Reactivation vs. Softening: Analysis of the Reversal of the Aging Impact through Use of a Novel Bio-based "Reactivator"

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Summary
Increasing incorporation of highly oxidized bitumen material into pavements has accentuated the need to ensure long term durability via effective "Rejuvenation." While it is understood that bitumen modifiers perform differently, consensus on the definition of "Rejuvenation" and the associated mechanisms does not exist. Thus, further clarification and assessment of impacts on aging and of various approaches to "Rejuvenation" is imperative.

The present study utilizes chemical fractionation and characterization to contrast the impact of "Solvators" with "Compatibilizers." The former defined as additives that supplement the solvent fraction of the bitumen colloidal structure, whereas the latter are defined as additives that in addition to the solvent phase, show greater affinity for the Resin fractions. Using these definitions, the term "Reactivator" has been proposed to represent recycling agents that simultaneously exhibit properties of both "Solvators" and "Compatiblizers" and a novel biobinder is introduced that can be thus defined as a "Reactivator." The ideal objective of a "reactivation" process is not the reversal of aging, but is rather the reversal of the "impact of aging" on bitumen mechanical and rheological properties, damage resistance, and overall durability and performance.

Keywords
Reclaimed Asphalt Pavements, Rejuvenators, Reactivators, Anova 1817, Cargill

1. Introduction

Aging affects the bitumen properties through a number of mechanisms, one of the most important of which is oxidation [1]. Perhaps one of the most useful descriptions of the effect of such oxidative aging on the mechanical and damage resistance properties of bitumen has been offered by Petersen [2]: "If during oxidative aging, the concentration of polar functional groups becomes sufficiently high to immobilize an excessive number of molecules through intermolecular association, the molecules or molecular agglomerates lose sufficient mobility to flow past one another under thermal or mechanical stress. The resulting embrittlement of the bitumen makes it susceptible to fracturing or cracking and resistant to healing." This statement clearly relates the loss of performance and durability observed with aging to structural changes and associations in the bitumen colloidal system, thus providing a useful basis for defining the objective of rejuvenation, as discussed in the next section.

2. Rejuvenation and Categorization of Recycling Agents

A large number of both petroleum- and biological-based additives proposed as recycling agents have been investigated in the literature [3, 4, 5, 6]. Although different types of categorization may be employed for such material based on the source or manufacturing process, the authors believe that the most useful categorization for discriminating between recycling agents would need to be based on the bitumen fraction most affected by the additive and the expected mechanism of affecting that compatible fractions upon addition to aged bitumen. Thus using this philosophy and the previously described aging mechanism, three broad categories of recycling agents are envisioned and proposed:

1. "Solvators", which supplement the "solvent" phase of the bitumen colloidal structure by being most compatible with the neutral naphthenic aromatic fraction of the bitumen. Such additives reduce the viscosity and modulus of the overall bitumen through lowering the viscosity of the continuous solvent phase, but may have little effect on the intermolecular agglomeration and self-assembly of the polar micelles.
2. "Compatibilizers", which have affinity for multiple fractions in the bitumen and may be derived through careful engineering of the source material, whether Petroleum- or bio-based. In addition to reduction in viscosity, these additives are hypothesized to result in a reduction in high molecular weight micelle agglomerations through disruption of the intermolecular associations and molecular self-assembly, similar to the postulated effect of the bitumen "resin" phase.
3. "Insoluble softeners", which often exhibit the most compatibility with the paraffinic phase of the bitumen and have low compatibility with the neutral naphthenic aromatic and polar fractions. Dispersion of such lower viscosity additives in the bitumen may still achieve a reduction in overall bitumen modulus. Increasing the dosages of "insoluble softeners" has in bitumen has been speculated to lead to colloidal instability and precipitation of the asphaltene fraction, especially after the bitumen is subjected to further aging. Thus although addition of such additives to bitumen may initially result in seemingly desirable rheological impact, long term durability and phase stability may be compromised [7].

Using these definitions, the term "Reactivator" has been proposed to represent recycling agents that simultaneously exhibit properties of both "solvators" and "Compatiblizers". The ideal objective of a "reactivation" process is not the reversal of aging, but is rather the reversal of the "impact of aging" on bitumen mechanical and rheological properties, damage resistance, and overall durability and performance.

3. Chemical Composition and Colloidal Stability

The present study uses chemical fractionation and Atomic Force Microscopy to compare the impact of different types of recycling agents that are believed to represent different degrees of the "Solvator" and "Compatiblizer" effect on aged bitumen. For this purpose, the following recycling agents were compared:

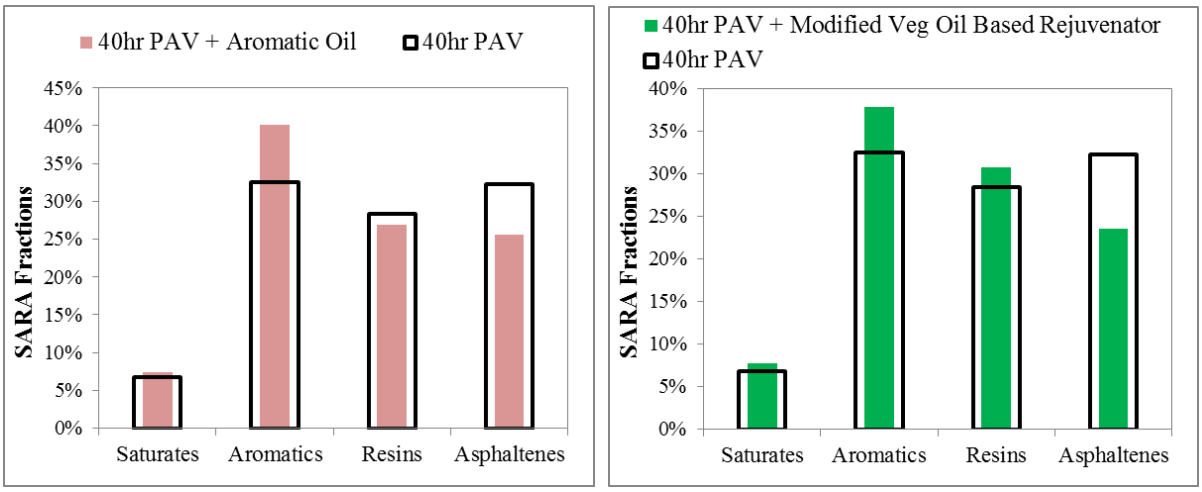
- A commercial aromatic petroleum-based recycling agent
    - Dynamic Viscosity at 1Hz and 60°C: 101 cSt
    - Dynamic Viscosity at 1Hz and 135°C: 6.3 cSt
    - Flash Point: >210°C
- A commercial chemically modified vegetable oil-based recycling agent (**Anova 1817**)
    - Dynamic Viscosity at 1Hz and 60°C: 28.5 cSt
    - Dynamic Viscosity at 1Hz and 135°C: 6.6 cSt
    - Flash Point: >290°C

Comparisons were performed on the 40hr PAV aged PG 64-22 (Pen 50-70) base binder using an equal 5% by weight dosage of recycling agent to the 40hr PAV aged bitumen. Previous work has shown that 40 hrs of aging can simulate the properties of a highly aged Reclaimed Asphalt Pavement (RAP) binder [8].

The categorization of recycling agents, as proposed in the previous sections, is mainly based on the bitumen chemical fraction with the most affinity with the recycling agent. In order to better understand the possible effect mechanisms of the Modified Vegetable Oil-Based Rejuvenator (Anova 1817) and the Aromatic Oil-based rejuvenator, SARA (Saturates, Aromatics, Resins, Asphaltenes) fractionation was performed on aged and rejuvenated bitumen binders. Asphaltene content determination was performed using an N-Heptane solvent extraction method. The fractionation of the N-Heptane soluble fractions (the "maltenes") was performed using an Iatroscan Thin Layer Chromatography methodology. The saturates were separated through an N-Pentane elution, followed by a Chloroform-Toluene blend (90:10 by volume) elution to separate the aromatic phase from the polar aromatic (resin) fraction. The Iatroscan employs a Flame Ionization Detector (FID) to quantify the fractions separated by each elution. The results are shown in Figure 1.

In both Figure 1(a) and (b), the rejuvenators increased the maltene phase of the aged bitumen, and as a result reduced the asphaltene to maltene ratio. Not surprisingly, Figure 1(a) indicates that the addition of the aromatic oil-based rejuvenator had the highest contribution to the aromatic fraction of the aged bitumen while the other maltene fractions remained relatively unchanged.

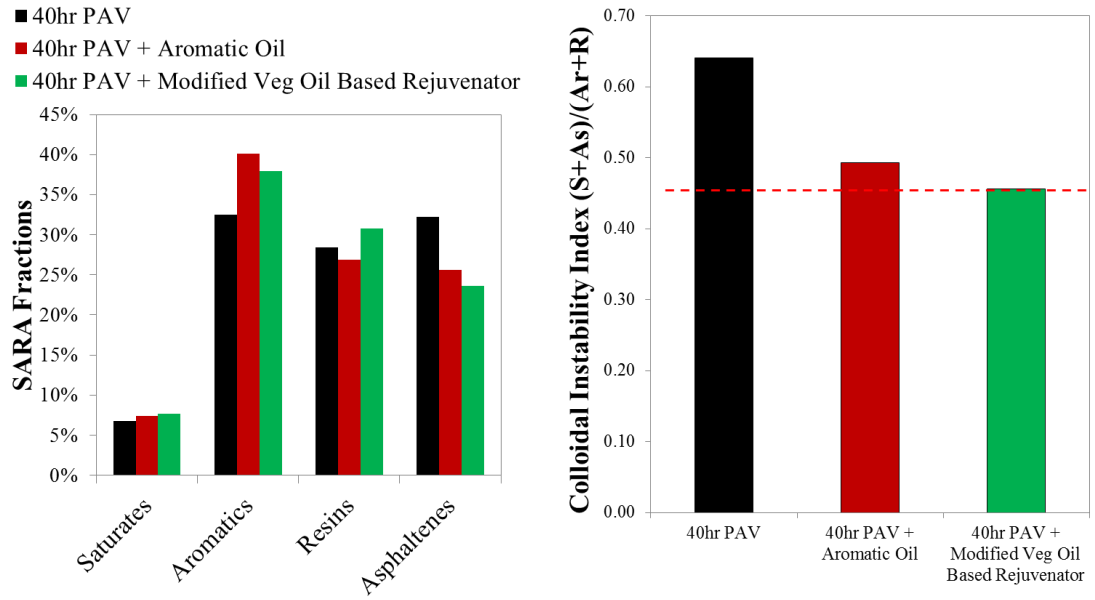
Based on the categorization used in the previous section this recycling agent would be most closely categorized as a "Solvator". On the other hand, the addition of the Modified Vegetable Oil-based rejuvenator (Figure 1(b)) increased both the aromatic and the resin content of the maltene phase, which would indicate sharing aspects of both the "Solvator" and the "Compatibilizer" categories using the aforementioned definitions. Thus in accordance to the previously presented definitions, the Modified Vegetable Oil-based Rejuvenator can be labeled a "Reactivator".



(a) *(b)*

Figure 1. Effect of rejuvenation on the SARA fractions of 40hr PAV-aged bitumen using (a) an aromatic oil-based rejuvenator, and (b) a Modified Vegetable Oil-based Rejuvenator.(Anova 1817)

The "Gaestel Index" (GI) has been used by researchers to describe the dispersion in polarity of the constituent molecules, especially when describing the bitumen using the dispersed polar fluid model. The parameter is sometimes referred to as the "Colloidal Instability Index" when describing the bitumen using the colloidal model. The index is calculated as the ratio of the sum of the asphaltene and saturates fractions (insoluble fractions) to the sum of the aromatic and resin fractions (the "solvent" phase). Smaller values of the index indicate a higher stability and better dispersion of the micelle fractions in the bitumen. Figure 2(b) shows that the Colloidal Instability Index was reduced significantly by the addition of both rejuvenators, with the most improvement occurring for the binder rejuvenated using the modified vegetable oil based rejuvenator.



(a) *(b)*

Figure 2. (a) Summary of SARA fraction results of aged and rejuvenated binders. (b) Effect of rejuvenation (Anova 1817) on the Colloidal Instability Index of highly aged bitumen (S = Saturates, As = Asphaltene, Ar = Aromatics, R = Resins)

4. Conclusions

The following main conclusions and summations are derived from the findings of this study:

- A method was proposed for the categorizing recycling agents based on the bitumen fraction most affected by the additive and the mechanism of expected effect as “Solvators”, “Compatiblizers”, and “Insoluble Softeners.”
- Using these definitions, the term “Reactivator” has been proposed to represent recycling agents that simultaneaously exhibit properties of both “Solvators” and “Compatiblizers.” The ideal objective of a “reactivation” process is not the reversal of aging, but is rather the reversal of the “impact of aging” on bitumen mechanical and rheological properties, damage resistance, and overall durability and performance.

- The addition of the chemical modified Vegetable Oil-based rejuvenator to aged bitumen increased both the aromatic and the resin content of the maltene phase, which would indicate sharing aspects of both the “Solvator” and the “Compatibilizer” categories using the aforementioned definitions. Thus in accordance to the previously presented definitions, the Modified Vegetable Oil-based Rejuvenator can be labeled a “Reactivator”.

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