for failure strain test?
  - >G-R parameter: an improvement over G\*.sin  $\delta$ , <u>but</u> with limitations including binder stiffness (G\*) and temp. (climate) dependencies
  - >∆Tc: most promising to differentiate binders according to their composition and thermal or aging conditioning.
    - Influenced by asphalt structure balance asphaltene / maltene
    - Relevance to field cracking propensity is under review for PMA's
- Care with hasty conclusions to avoid "Fort-T syndrome"
  - Clear behavioral trends and correlations for unmodified binders, not true in general for modified binders or complex blends
  - Understanding the trends and outliers need holistic approach

### **Perspectives 9-60**

#### Relations Field cracking – Specification parameters

- Thorough analysis of field cracking data is ongoing to differentiate binder / mix related cracking from construction issues or poor subgrade (field data reports / google maps data as a function of time, climate temperature records...)
- Review of the relationships of block/thermal/fatigue cracking extent with rheological parameters and possibly failure parameters
- Impact of binder composition using a holistic approach
  - >Understand outliers
  - >Establish qualitative composition guidelines (under 09-60)
- > 9-60 RECOMMENDATIONS FOR NEW SPECS: END OF 2019
  - Final report draft: September 2019
  - Discussions with Panel
- Presentations to stakeholders in 2020

>Webinars, TRB 2020 lectern session (?)

![](_page_69_Picture_0.jpeg)

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# Summary / Perspectives

![](_page_69_Picture_10.jpeg)

- Asphalt supply chain has changed since SHRP
   Crudes, refining processes, blends, additives, recycling
- Superpave is not enough to assess the changes
- Rheological assessment beyond (current) Superpave can give important insights
  - >Black space, ∆Tc, MSCR, G-R, R-value...
  - T<sub>IR</sub> (Intermediate Region Temperature Range)
    - Temperature difference: Crossover (Tx) Glass transition (Tg), both temperatures determined by DSR
    - Tg correlated to Tc(S) and Tx to Tc(m)
    - Based on fundamental material properties, represents S- and mcontrolled binders, relates to \DeltaTc, cracking, and healing propensities

Most production/formulation changes have their own chemical signature and rheological features

# **Summary - Perspectives**

#### Fingerprinting is feasible & helps cope with changes

Large and relevant binder database = key

Association of analytical techniques to assess differences

Useful for suppliers, users, owners for formulation and control

#### ➢ New relevant tools - SAR-AD<sup>™</sup> 2G coming into play

Holistic analysis combining various conditions, detectors
 Qualitative and quantitative data - allow correlations + predictions
 Can be specifically designed for given formulation / application

Machine learning to tie Chemistry to Structure to Thermal to Rheology and ultimately to Performance


## **Acknowledgements**

- FHWA / NCHRP
  - FP of Asphalts and Products Validation
  - Asphalt Research Consortium
  - 9-60 Panel and Team
- WRI Industry Partners
  - WRI-Asphalt Industry Research Consortium
  - Paving and Roofing stakeholders
- WRI-APT team
- Note:
  - AIRC outcomes presented in/at
    - TRB / AMAP / PARC 2018
    - TRB and AMAP 2019
    - ACS Energy & Fuel Journal 2019
  - NCHRP 9-60 outcomes presented at
    - AAPT 2019
- Stay tuned!





Please join us to PARC 2019!

56th Petersen Asphalt Research Conference

July 14-17, 2019 Laramie, Wyoming

Thank You!



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