Rejuvenation vs. Softening
of Recycled Binders

Tony Sylvester
Hassan Tabatabaee, Ph.D.
Cargill Industrial Specialties

Illinois Asphalt Pavement Assn.
iapa

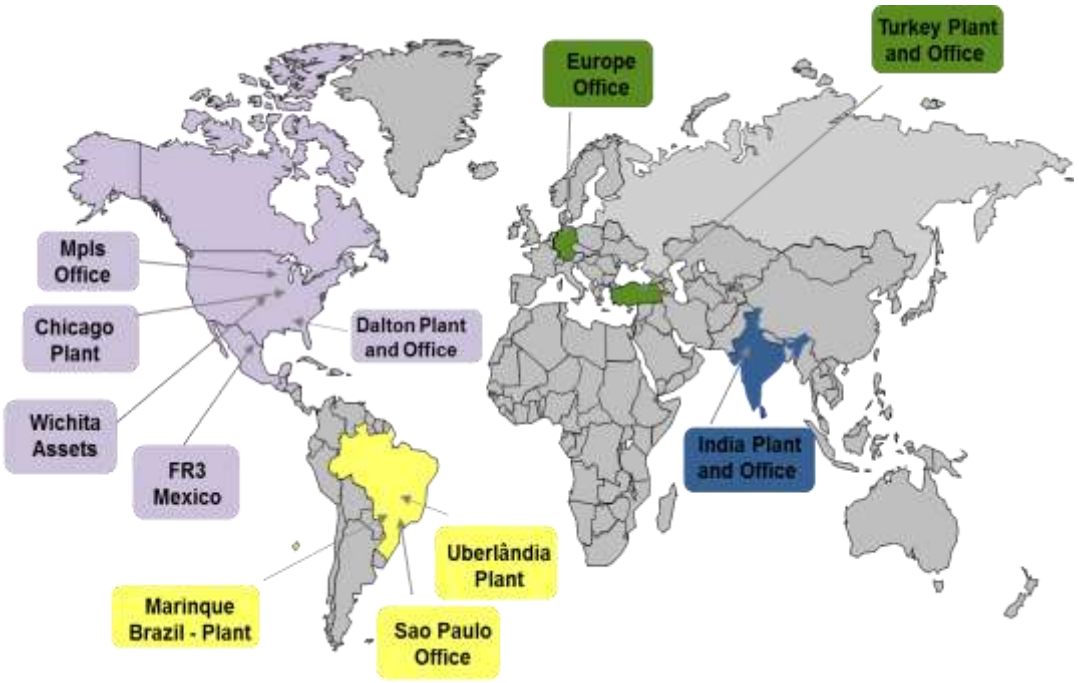
March 13, 2017
Springfield, IL

Cargill

Cargill's Role in Asphalt

- Cargill is a large, global provider of solutions in agricultural, food, financial and bio-industrial markets.

1. Cargill Anova™ Modifiers
2. Cargill Anova™ Rejuvenators
3. Cargill Anova™ Green Diluents
4. Cargill Anova™ Anti-strips
5. Cargill Anova™ WMA
6. Cargill Anova™ Emulsifiers



Agenda

- Background
- Softening vs. Rejuvenation
- Balanced Performance: Cracking vs. Rutting
- ΔT_c Parameter
- Conclusions

Definitions

- **"Rejuvenation" is an inaccurate, but popular term.**
  - Rejuvenators do not undo oxidative aging!!!
- **A good rejuvenator** reverses the impact of aging on asphalt performance, properties, and durability.

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

1. **Soluble Softeners:**

   Add to solvent phase and perform as diluents

2. **Compatiblizers:**

   Disrupt asphaltene associations

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

   Low viscosity additions to saturate fraction

Softening vs. Rejuvenation

Softening

- Reduce modulus/viscosity

Rejuvenating

- Restore balance of asphalt fractions
- Restore phase/colloidal stability
- Reduce brittleness / improve damage resistance
- Restore “healing” ability
- Equal (or better) aging behavior than original binder!

Material Considered in this Presentation

The Rejuvenator:

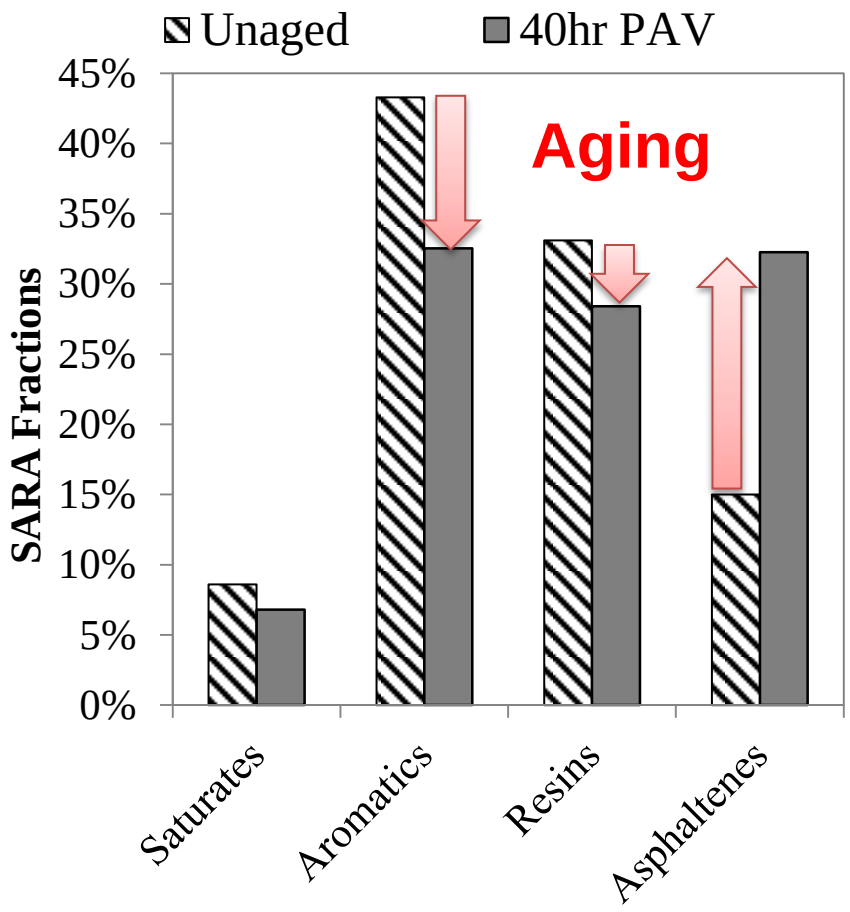
Description	Flash Point	Viscosity at 60°C
Chemically Modified Veg oil-based Rejuvenator	>290°C	28.5 cP
	TFO Mass loss	**TFO Visc Ratio**
	<1%	1.1

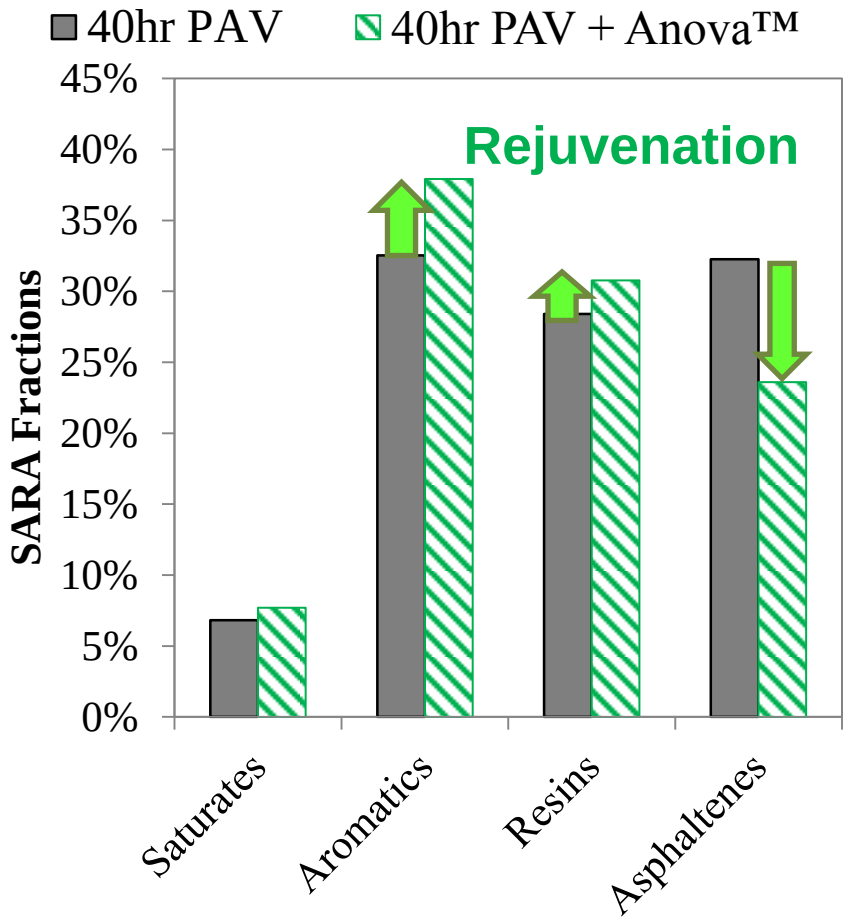
The Asphalt Binders Considered:

- A PG64-22 from Flint Hills Refinery
- A PG58-28 from Flint Hills Refinery
- An Extracted Mid-west RAP Binder
- An Extracted Northeast RAP Binder
- An Extracted SC RAP from ARC/WRI
- SHRP Binder AAA-1
- Conditioned to RTFO, 20hr PAV, 40hr PAV, and 60hr PAV

Re-Balancing Bitumen Fractions

- Decreasing asphaltenes content and association through balanced addition of bio-based “aromatic” and “resin” functionality.



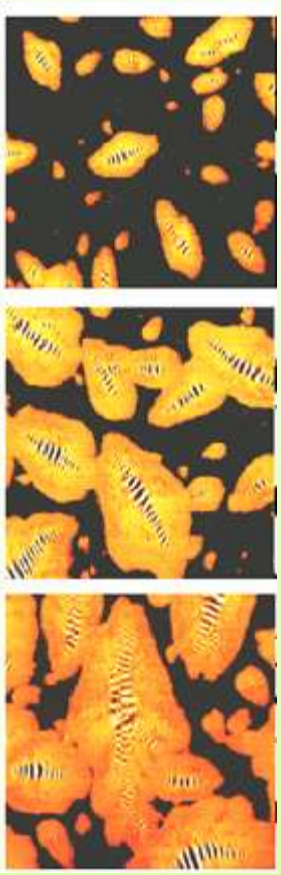


Thin Layer Chromatography (TLC) using an Iatroscan

Cargill

Reversal of Aged Asphalt Morphology

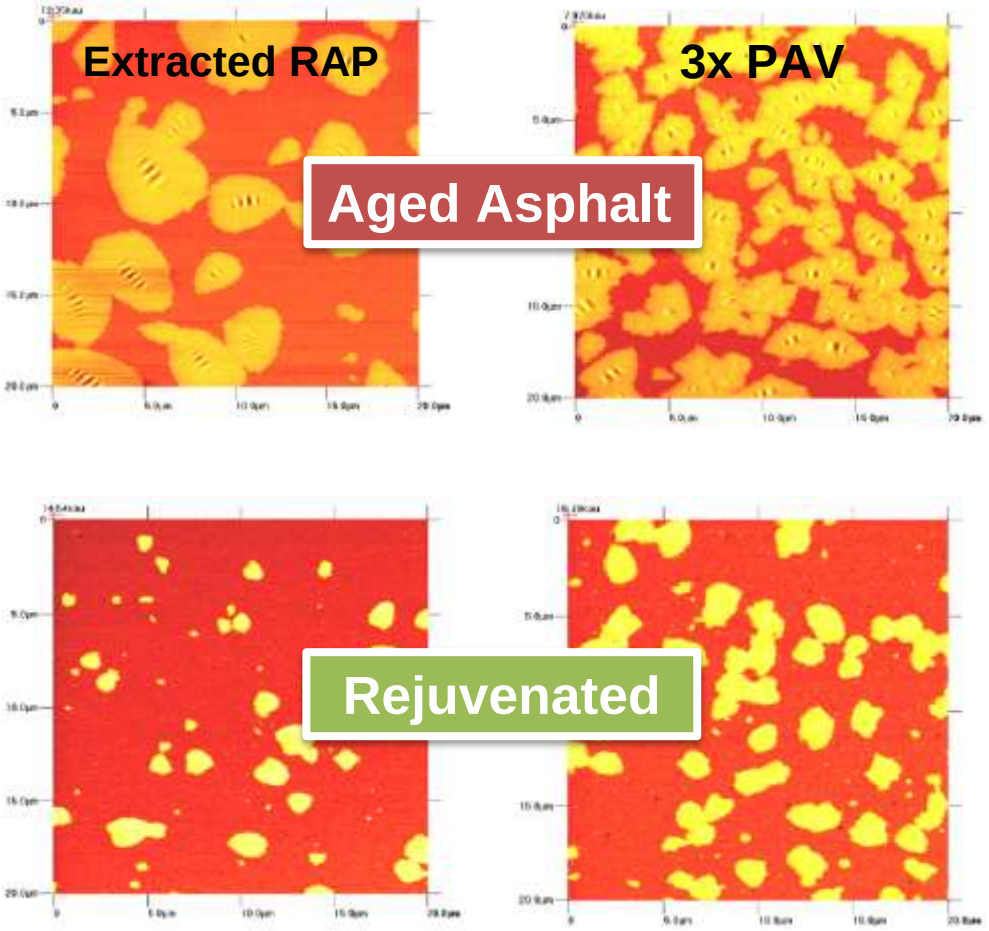
Atomic Force Microscopy



Increase in Wax Content

Has been correlated to more *Aging*, Increase in *Asphaltene* or *Colloidal Instability*

(Image from Pauli et. al., 2014)

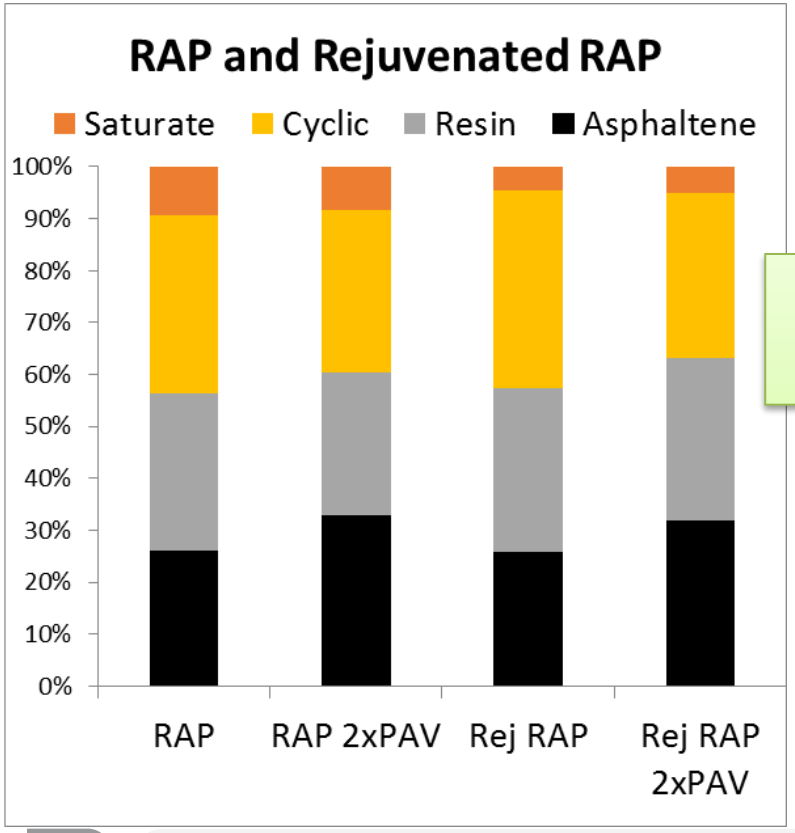


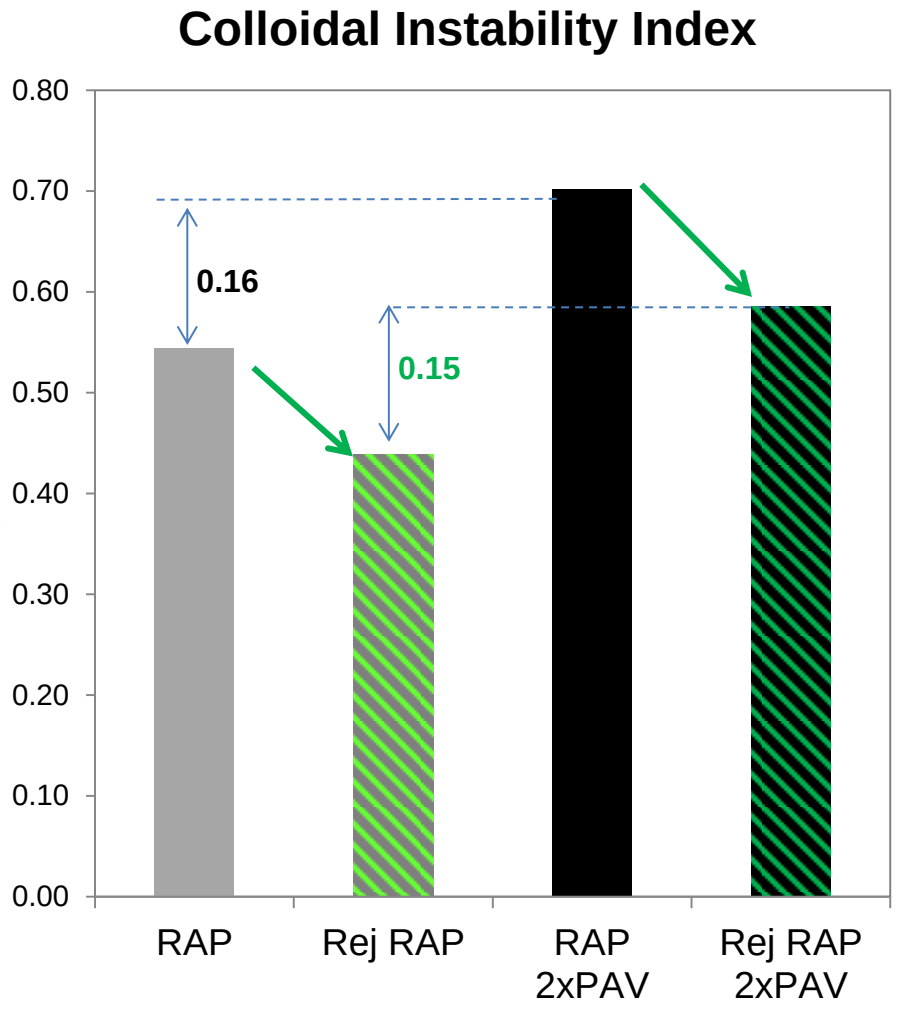
Phase image scans of solvent spin-cast films of asphalt air-dried in a vacuum desiccator for 48 hours.

Aging Resistant Fractional Balance

Extracted RAP > RTFO > 1x PAV > 2xPAV

$$CII = \frac{Asphaltenes + Saturates}{Aromatics + Resins}$$





Balanced Performance
Cracking vs. Rutting

RAP Blend Charts

- The allowable RAP dosage is often estimated using a blending chart in accordance to AASHTO M323:

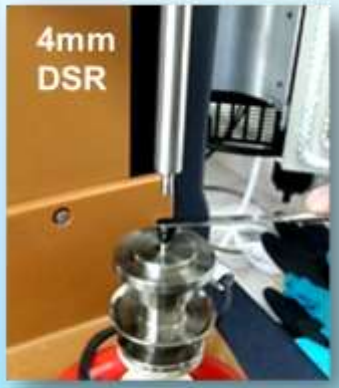
$$\%RAP = \frac{\left(T_{\text{blend}} - T_{\text{virgin}}\right)}{\left(T_{RAP} - T_{\text{virgin}}\right)} \times 100$$

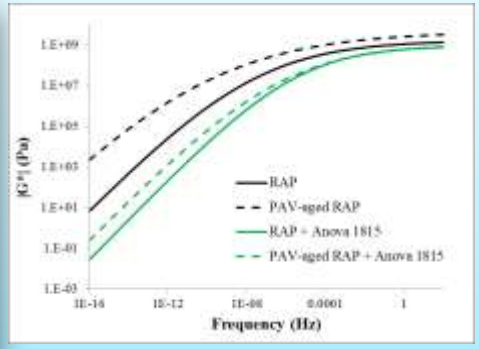
- Extraction techniques AASHTO T-164, AASHTO R-59, ASTM D7906, ASTM D1856, ASTM D2172

Extraction & Recovery

High Temperature Rutting Resistance

Low Temperature Cracking Resistance



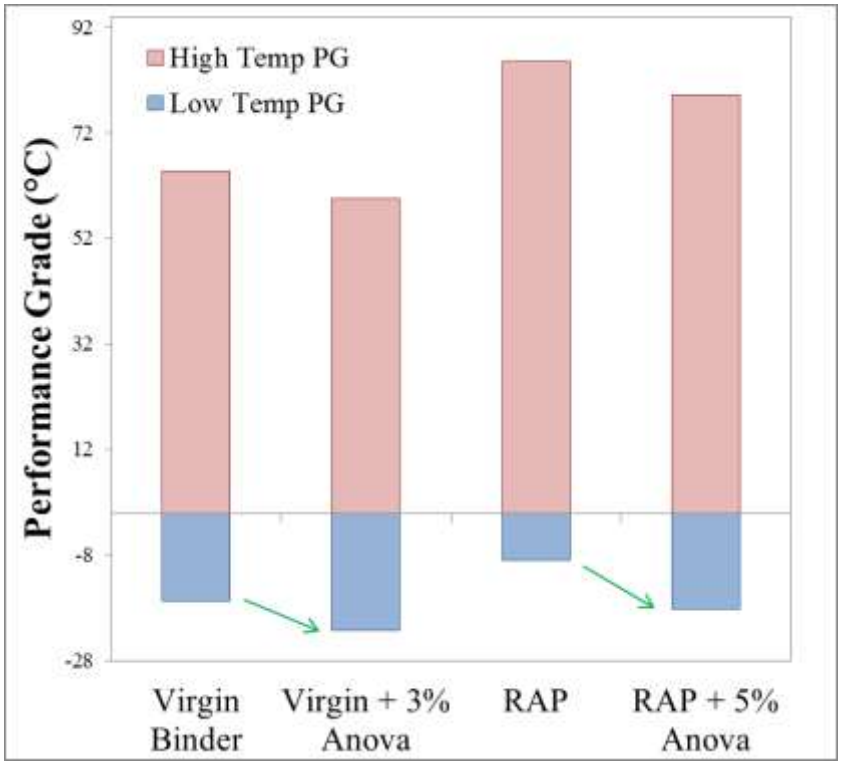


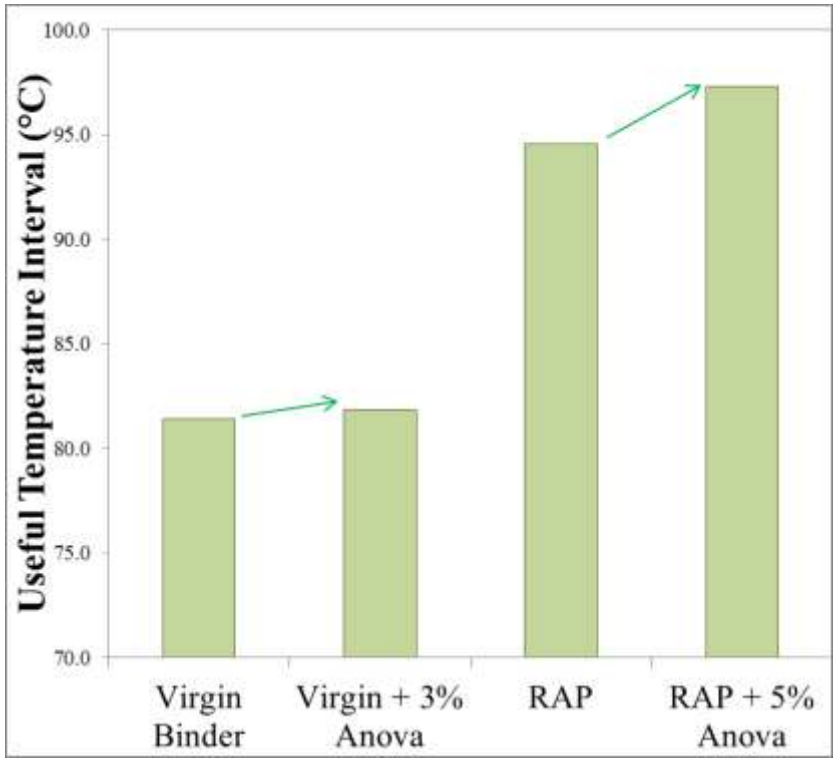
High and Low Temperature

RAP PG
Rejuv'd RAP PG

Rejuvenator Dosage vs. %RAP

Rejuvenated RAP PG



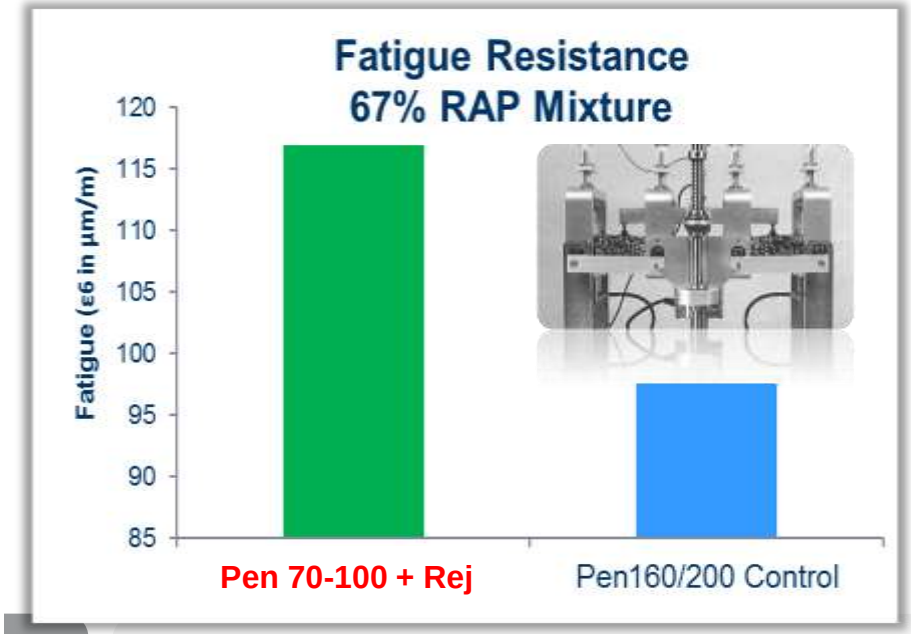


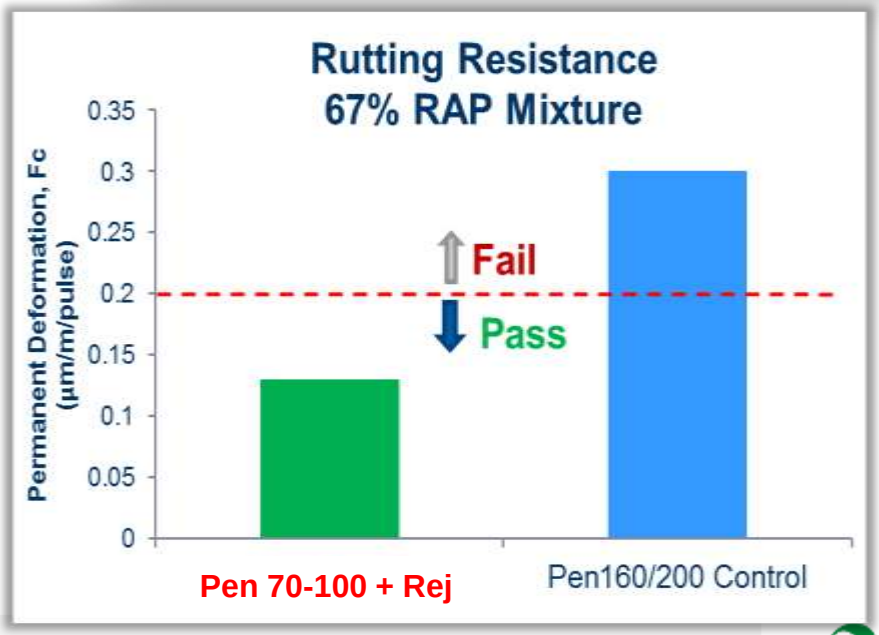
- Among other things, proper “rejuvenation” will affect the low temperature PG more than the high temperature PG.
  - Resulting in an increased “Useful Temperature Interval”.
  - This quality is essential for stiff high RAP mixes to prevent rutting issues while treating cracking resistance and durability.

Cargill

Rutting vs. Fatigue #1

- Beam fatigue test showed that the **rejuvenator** significantly improved the fatigue resistance.
- The **rejuvenated mix easily** passed the rutting requirement
- The mix using soft bitumen failed the rutting test.

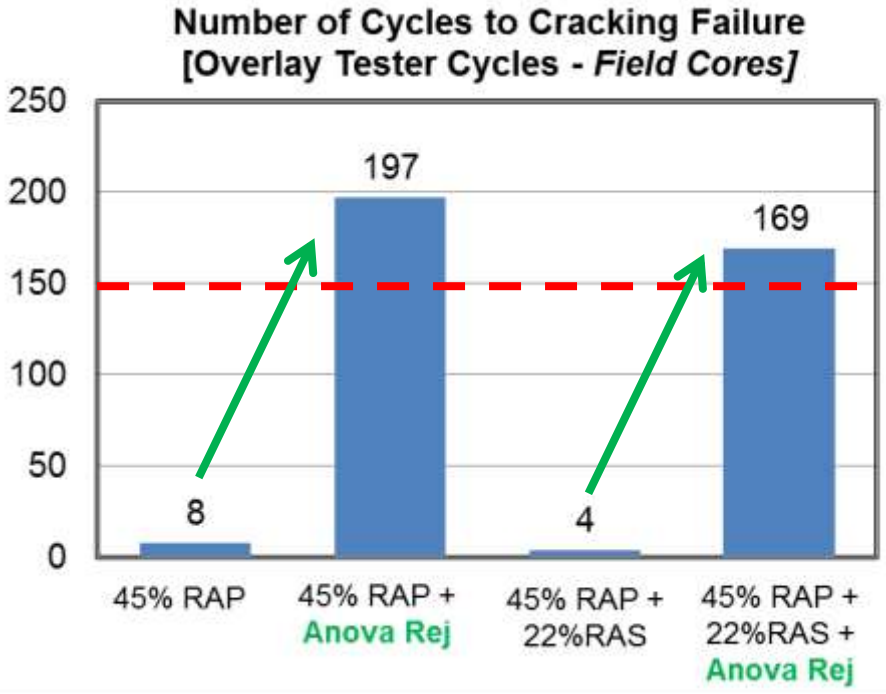


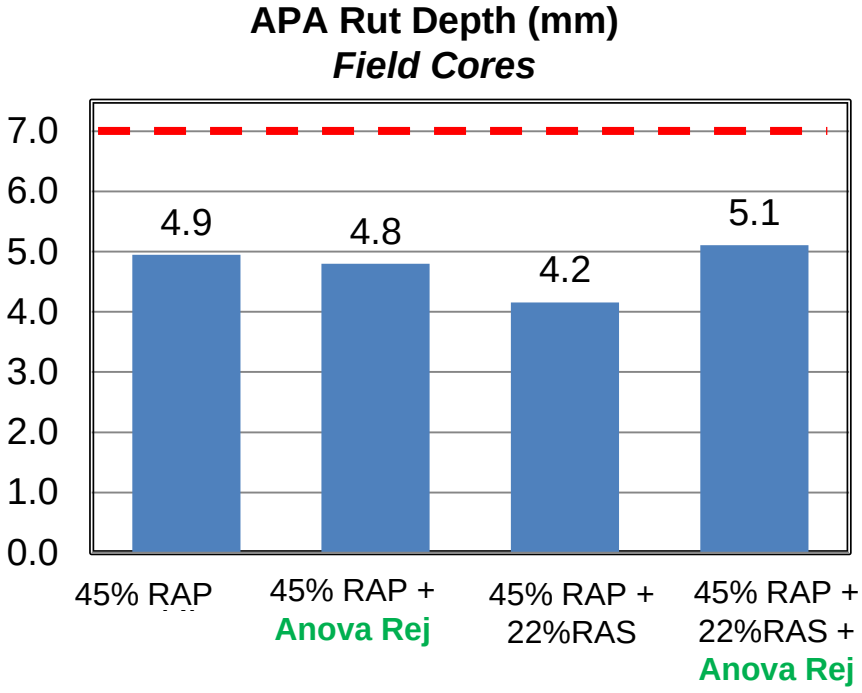


Cargill

Rutting vs. Fatigue #2

- In this project rejuvenation resulted in a **25 time improvement** in cycles to cracking.
- Change in rutting resistance was relatively small.

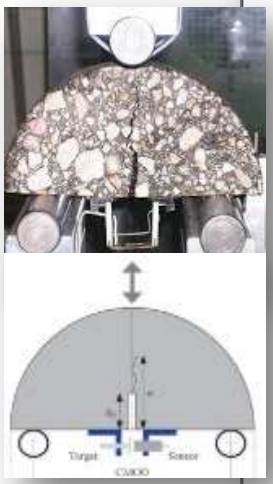


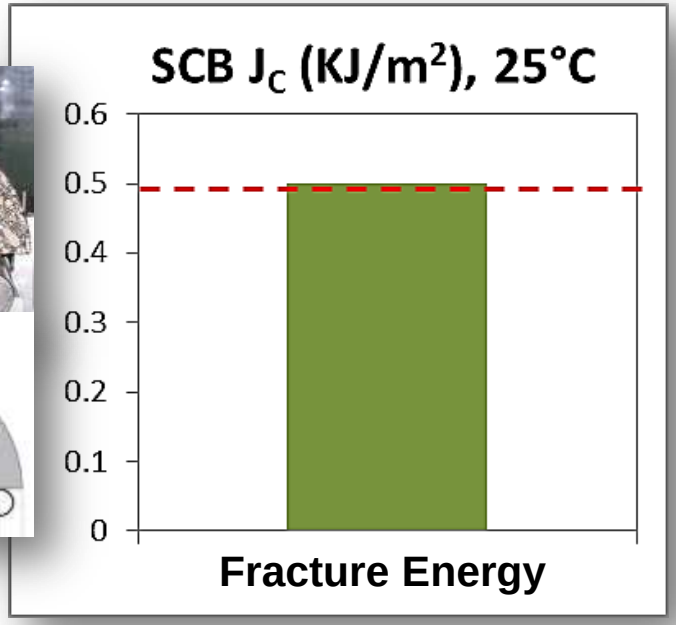


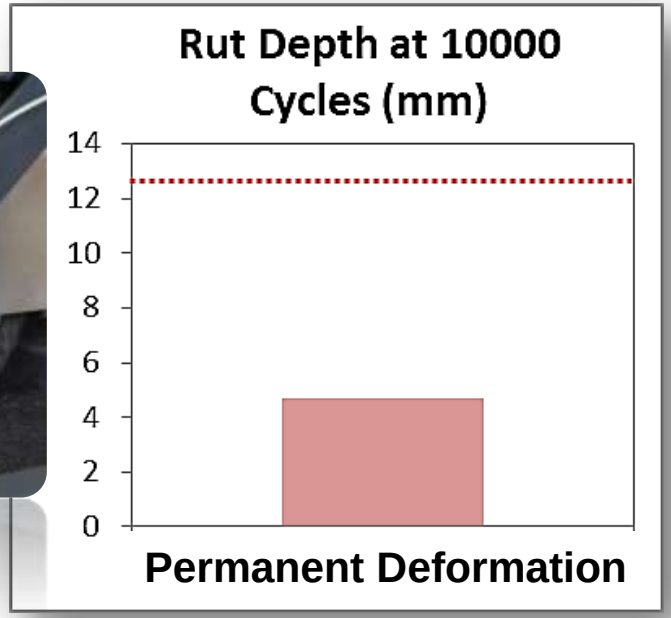
Cargill

Rutting vs. Fatigue #3

- HMA solely consisted of RAP and Rejuvenator
- Rejuvenator sufficiently activated RAP to achieve **+500 J/m^2 fracture energy**.
- No rutting issues observed.

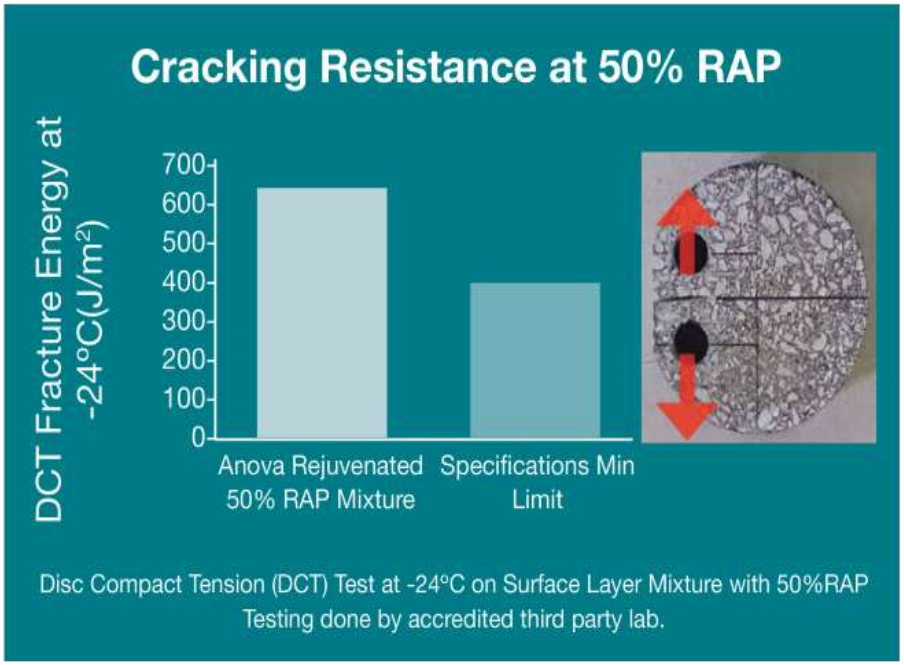


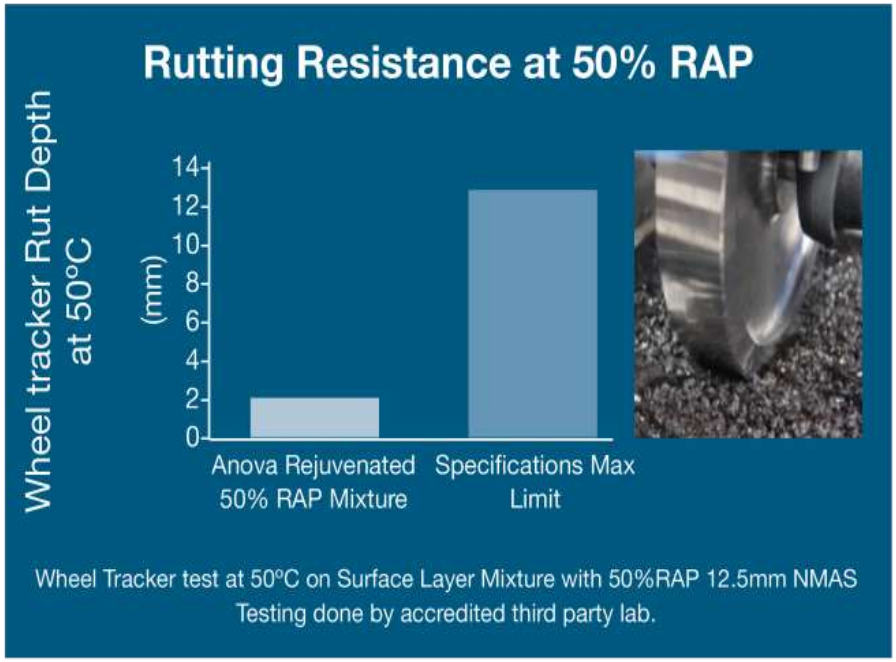




Rutting vs. Thermal Cracking #4

- A 50% RAP mixture placed in a cold climate.
- Rejuvenating RAP achieved a **+600 J/m^2 fracture energy at -24°C**.
- No rutting issues observed.



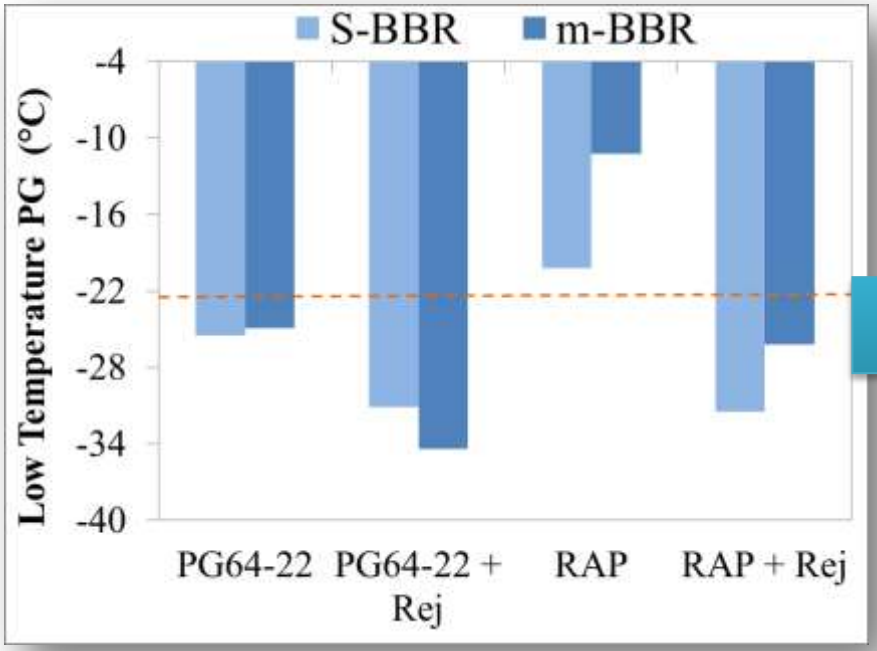


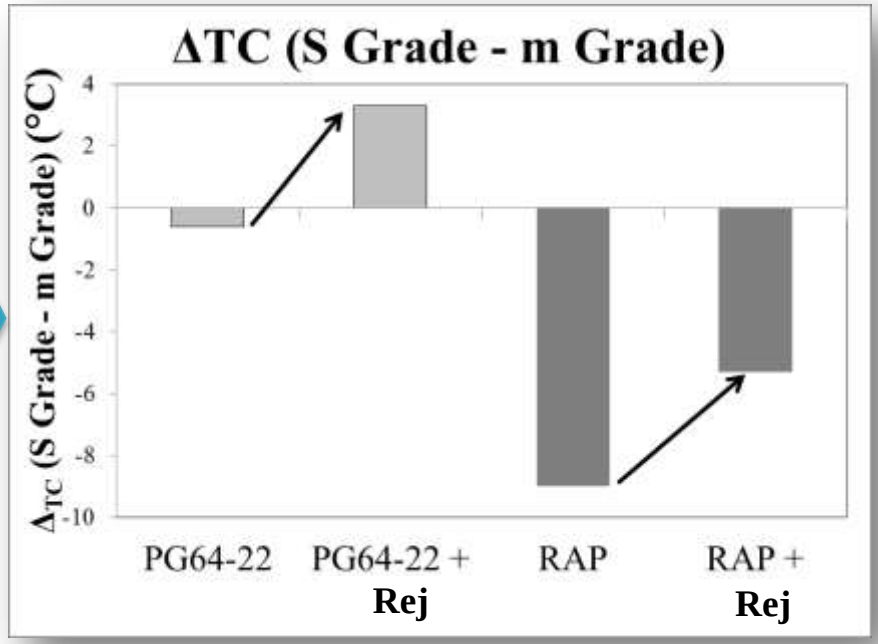
Relating ΔT_c to Aging & Rejuvenation

Future Specification: ΔT_c Parameter

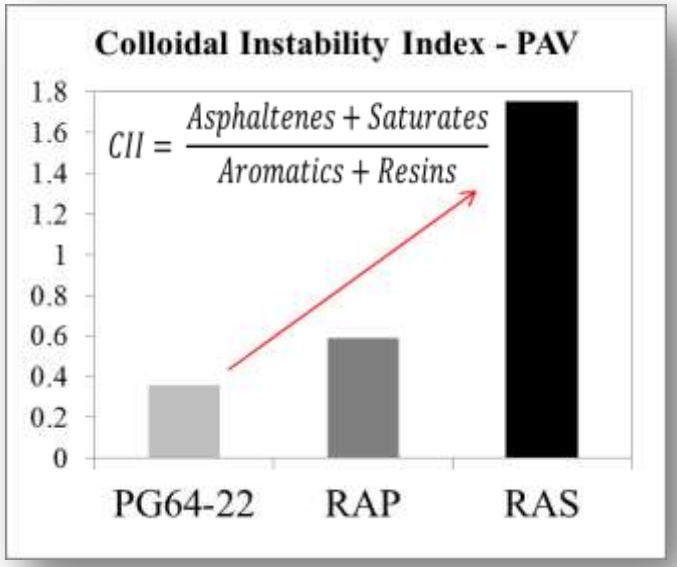
ΔT_c = [S(t) Grade] – [m-value Grade]

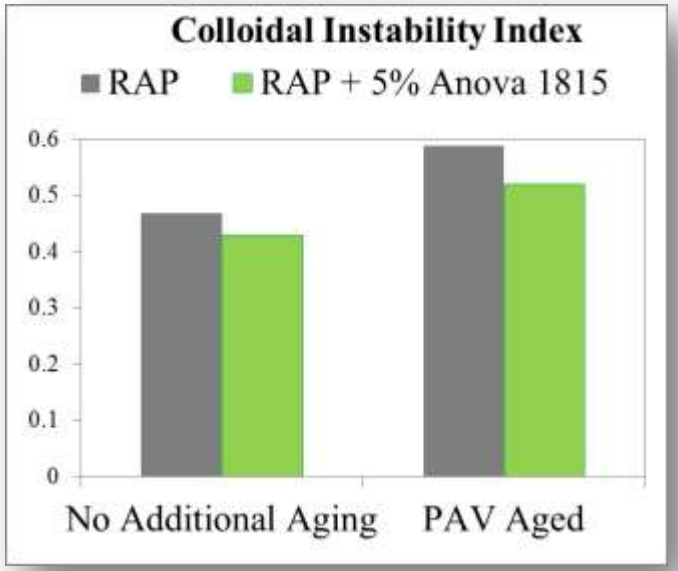
- A positive value (S controlled) is desired:
  - **Positive ΔT_c**: Better bitumen fraction balance.
  - **Decrease in ΔT_c** due to aging or low compatibility bitumen blends

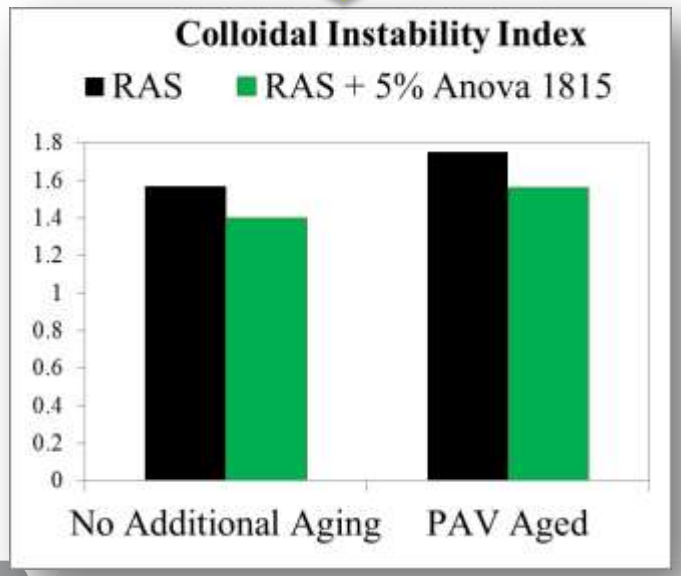


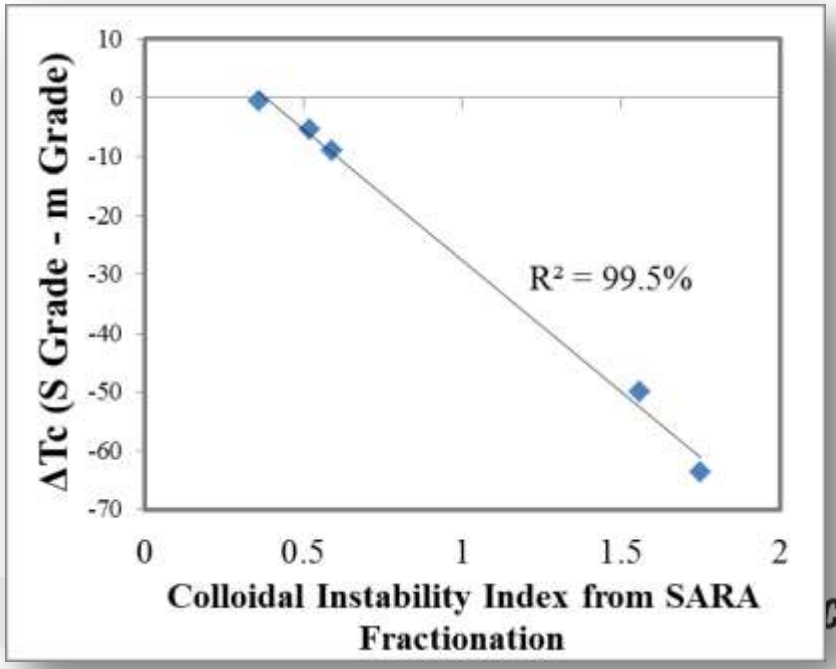


Cargill


Colloidal Instability Index - PAV
$CII = \frac{Asphaltenes + Saturates}{Aromatics + Resins}$
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
PG64-22
RAP
RAS


Colloidal Instability Index
RAP
RAP + 5% Anova 1815
0.6
0.5
0.4
0.3
0.2
0.1
0
No Additional Aging
PAV Aged


Colloidal Instability Index
RAS
RAS + 5% Anova 1815
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
No Additional Aging
PAV Aged


ΔTc (S Grade - m Grade)
10
0
-10
-20
-30
-40
-50
-60
-70
$R^2 = 99.5\%$
0
0.5
1
1.5
2
Colloidal Instability Index from SARA Fractionation

Cargill

Conclusions

SOFTENING VS. REJUVENATION

- In addition to "softening", a "rejuvenation" requires rebalancing the bitumen fractions in oxidatively stable and compatible manner.
- **Balanced Performance**- Proper rejuvenation will improve cracking resistance and durability without compromising on rutting resistance.
    - *Balanced mix design and performance based testing are found to be very useful tools to optimize high RAP high performance mixes*
- The ΔT_c parameter seems to relate rheology to fractional balance of aged bitumen.
    - *This parameter can be simple and efficient measure of binder quality and balance.*

Tony Sylvester
Tony_Sylvester@cargill.com

Cargill®

Hassan Tabatabaee, Ph.D.
Hassan_Tabatabaee@cargill.com

Analysis Approach

Aging and rejuvenation can be assessed at multiple levels:

1. *Physical-Chemical Analysis Aspect*
2. *Binder Performance and Rheology aspect*
3. *Mixture Performance and damage aspect*

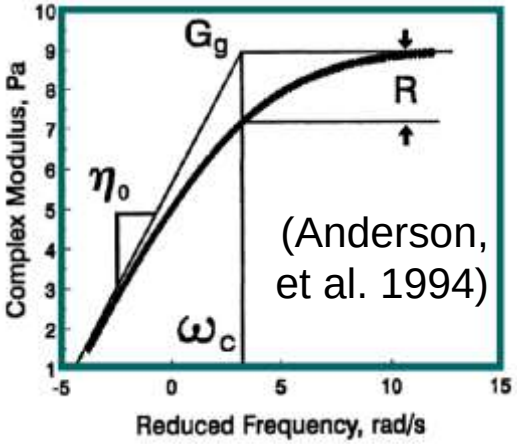
REFERENCE:

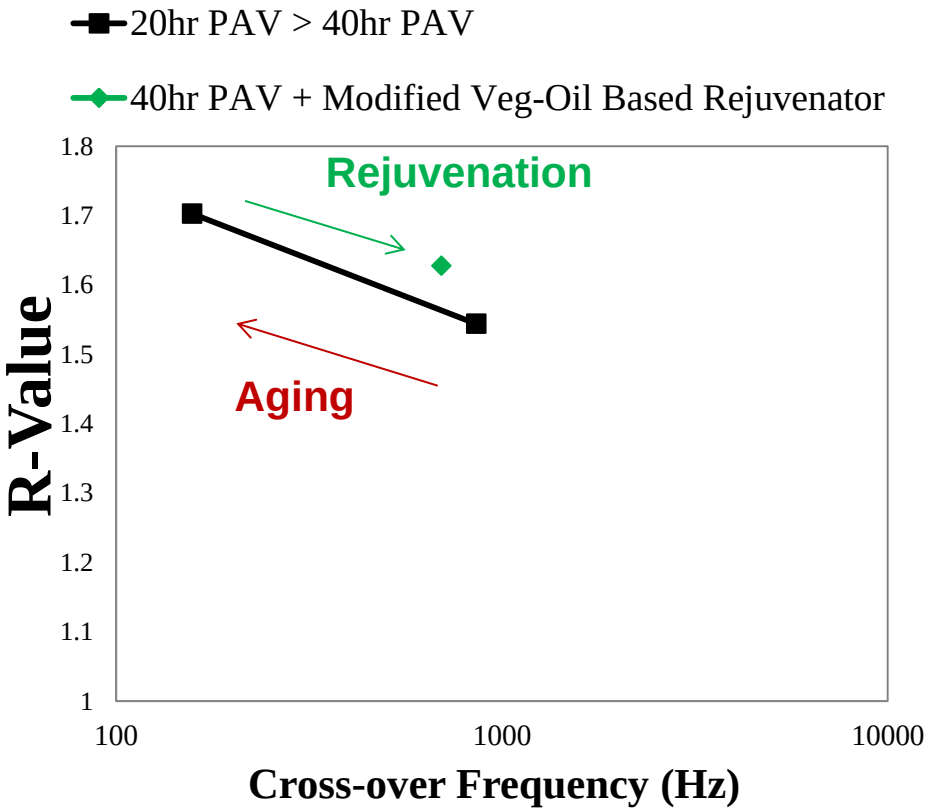
- Tabatabaee, H.A. and Kurth, T.L., "*Rejuvenation vs. Softening: Reversal of the Impact of Aging on Asphalt Thermo-Rheological and Damage Resistance Properties*," Proceedings of the International Society for Asphalt Pavers, 2016, Jackson, WY, USA.
- Tabatabaee, H.A. and Kurth, T.L., "*Critical Comparison Of Asphalt Recycling Agents From Bio-based and Petroleum Sources*," Proceedings of the 22° Encandro de Asfalto, 2016, Rio de Janeiro, Brazil.
- Tabatabaee, H.A. and Kurth, T.L., "*Analytical Investigation of the impact of a novel bio-based recycling agent on the colloidal stability of aged bitumen*," Proceedings of EATA 2017, Switzerland.

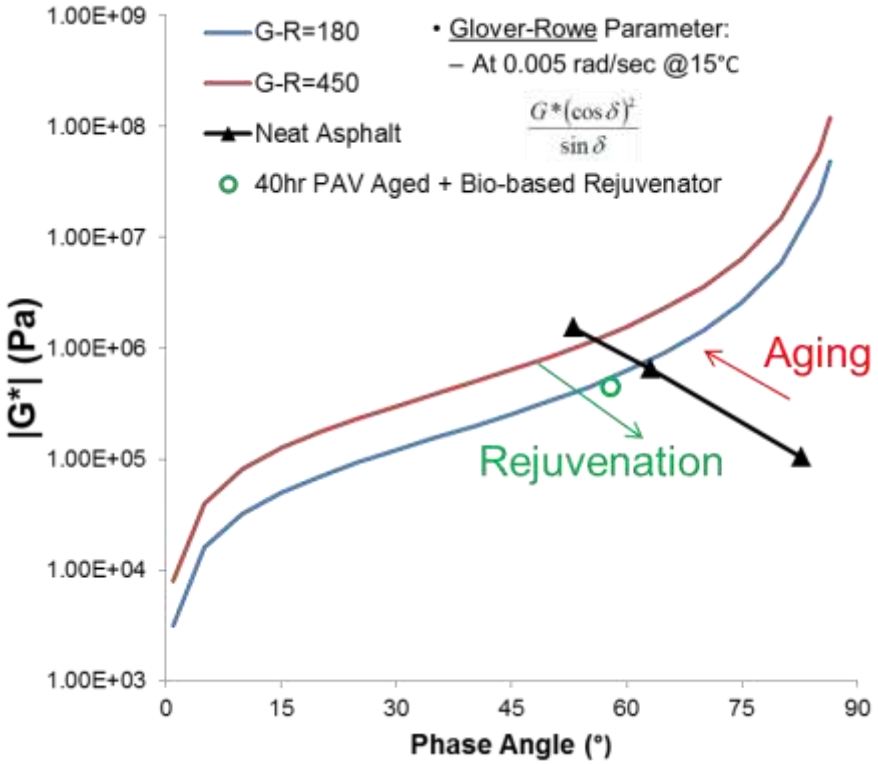
Cargill

Rheological Parameters

- The “Rheological Index” or R-Value can be related to a number of performance-based rheological properties.
- Aging increases the R-value, decreases the crossover frequency, and increases the crossover temperature.

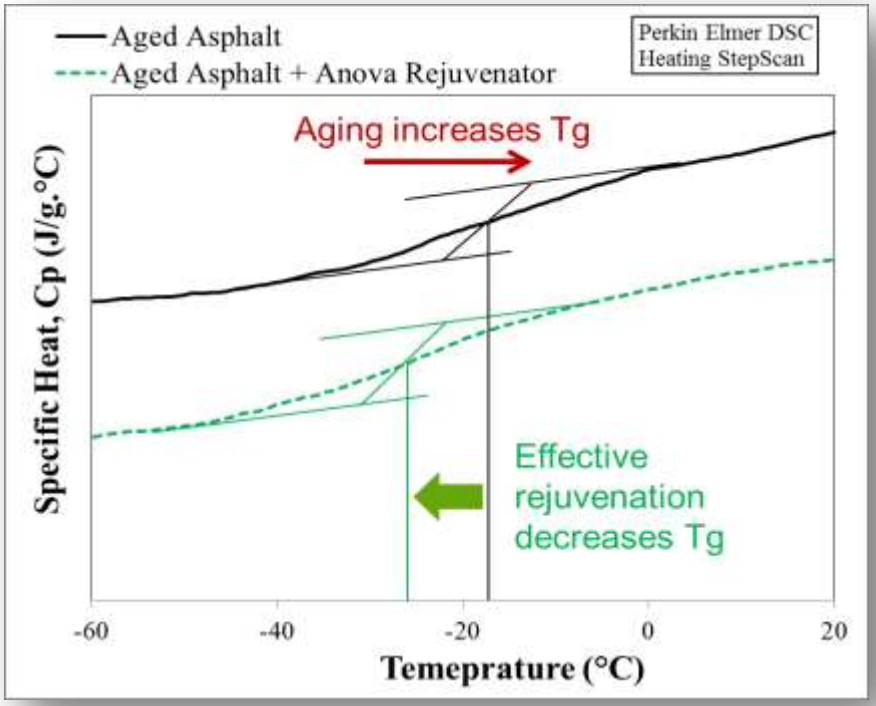


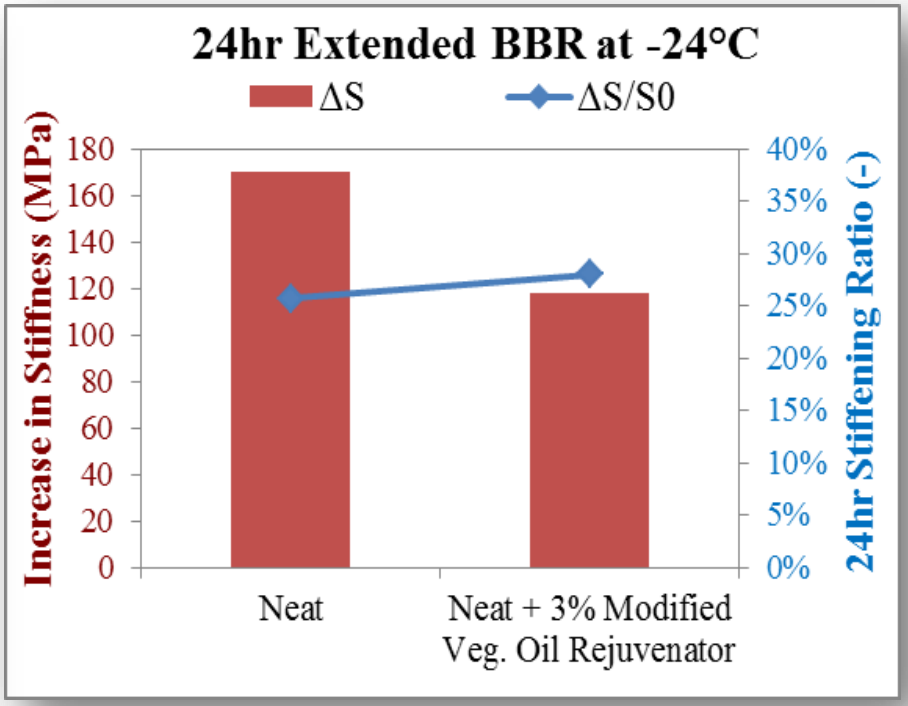




Thermo-volumetrics & Physical Hardening

- Asphalt undergoes “physical hardening” over extended low temperature exposure. Physical hardening can gradually deteriorate low temperature PG.
- Extended BBR following MTO LS-308 covers the effect of physical aging on asphalt.
- Aging and rejuvenating additives can affect the rate of physical





Fourier Transform Infra Red Spectroscopy (FTIR)

Extracted RAP > RTFO > 1x PAV > 2xPAV

Carbonyl index (C=O): $A_{1700}/\Sigma A$

Sulfoxide index (S=O): $A_{1030}/\Sigma A$

Aromaticity index: $A_{1600}/\Sigma A$

The sum of the area ΣA represents: $A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$

(Permenyar et.al. 2002)