Rejuvenator Use in Plant Mix Asphalt Production

Rejuvenation vs. Softening

Dallas C Little, PE

2021 Asphalt Conference & Expo

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Cargill® Helping the world thrive

Cargill's Role in Asphalt

To be the industry leader in high-performance and sustainable asphalt additives.

- Rejuvenation
- Warm Mix
- Cold Mix
- Emulsions
- Rheology
- Stabilizers

State-of-the-art Asphalt Lab

- Customer custom formulation services
- Compositional and analytical evaluation
- Advanced rheology and thermal analysis

155,000 employees

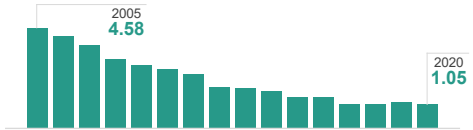
155 years of experience

Working in **70** countries

$114,6 billion in annual revenue

Our commitments

Safe
We relentlessly work to improve the safety of our people. Reduction in injuries per 200,000 hours worked over 15 years.



Responsible
We strive to strengthen the communities where we live and work.

$115 million
Total charitable contributions last year across 56 countries

Attendance at our farmer trainings for sustainable agricultural practices totaled 860,000 last year

Sustainable
- Agriculture is how we will protect the planet and our shared future.
- Climate change: Reducing supply chain emissions per ton of product 30% by 2030, and absolute operational emissions 10% by 2025
- Water resources: Achieving sustainable water management in all priority watersheds by 2030
- Land use: Eliminating deforestation in our supply chains by 2030

Agenda:

1. Background on use of Recycling Agents
2. Introduction to Rejuvenation and Softening
3. How to Differentiate between Rejuvenation and Softening

Part 1: Background on Recycling Agents

“Rejuvenation” is an inaccurate, but popular term for recycling agents.

- Recycling agents do not undo oxidative aging!!!
- A **Recycling Agent** is used to reverse the impact of aging on asphalt performance and durability.

- The use of Petroleum-based recycling agents dates to the 1970’s and 1980’s, e.g. lube oil processing by-product.

- Late 2000’s: A wide range of recycled oil and bio-based recycling agents were developed resulting from high asphalt prices.

– *NAPA QIP 131: Practical Guide for Using Recycling Agents in Asphalt Mixtures….*

Classification of RAs

- Early classifications of Recycling Agents focused on raw material type (e.g. aromatic oil vs. tall oil).
  - This was adequate when most additives were chemically unmodified.
  - However, with advent of engineered and chemically modified additives, raw material designations are less useful.
- There are several recently completed and on-going efforts to develop a classification system and specification to accurately describe the chemical, physical, and engineering properties of recycling agents, regardless of their composition.
- Currently only one ASTM standard addressing Recycling Agents exists:
  - ASTM D4552: Classification of Hot Mix Recycling Agents

Recycling Agent Categorization - ASTM D4552-20

Assesses basic safety, thermal stability, storage stability, and compatibility property for use in asphalt plants.

Most Bio-oils Most Petro. oils

Test	ASTM Test Method	RA 1		RA 5		RA 25		RA 75		RA 250		RA 500	
		Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Viscosity • 60 °C [140 °F], mm²/s	D2170	50	175	176	900	901	4500	4501	12500	12501	37500	37501	60000
Flash Point, COC, °C	D92	219	...	219	...	219	...	219	...	219	...	219	...
Tests on Residue from RTFO 163 °C [325 °F]	D2872												
Viscosity Ratio[5]	"	...	3	...	3	...	3	...	3	...	3	...	3
Wt Change, ±, %	"	...	4	...	4	...	3	...	3	...	3	...	3
Specific Gravity at 25 °C [77 °F]	D70 or D1298	0.900	1.100	0.900	1.100	0.900	1.100	0.900	1.100	0.900	1.100	0.900	1.100

$$ViscosityRatio = \frac{Viscosity\ of\ Residue\ from\ RTFO\ Test\ at\ 60°C\ [140°F]}{Original\ Viscosity\ at\ 60°C\ [140°F]}$$

Defining Rejuvenation vs. Softening

The following definitions were provided by the **NAPA RA Usage Guide (2020)**:

- **Softeners** are low-viscosity oils that reduce the stiffness of a blend of virgin and recycled binders.
- **Rejuvenators** reduce the stiffness of binder blends, and can help to partially restore chemical balance, reduce brittleness, and/or improve aging sensitivity.

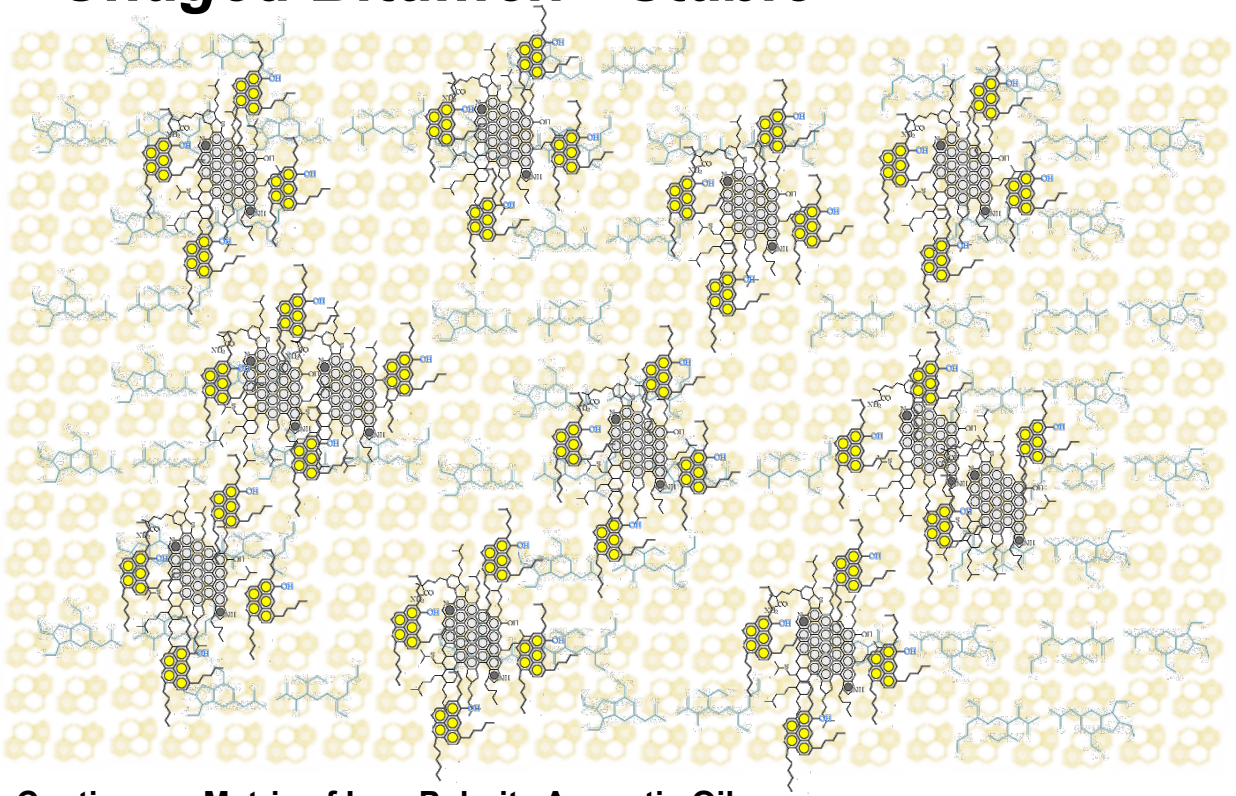
- The definitions of “Rejuvenation” and “Softening” are rooted in the mechanisms of impact upon asphalt.
- To understand these definitions, we need a working mechanism theory.

Defining Rejuvenation vs. Softening

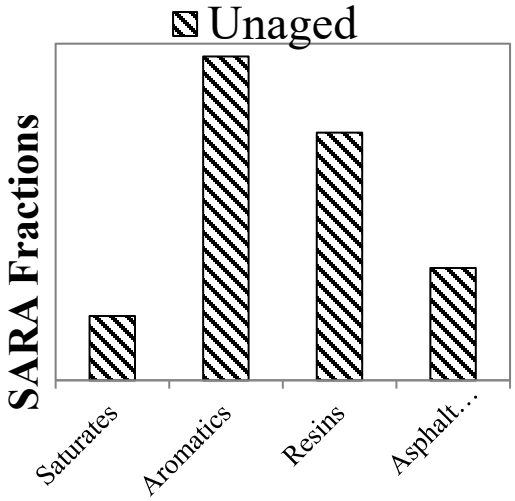
– Link to video: https://youtu.be/uwfYjy4PHDU

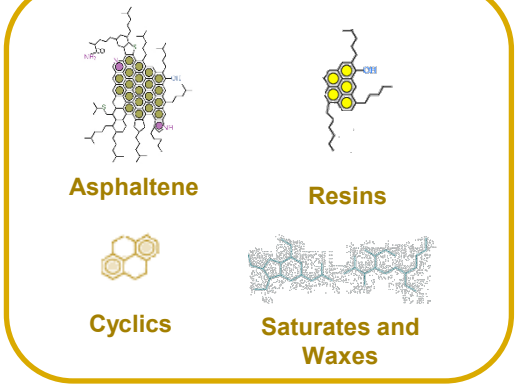
Simplified Bitumen Colloidal Model

Unaged Bitumen - Stable



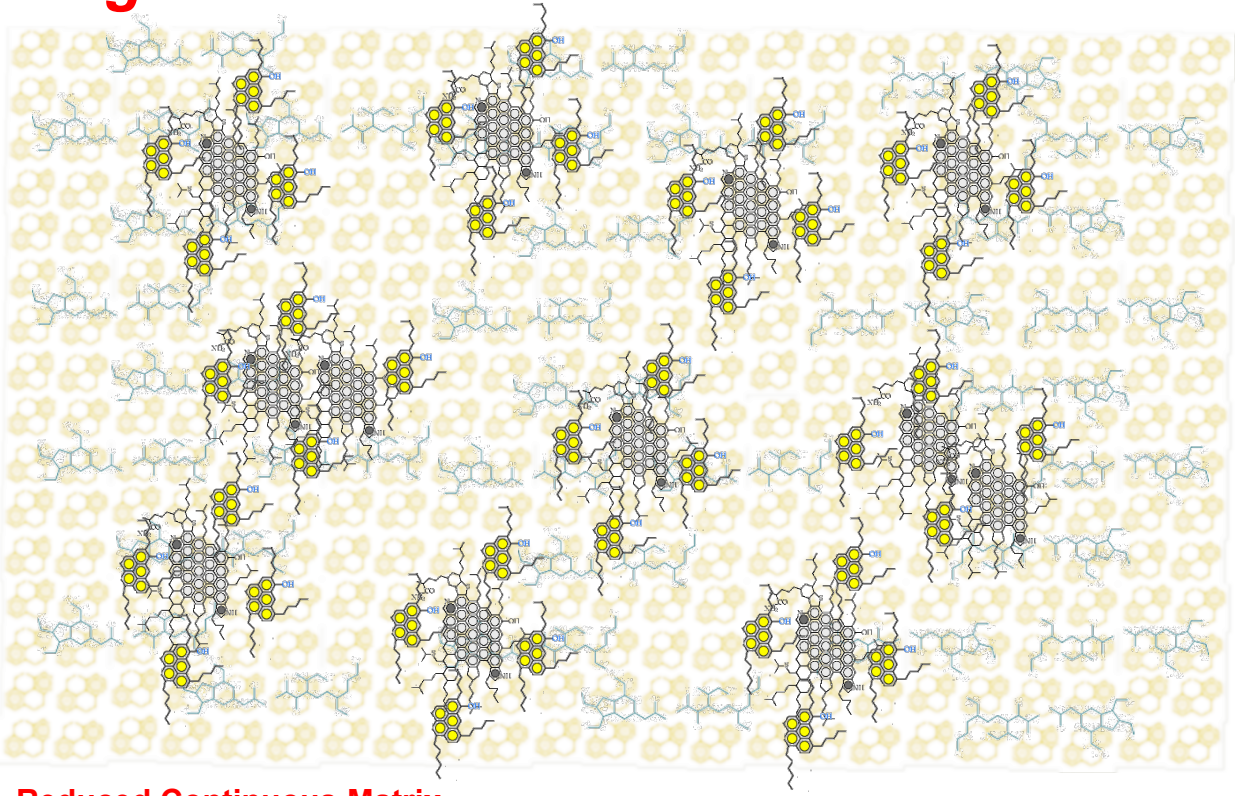
Continuous Matrix of Low Polarity Aromatic Oil



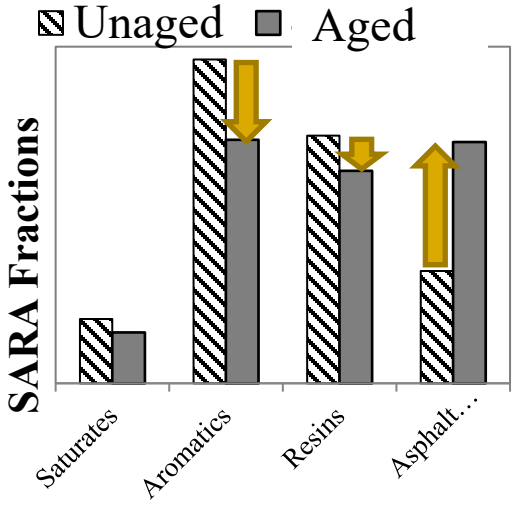


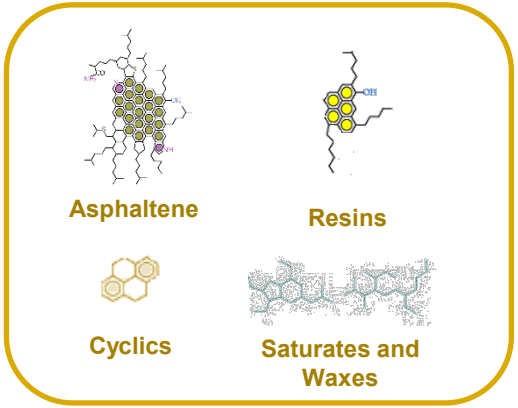
Simplified Bitumen Colloidal Model

Aged – Loss of softer fractions



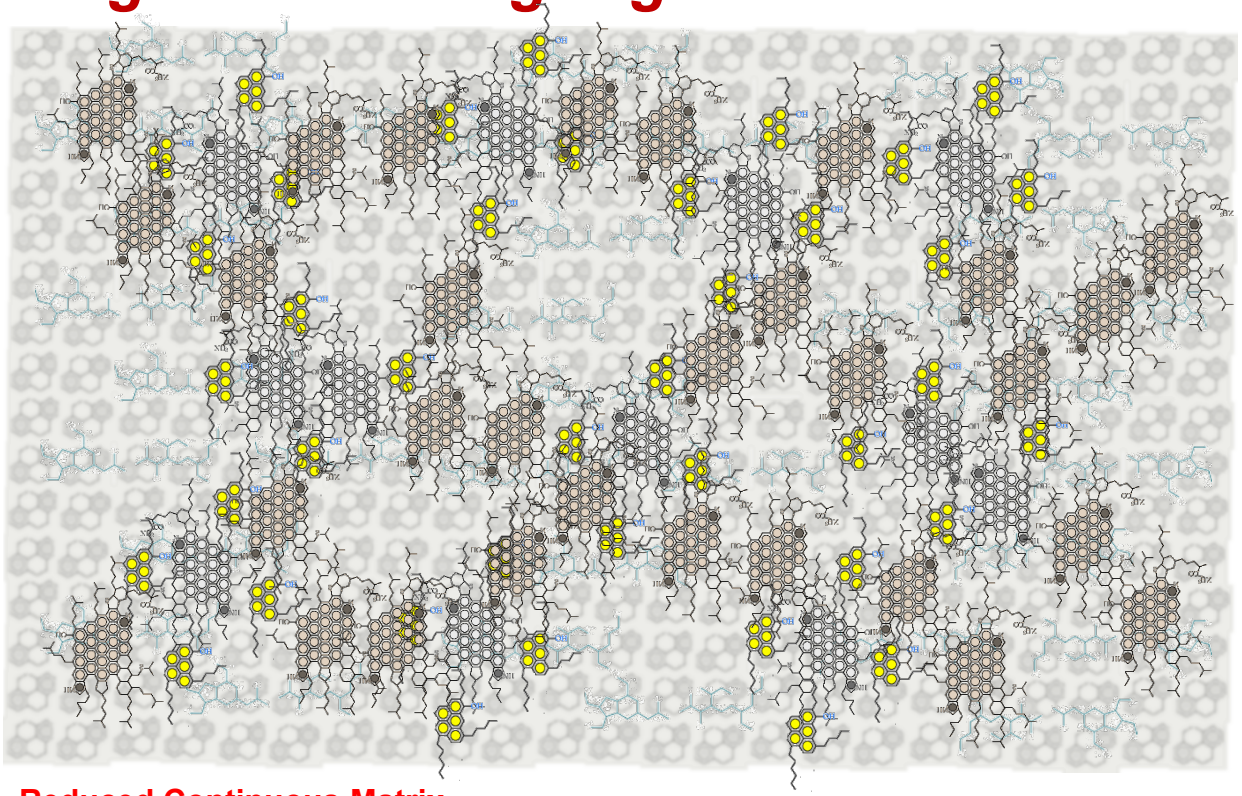
Reduced Continuous Matrix



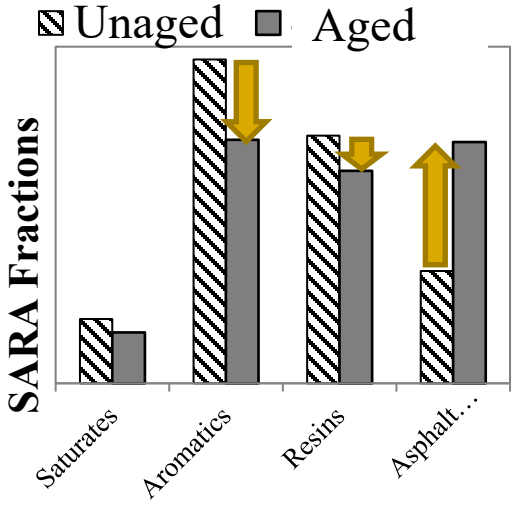


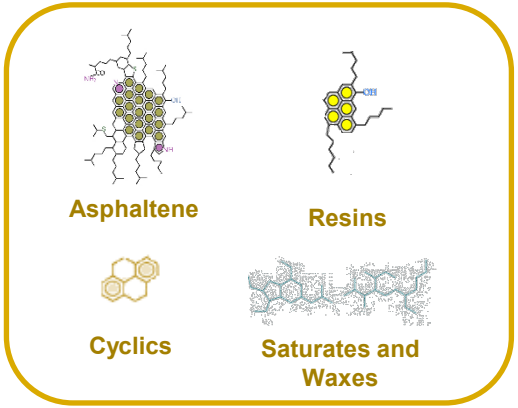
Simplified Bitumen Colloidal Model

Aged – Forming Rigid Structures



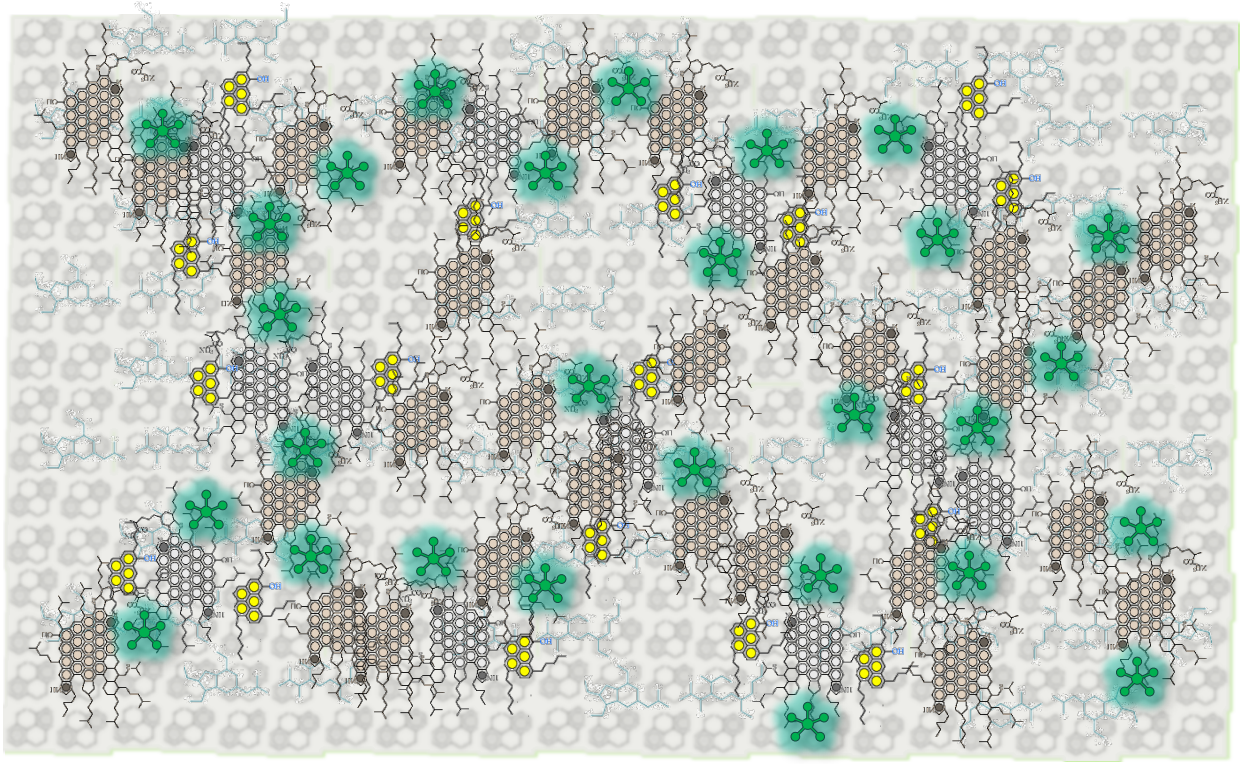
Reduced Continuous Matrix



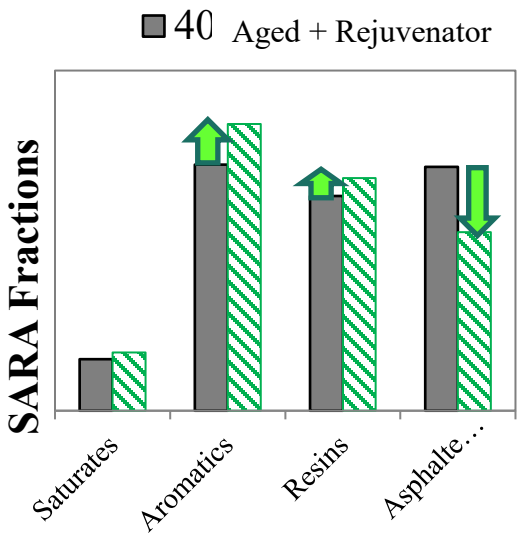


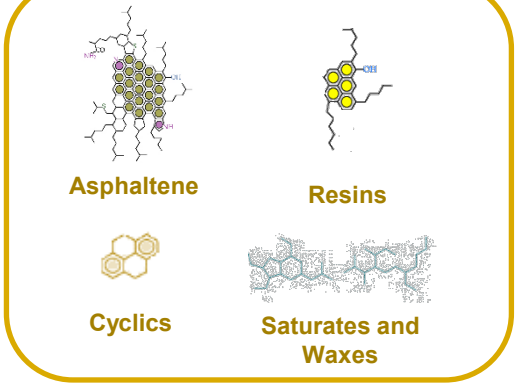
Simplified Bitumen Colloidal Model

Rejuvenated with Appropriate Rejuvenator



Replenished Continuous Matrix





Summary of the Mechanisms of Impact?

Three broad **mechanisms** to treating aged asphalt are envisioned:

1. **Softening through Dilution of Maltenes:**

   Adds to solvent phase and performs as diluents or "Fluxing"

2. **Compatibilizing Asphaltene and "Gel" Structure:**

   Disrupt asphaltene associations

3. **"Non-balancing" Softening:**

   Low viscosity additions to saturate fraction

How do we Differentiate Rejuvenators from Softeners?

- The difference between “Rejuvenation” and “Softening” is in the ability to “compatibilize” asphaltene-association structures in asphalt.

- Directly measuring asphalt compatibility is not easy. However:
  - We know that **long term-aging** decreases the compatibility of asphalt
  - We can **measure the change** in properties as a result of aging.

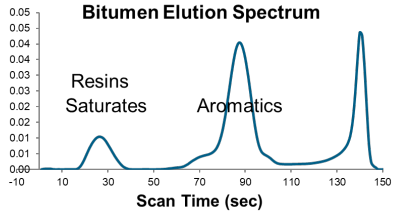
- Examples of property changes compared after long term aging:
  - Measuring the change in Analytical indices (e.g. “Colloidal Instability Index”, AFM structures)
  - Measuring change in Miscibility thermal analysis (i.e. Tg properties)
  - Measuring the change in BBR m-grade or ΔTc

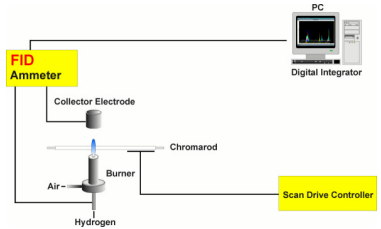
Impact of Further Aging on Colloidal Stability

Extracted RAP > RTFO > 1x PAV > 2xPAV

Extraction & Recovery

+ Aging

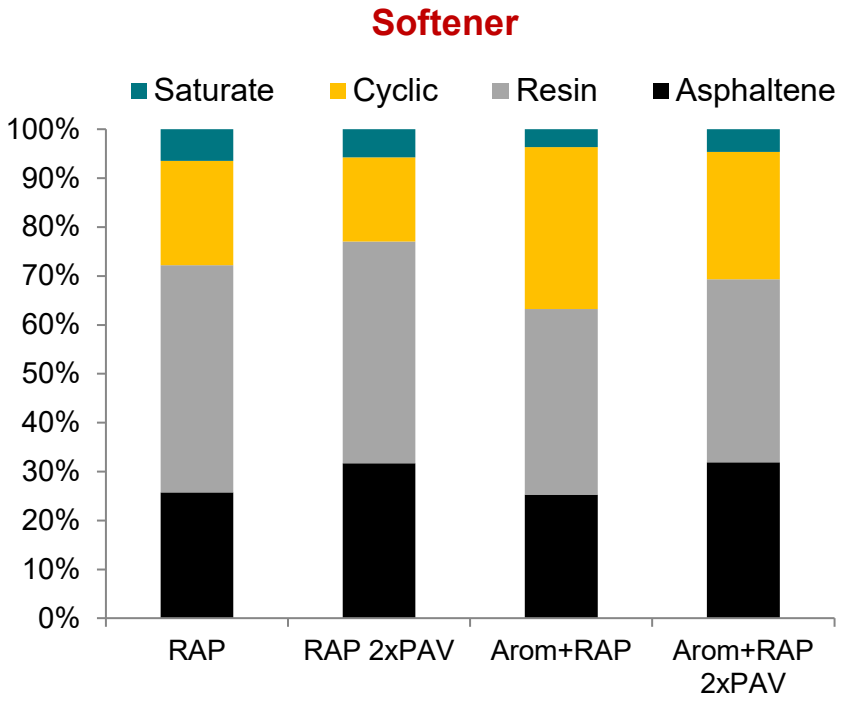


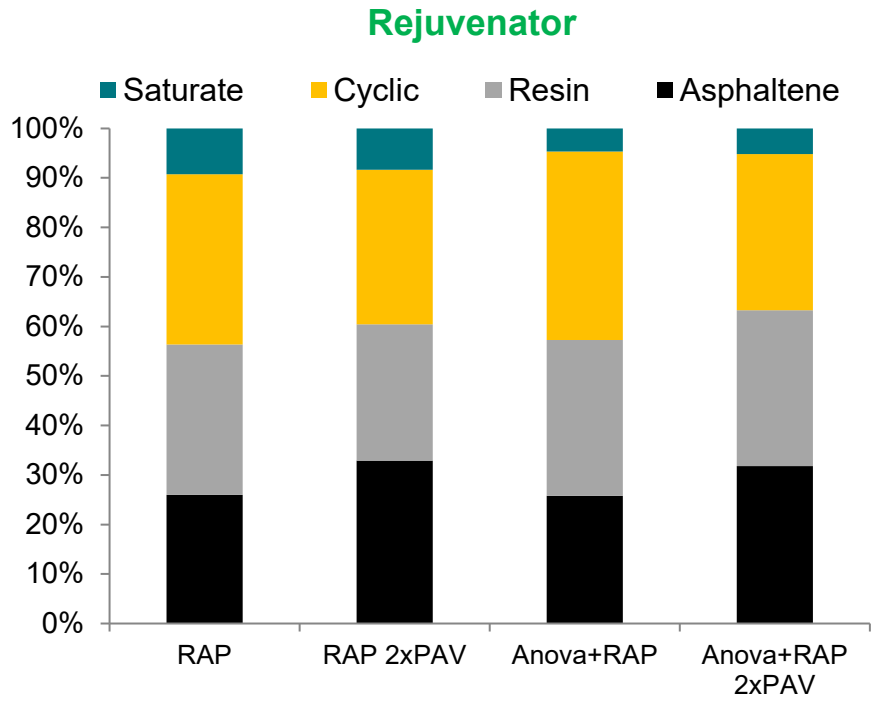


Bitumen Fractionation

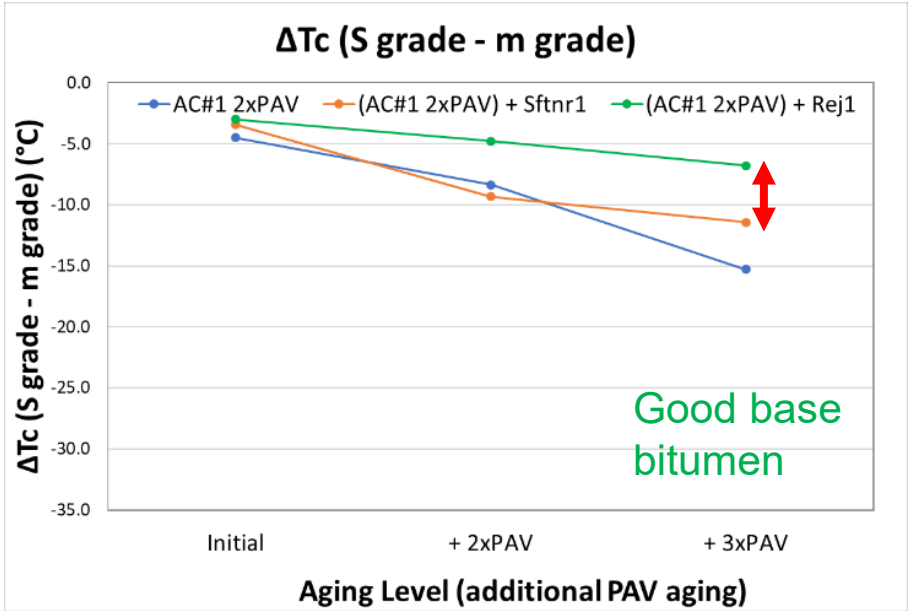
Impact of Further Aging on Colloidal Stability

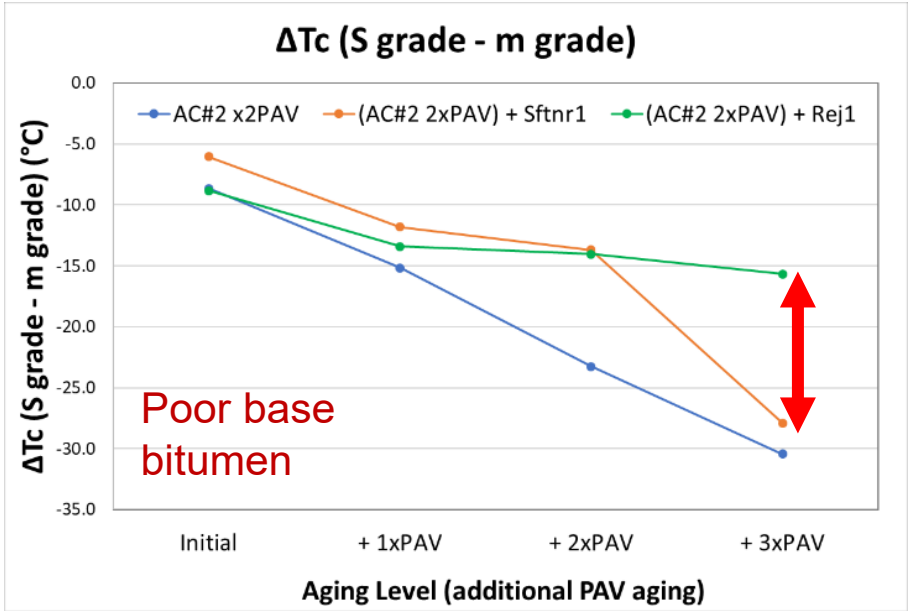
Extracted RAP > RTFO > 1x PAV > 2xPAV





Measuring Change in Rheological Properties



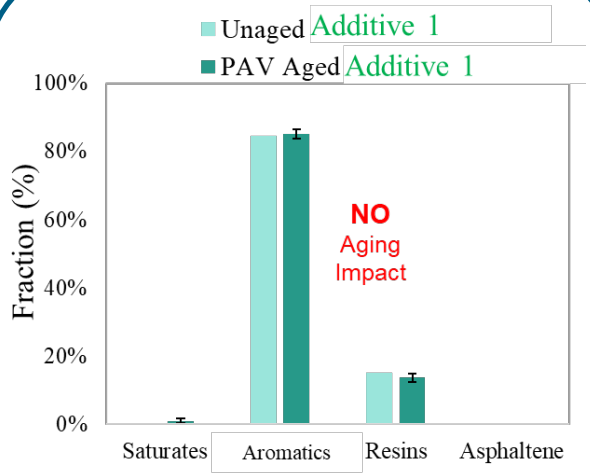


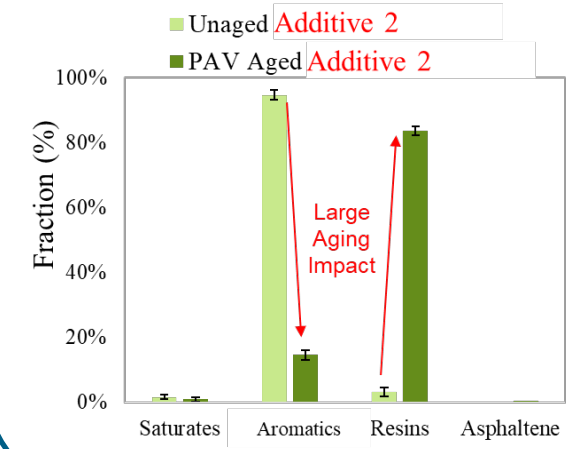
- Rejuvenating power of additives compared through ability to ***maintain ΔTc*** with aging.
- Relative value of ΔTc at a single aging level can be misleading (example: PMAs)
  - The change in ΔTc with aging is the differentiator, not the value at a given condition.

Quick Checks

- Additive stability can be quickly checked through direct aging in an RTFO or PAV.
- Compare viscosity… or even perform SARA fractionation!

Property	Additive 1	Additive 2	Comment
Viscosity at 60°C	29.25 cP	16.25 cP	Brookfield, #18
Viscosity Aging Ratio (Additive Viscosity after aging / Viscosity unaged)			
TFO (5hrs at 163°C)	1.05	2.2	< 3.0 (ASTM D4552)
TFO (5-days at 85°C)	1.0	50.5	< 3.0 (proposed)
PAV (20hrs at 100°C)	1.07	31.8	< 3.0 (proposed)





Summary of Rejuvenation vs. Softening

- Reduce modulus/viscosity

Softening

- Restore balance of asphalt chemical fractions
- Reduce brittleness / improve damage resistance and healing
- Equal (or better) aging behavior than original binder!

Rejuvenating

- We can assess rejuvenation through its impact on the compatibility of asphalt as it ages.
- Although directly measuring combability is difficult, indirect assessment is possible by measuring the change in properties as a result of aging.
  - For example: Measuring the change in BBR m-grade or ΔTc
- More clarity on this topic expectes from the results of in-progress NRRA project:

National Road Research Alliance

Project in Progress: AN INNOVATIVE PRACTICAL APPROACH TO ASSESSING BITUMEN COMPATIBILITY AS A MEANS OF MATERIAL SPECIFICATION

- *PI: University of New Hampshire, Co-PI: Cargill*

What Should Be Discussed Next?

- How can Recycling Agents be practically used to meet Balanced Mix Design Requirements?
  - What performance and operational impact can be expected?
- What is the process of optimizing mix designs containing Recycling Agents?
- Case Studies and practical examples of use of RAs to meet BMD in Illinois and other states.