National Center for Asphalt Technology NCAT at AUBURN UNIVERSITY

Development of Aging Resistant Binder Technologies

FHWA Project 19-0011

SEAUPG Southeastern Asphalt User/Producer Group

November 20th, 2024

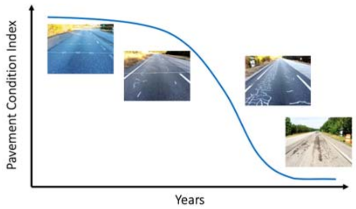
Background
Research Project

Can asphalt binders be improved by adding certain additives?

- FHWA 2018 Exploratory Advanced Research (EAR) Program funded a research project to identify aging-resistant technologies.
- NCAT and GHK partnered with five industry collaborators—*Blacklidge Emulsions, Chemco Systems, Iowa State University, Kraton Corporation, and Lehigh Technologies*—to evaluate five candidate aging-resistant additives, each with a Technology Readiness Level (TRL) of 2 or 3.

Background
Asphalt Aging

- Environmental exposure leads to the degradation and hardening of asphalt binders, which eventually causes cracking and raveling of the pavement surface.
- Most asphalt pavements in the United States deteriorate due to cracking.



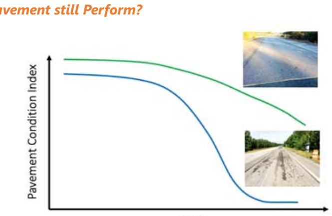
What Component of the Mix Changes?

Technologies Evaluated

- *Additive 1*: A two-component chemical system of low-modulus epoxy polymer and a blend of asphalt and oil-based flexible modifiers.
- *Additive 2*: A hybrid system of ground tire rubber powder and a functional elastomer, a stabilizer, and a dispersant additive.
- *Additive 3*: A hybrid system of a continuous-phase styrene block copolymer with a pine-based performance chemical additive.
- *Additive 4*: An additive made from sub-epoxidized soybean oil.
- *Additive 5*: A blend of biosynthetic oils, petroleum-based oils, and rheology modifiers.

Background
Asphalt Aging

Can an Aged Pavement still Perform?



- Both sections were constructed in the same year with similar thicknesses and mixed designs, but different binders were used, leading to different performances.

Project Objectives

- Understand how asphalt changes and how additives work with respect to aging.
- Determine the effects of additives on the rheological and chemical characteristics of binders.
- Demonstrate effects of additives on mixture cracking resistance.
- Determine pavement life extension benefits.

Study divided in three phases

- **Phase 1**: Selection of two base binders by rheological and chemical evaluation before and after oxidation.
- **Phase 2**: Rheological and chemical evaluation of the base binders and their blends with each additive and RAP binder before and after exposure to oxidation and UV radiation.
- **Phase 3**: Asphalt mixture cracking evaluation and simulation of the potential life-extending benefits of these additives using FlexPAVE™.

Base Binder Selection
Phase 1

Six Base Asphalt Binders

Binder 1	Binder 2	Binder 3	Binder 4	Binder 5	Binder 6
PG 64-16	*PG 58-22*	*PG 67-22*	*PG 64-22*	*PG 64-28*	*PG 64-22*
South Central	West Coast	Southeast	West Coast	Western Canada	Western Canada

RTFO/PAV20 and RTFO/PAV60

Performance Grade and ΔT_c

SARA Fractions

Elemental Analysis
(Inductively Coupled Plasma Optical Emission Spectrometry ICP OES)

Selection of two base binders

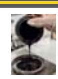
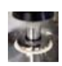
The six base binders were sent to each research partner for internal evaluation with the partner's proposed aging-resistant technology.

Asphalt Binder Experiment
Phase 2

Chemical Testing

Property	Test	Aging Level	Research Parameters
Molecular Size Distribution	Gel Permeation Chromatography (Kraton)	Unaged RTFO+60hPAV	Molecular Weight
Thermal Behavior	Differential Scanning Calorimetry (WRI)	RTFO+60hPAV	Glass Transition (T_g) Temperature
Oxidative Aging Products	FTIR-ATR (NCAT)	Unaged RTFO+60hPAV UV Radiation	Carbonyl and Sulfoxide Groups
Fatty Acids	GC/MS (WRI)	Unaged RTFO+60hPAV	Fatty Acids
Chemical Composition	SARA Fractionation (Kraton)	Unaged RTFO+60hPAV	Colloidal Index, SARA Fractions

Asphalt Binder Experiment
Phase 2

- 2 base binders
- 1 extracted RAP binder
- 5 aging resistant additives

20% RAP blends

2 dosages each

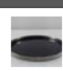
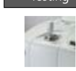
Blends:
- Control
- Aging resistant

Multiple aging conditions

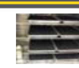
Rheological Testing

Chemical Testing

Effect on binder

Asphalt Mixture Experiment
Phase 3




- 1 aggregate
- 1 RAP
- 2 base binders
- 5 additives

1 dosage each

20% RAP mixes:
- Control mixes
- Aging resistant mixes

LTOA 5 days, 95°C

STOA 4 hours, 135°C

NCAT Accelerated Pavement Weathering (NAWS)

AMPT |E*|, Cyclic Fatigue

Effect on mix aging

12 Binders extracted & tested

Effect on binder

Asphalt Binder Experiment
Phase 2

Rheological Testing

Temperature Range	Test	Standard	Research Parameters	Aging Level
High-Temperature	DSR	AASHTO M 320	|G*|/sin(δ) |G*|.sin(δ)	Unaged, RTFO, RTFO+20hPAV RTFO+60hPAV
	DSR	AASHTO M 332	$J_{nr3.2}$ and $\%R_{3.2}$	RTFO
Intermediate-Temperature	DSR LAS	AASHTO T 391	Cycles to failure (N_f), strain at peak stress	RTFO+60hPAV
	DSR Master curve	AASHTO T 315	G-R, |G*|, δ Black space diagram	Unaged RTFO+60hPAV UV Radiation
Low-Temperature	BBR	AASHTO T 313	Stiffness, m-value & ΔT_c	RTFO+20hPAV RTFO+60hPAV UV Radiation
	BBR	AASHTO TP 122 (Adapted)	Physical hardening behavior, stiffness, m-value & ΔT_c	RTFO+60hPAV

Pavement Analysis
Phase 3

Rheological Properties
Dynamic modulus
(|*E**|)

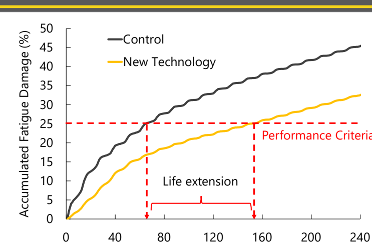
Damage Characteristics
AMPT cyclic fatigue

FlexMAT™

Same thickness, traffic, climate inputs

FlexPAVE™ version 1.1

Life extension benefits



Performance Grade
Base Binders

Asphalt Sample	PAV Cycle	Unaged, RTFO and RTFO + PAV (°C)							
		T_{cont} High Original	T_{cont} High RTFO	T_{cont} Intermediate	T_{cont} Low S	T_{cont} Low m-value	ΔT_c	PG HT	PG LT
Binder 1	20-hour	65.7	66.6	25.0	-26.1	-19.9	-6.2	64	-16
	60-hour	100.7		30.2	-24.4	-9.7	-14.7	100	-4
Binder 5	20-hour	65.6	67.4	20.8	-28.4	-28.8	0.4	64	-28
	60-hour	103.4		25.2	-26.5	-22.7	-3.8	100	-22

- *RTFO/PAV20 ΔT_c*: Canadian binder (Binder 5) showed much better relaxation properties than the West Texas source (Binder 1).
  - Binder 5 is S-controlled , and Binder 1 is highly m-controlled.
- *RTFO/PAV60 PGL grade loss*: +10.2°C for Binder 1 and +5.7°C for Binder 5.
  - Binder 5 changed from S-control to m-control.
- Rheological modifiers impacting molecular relaxation that are beneficial to Binder 1 will likely have little influence on Binder 5.

Effects at Low-Temperature
Binder 5 + RAP + Additive after RTFO/PAV60

- Additive blends were ranked from best to worst according to the difference in ΔT_c/PGL versus the control/RAP blend. Relative improvements in °C are included in parentheses.

Improvement in ΔT_c

Additive 4 AD (+3.8) > Additive 5 OD (+2.7) > Additive 3 AD (+1.6) > Additive 2 OD (-1.3).

Improvement in PGL

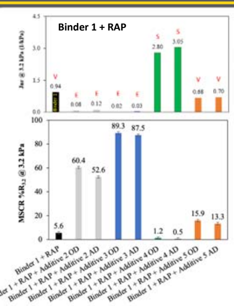
Additive 4 AD (-7.8) > Additive 5 OD (-5.9) > Additive 2 OD (-1.2) > Additive 3 AD (+0.3).

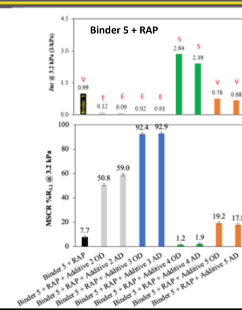
- ❑ Additive 4 recovers the ΔT_c loss of 2°C caused by adding RAP and reduces PGL by almost 8°C.
- ❑ Results for Additive 5 are also encouraging.
- ❑ Slightly positive results for Additive 3 were probably not statistically significant, and Additive 2 is relatively ineffective.

Useful Temperature Interval (UTI)
RTFO/PAV60, without RAP

Binder ID	PG	UTI (°C)	Binder ID	PG	UTI (°C)
Binder 1	100-4	104	Binder 5	100-22	122
Binder 1 + Additive 1 OD	94-22	116 ↑	Binder 5 + Additive 1 OD	118-22	140 ↑
Binder 1 + Additive 2 OD	112-10	110 ↑	Binder 5 + Additive 2 OD	118-16	134 ↑
Binder 1 + Additive 3 OD	136-22	134 ↑	Binder 5 + Additive 3 OD	124-22	102 ↓
Binder 1 + Additive 4 OD	88-22	110 ↑	Binder 5 + Additive 4 OD	94-28	122 =
Binder 1 + Additive 5 OD	94-16	110 ↑	Binder 5 + Additive 5 OD	100-28	128 ↑

Multiple Stress Creep and Recovery @ 64°C
After RTFO





Effects at Low-Temperature
Binder 1 + RAP + Additive after RTFO/PAV60

- Additive blends were ranked from best to worst according to the difference in ΔT_c/PGL versus the control/RAP blend. Relative improvements in °C are included in parentheses.

Improvement in ΔT_c

Additive 4 OD (+8.9) > Additive 3 AD (+2.8) > Additive 5 OD (+2.6) > Additive 2 AD (0.0).

Improvement in PGL

Additive 3 AD (-16.5) > Additive 4 OD (-13.5) > Additive 5 OD (-4.5) > Additive 2 AD (-4.2).

- ❑ Additive 4 effectively restores relaxation and adds over two PG grades to the RTFO/PAV60 PGL.
- ❑ Additive 3 lowers the PGL but is less effective in restoring ΔT_c.
- ❑ Additive 5 shows modest improvement in both values and Additive 2 is relatively ineffective.

Linear Amplitude Sweep Test
RTFO/PAV60

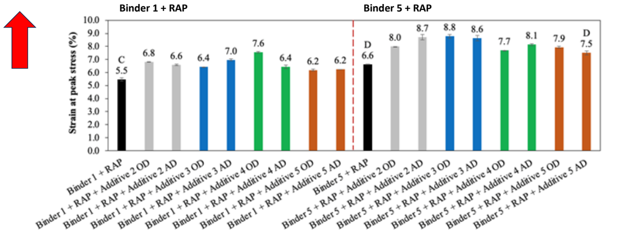
- AASHTO T 391 adapted.

Modifications

- Damage was calculated based on changes in pseudo stiffness (|G*|/|G*|initial), whereas in the past, it was calculated based on changes in |G*|sindelta.
  - ❑ The reason is that the effect of damage on |G*| is very clear, but damage does not necessarily cause a change in phase angle.
- The failure definition was a drop from the peak stress by 10%, whereas in the past, a 35% reduction in |G*|sindelta was used.
  - ❑ This better reflects ultimate failure and distinguishes unmodified vs. polymer-modified binder performance.
- Binders presented similar $|G^*|_{LVE,\ 10\ Hz}$ values within the 12 to 60 MPa range at a testing temperature of 20°C.

Linear Amplitude Sweep Test
Strain at peak stress

- Aging often causes strain intolerance and the inability to relax stresses induced by traffic. Thus, it is believed that a higher strain at a maximum stress level is beneficial.



Glover-Rowe (G-R) Effectiveness Index
***G-R** 15°C, 0.005 rad/s*

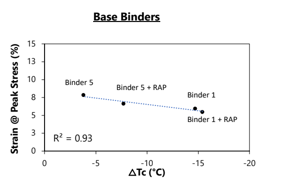
- Polymers typically shift failure moduli to higher values of |G*| (i.e., the *G-R* failure envelope moves higher on the Black Space Diagram).
- Because the $G\text{-}R_{effectiveness\ index}$ has no reference to the *G-R* parameter failure envelope and is strictly driven by rheological changes in Black Space for a single binder, it should apply to all binders, whether modified or not.

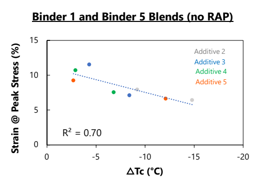
$$G-R_{Effectiveness\ Index} = \frac{(G-R_{After\ aging})_{Binder+RAP+Additive}}{(G-R_{After\ aging})_{Control\ Binder+RAP}}$$

- A lower index value is desired for additives that are more effective in restoring the *G-R* parameter of the control binders after aging.

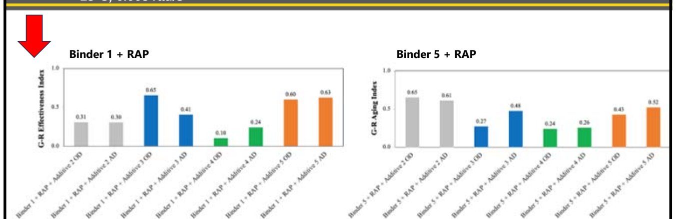
LAS Strain @ Peak Stress *vs.* $\triangle T_c$
RTFO/PAV60

- Higher strain tolerance resulting in less negative $\triangle T_c$ (better) values.



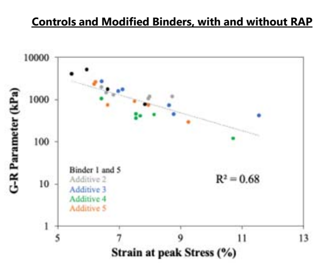


Glover-Rowe (G-R) Effectiveness Index
G-R** 15°C, 0.005 rad/s **after RTFO/PAV60



- Additives were more effective in limiting the change in binder modulus and restoring binder phase angle after RTFO/PAV60 than neat binders could do independently.

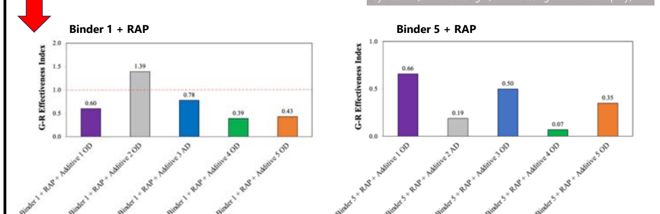
LAS Strain @ Peak Stress *vs.* ***G-R** 15°C, 0.005 rad/s*
RTFO/PAV60



- Higher strain tolerance resulting in lower *G-R* parameter values.
  - Potential indication that strain intolerance is correlated with stiffness and embrittlement of binders

Glover-Rowe (G-R) Effectiveness Index
G-R** 15°C, 0.005 rad/s **after NAWS

Irradiance Level: 0.55W/m² (at 340nm)
Chamber Temperature: 60°C
Water Temperature: 45 +/- 5°F (7.2 +/- 3C)
Cycles: 1h (51 minutes light; 9 minutes light and water spray)



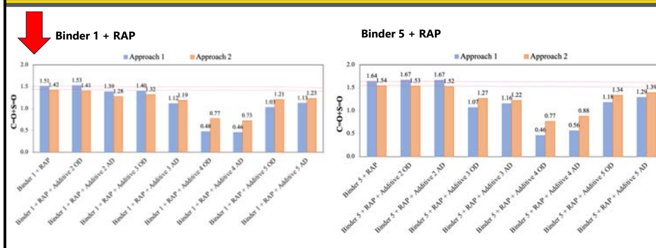
- Even soft asphalts with good relaxation properties (Binder 5) may benefit from rheology modifiers when formulating more age-resistant recycled mixes.

Classification of Additives Using Various Binder Cracking Parameters

- Best performance is judged to be the smallest $G\text{-}R_{\text{effectiveness index}}$, the highest positive value of ΔT_c, and the highest strain tolerance from the LAS test.

Binder 1 + RAP			Binder 5 + RAP		
G-R Effectiveness Index	ΔT_c	LAS Strain at Peak Stress	G-R Effectiveness Index	ΔT_c	LAS Strain at Peak Stress
Additive 4 OD	Additive 4 OD	Additive 4 OD	Additive 4 OD	Additive 4 OD	Additive 3 OD
Additive 4 AD	Additive 4 AD	Additive 3 AD	Additive 4 AD	Additive 5 OD	Additive 2 AD
Additive 2 AD	Additive 3 AD	Additive 2 OD	Additive 3 OD	Additive 4 AD	Additive 3 AD
Additive 2 OD	Additive 5 OD	Additive 2 AD	Additive 5 OD	Additive 3 AD	Additive 4 AD
Additive 3 AD	Additive 5 AD	Additive 4 AD	Additive 3 AD	Additive 5 AD	Additive 2 OD
Additive 5 OD	Additive 2 AD	Additive 3 OD	Additive 5 AD	Additive 3 OD	Additive 5 OD
Additive 5 AD	Additive 3 OD	Additive 5 AD	Additive 2 AD	Additive 2 OD	Additive 4 OD
Additive 3 OD	Additive 2 OD	Additive 5 OD	Additive 2 OD	Additive 2 AD	Additive 5 AD

FTIR-ATR
C=O+S=O areas after RTFO/PAV60

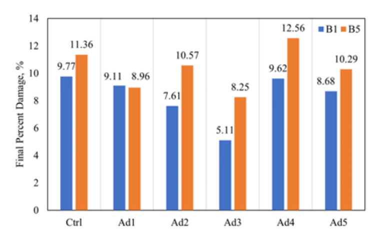


- Additive 4, a bio-based rejuvenator, somehow blocks or redirects a significant amount of available oxygen during aging. $G\text{-}R_{\text{effectiveness index}}$ was consistent with this finding.

Classification of Additives Using Various Binder Cracking Parameters

- Additive 2 and Additive 3 contain a high dosage of polymeric modifiers, as identified by MSCR $\%R_{3.2}$, yet displayed less favorable rankings for both *G-R* and ΔT_c parameters.
  - Polymer systems increase binder stiffness and lower phase angle, leading to more negative ΔT_c.
  - Rankings were mid-range for ΔT_c and *G-R* but high for LAS strain-at-peak-stress.
    - *These results suggest that these additives deserve a boost in crack performance rating over those for rheology-based relaxation properties alone.*
  - Without adjustment, Additive 2 and Additive 3 may be penalized in performance rankings.
- The oil-based modifiers (Additive 4 and Additive 5) reduced the stiffness and increased the binders' phase angle, a behavior captured by both *G-R* and ΔT_c parameters.

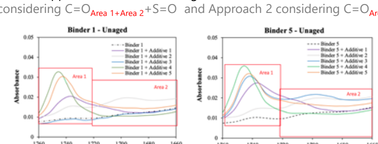
Pavement Analysis using FlexPAVE
Mixture Percent Damage



- To assess the fatigue damage that occurred in the surface layer of the pavement following a 20-year service life.
- All the additives yielded a lower percent damage than the control.
  - Except for the Additive 4 with base Binder 5 mixture.

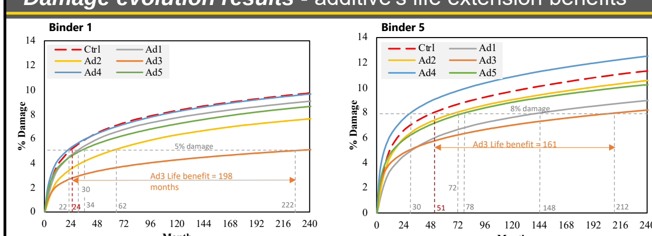
FTIR-ATR
C=O+S=O areas

- Asphalt binders with higher C=O+S=O areas are typically thought to have experienced greater oxidative aging than those with lower C=O+S=O areas.
- This study evaluated two approaches for determining C=O+S=O areas:
  - Approach 1 considering $C{=}O_{\text{Area 1+Area 2}}$+S=O and Approach 2 considering $C{=}O_{\text{Area 2}}$+S=O



- Approach 2 subtracts out the carbonyl oxygen attributable to the fatty acids (i.e., secondary peak within the region of the C=O functions) in the bio-oils but keeps the ketone carbonyls responsible for the loss of relaxation properties during asphalt aging.

Pavement Analysis using FlexPAVE
Damage evolution results - additive's life extension benefits



- A 5% threshold was used based on the fatigue damage observed in the mixture with Additive 3 after 20 years of service.
- An 8% threshold was used based on the fatigue damage observed in the mixture with Additive 3 after 20 years of service.

Pavement Analysis using FlexPAVE

Damage evolution results - additive's life extension benefits

Mix ID	Months to reach 5% damage	Life extension compared to Control, months
Control Binder 1	24	0
Binder 1 + Additive 1	30	6
Binder 1 + Additive 2	62	38
Binder 1 + Additive 3	222	198
Binder 1 + Additive 4	22	-2
Binder 1 + Additive 5	34	10

Mix ID	Months to reach 8% damage	Life extension compared to Control, months
Control Binder 5	51	0
Binder 5 + Additive 1	148	97
Binder 5 + Additive 2	72	21
Binder 5 + Additive 3	212	161
Binder 5 + Additive 4	30	-21
Binder 5 + Additive 5	78	27

Conclusions

- The effectiveness of the aging-resistant additives varied based on the base binder and the presence of RAP.
- All five additives helped reduce the negative effects of aging in both neat and their blends with RAP.
  - However, they proved more effective in Binder 1 (m-controlled, more negative ΔT_c), where improvements in the phase angle directly translated to better low-temperature performance.
- Although no direct evidence indicates that these additives slow oxidation kinetics, they may offer significant benefits in stabilizing low-quality virgin binders or brittle RAP binder blends.
- While the additives were selected for their aging-resistant potential to disrupt and decelerate oxidation, which leads to the formation of ketones (carbonyl groups), the complex nature of asphalt oxidation has long resisted a purely chemical solution.
  - Instead, the most practical strategy involves using age-stable rheological modifiers that restore molecular mobility and enhance relaxation properties where needed most.

Thank You

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