Binder performance and testing

Use of plant derived sterols as an age retarding additive for bitumen and asphalt mixtures

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Abstract

Rejuvenating additives for bitumen and bituminous mixtures is subject of much current research to facilitate the use of greater levels of aged bitumen in form of RAP and/or RAS. The additives are typically petroleum or plant derived oils that function as softening agents for aged bitumen and therefore reduce high and low temperature stiffness properties but do not reverse the aging of the bitumen. More importantly these additives do not significantly alter the rate at which treated, aged bitumen (RAP) is impacted by subsequent aging. Our research has shown that plant (phytosterols) can significantly retard the aging of virgin bitumen and can slow down the rate at which aged bitumen when treated with sterols undergoes additional aging. The sterol additive mainly acts to reduce the rate at which bitumen relaxation properties degrade with aging. Because as bitumen ages it becomes more m-controlled the ability of an additive to retard the rate at which bitumen relaxation degrades results in bitumen with a longer service time to failure. The economic benefits of extending the aging time of binder is obvious for long term performance. The use of higher RAP levels is also possible because the age retarding impact of sterol results in RAP binder aging at a slower rate compared to other additives. Sterol also acts to reduce the rate at which high temperature stiffness properties increase due to aging. The rate at which low temperature stiffness properties increase is the least affected property. Test sections in Wisconsin and Iowa have been constructed. Additional laboratory testing has shown that surface applications with emulsion containing sterol reduce the aging rate of the bitumen in the mixture surface compared to no treatment or emulsion treatment without sterol

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1. INTRODUCTION

Research into performance of rejuvenating additives to facilitate use of increased amounts (greater than 30% bitumen replacement) of reclaimed asphalt pavement (RAP) and reclaimed asphalt shingles (RAS) in bituminous pavements has increased in the past 10 years. Aromatic petroleum derived additives or soft bitumen materials have typically been used to accomplish this task. More recently there has been an increasing development and use of bio-derived products to fill rejuvenation needs. These bio-derived products are obtained from vegetable-based sources such as soybean, corn, rape seed and similar products or tree-based oils obtained from the Kraft pulping process as tall oil and various fractions of tall oil. These bio-based sources have been marketed in crude form with little or no processing as well as products that have undergone substantial reaction chemistry to provide products with improved bitumen compatibility and reduced aging potential. MTE and Paragon Technical Services joint development group has investigated many of the bitumen products and found that while these additives are very good at softening aged bitumen the resultant bitumen does not age well. Similar findings were published by (Ongel, 2015). We have also found that bio oil containing aged bitumen materials do not exhibit characteristics that are considered to identify a bitumen that has been "rejuvenated". Properties such as Black Space Plots and Rheological Index data should be improved if rejuvenation has occurred (Mogawer, 2015). In our search for chemistry to accomplish this goal we evaluated many products including plant-based sterols. Initial results were presented at the 2017 TRB meeting (Reinke G. ,., 2017). We reported sterol retards the aging rate of bitumen compared to the aging rate of the same bitumen with no sterol additive. We also showed 5% sterol retarded aging of PG 52-34 bitumen containing 20% bitumen recovered from tear-off shingles compared to the same blend without sterol. In the current work we investigate the impact of aging on laboratory aged bitumen combined with varying amounts of sterol subjected to additional aging. Additionally, aging analysis of several bio-derived oil blends with the same aged bitumen were conducted. Further aging of the aged bitumen plus sterol and bio oils was conducted because RAP in mixes will be subjected for further aging on the road in actual service. A possible mechanism of action is also presented.

2. STUDY DESIGN

2.1. Aged bitumen at seven sterol loadings and four aging times

PG 58-28 bitumen was aged in six large pans in a 135°C forced draft oven for an average of 72 hours to produce a surrogate RAP bitumen. The mass in the pans was ≈195 grams; equivalent film thickness of 17 grams in standard PAV pans. Three such aging cycles of six pans each were conducted, the resulting bitumen was comingled, mixed and aliquoted into 200-gram containers to serve as base bitumen for evaluating rejuvenating additives. Table 1 reports the rheological and Iatroscan results of the aged bitumen. Asphaltenes were determined as n-heptane insolubles according to ASTM D3279.

Table 1. Rheological and compositional properties of lab aged bitumen

RHEOLOGICAL PROPERTIES OF AGED BITUMEN				
PG @ 2.2 kPa	R-Value[1]	$T_{S\text{-}Critical}$, °C	$T_{m\text{-}Critical}$, °C	ΔT_c, °C
116.9	2.683	-24.14	-18.36	-5.78
COMPOSITIONAL PROPERTIES OF AGED BITUMEN				
Asphaltenes	Resins	Cyclics	Saturates	Colloidal Index (Loeber, 1998)
32.4	25.7	36.4	5.5	1.639

Sterol was added to 200-gram samples of the aged bitumen described in Table 1. The dosage level was 0%, 0.5%, 2.5%, 5%, 7.5%, 10% and 12.5%. All samples were tested in the as blended condition and after 20, 40 and 60 hours of PAV aging. The high temperature stiffness properties of all samples at all aging conditions was determined using ASTM D7175 and low temperature properties were determined using 4 mm Dynamic Shear Rheometer (DSR) procedure according to (Sui C. ,., 2010), (Sui C. F., 2011), (Farrar, 2012). Data analysis was performed using RHEA software (ABATECH, 2018) Using 4 mm DSR geometry is it possible to determine the low temperature limiting stiffness (S-value) grade and low temperature limiting relaxation (m-value) grade of the bitumen after each aging step. These parameters will be referred to $T_{S\text{-}Critical}$ and $T_{m\text{-}Critical}$ respectively. Based on these data the parameter Delta Tc (ΔT_c) is calculated as ($T_{S\text{-}Critical}$ - $T_{m\text{-}Critical}$) which is an industry adopted modification of work reported by Anderson et al (Anderson, 2011). Iatroscan analysis and FTIR data was collected for all samples at all aging conditions. Atomic Force Microscopy was performed on selected samples due to the time required to investigate all samples at all aging times.

2.2. Aged bitumen plus rejuvenating oils and rejuvenating oils plus sterol at four aging times

[1] R-value data in this paper is based on assuming glassy modulus to be 1E9 Pa. R-Value is defined as the difference of the Log (glassy modulus) and Log (modulus at the crossover frequency)

Testing was performed on several commercially available rejuvenating oils using the aged bitumen described above. Additionally, blends with some of those rejuvenating oils plus sterol were also tested at the four aging periods. Rheological properties, Iatroscan results and FTIR analysis were performed on these samples. ΔTc ΔTc

3 TEST RESULTS

3.1 Aged bitumen at seven sterol levels and four aging conditions

Table 2. Rheological properties of aged bitumen plus sterol at all aging times

PAV Aging hours	1 kPa PG Grade	2.2 kPa Grade	$T_{S\text{-}Critical}$	$T_{m\text{-}Critical}$	ΔT_c	R-Value
	AGED BASE BITUMEN 0.0% STEROLΔΔcc					
0	124.8	116.9	-24.14	-18.36	-5.78	2.683
20	130.1	122	-21.85	-10.26	-11.59	2.967
40	136.4	128.1	-20.26	-4.13	-16.13	3.192
60	148.4	139.5	-20.53	-0.32	-20.21	3.302
	AGED BASE BITUMEN 0.5% STEROL					
0	117.6	109.7	-24.92	-19.63	-5.28	2.663
20	128.4	120.2	-23.60	-14.01	-9.59	2.871
40	136	127.6	-22.05	-9.13	-12.92	3.064
60	143.7	135	-20.05	-0.47	-19.58	3.284
	AGED BASE BITUMEN 2.5% STEROL					
0	113	106.2	-24.36	-21.09	-3.27	2.482
20	122.4	114.5	-23.27	-16.51	-6.76	2.677
40	130.1	121.9	-21.36	-12.01	-9.35	2.842
60	137.9	129.5	-20.53	-7.01	-13.52	3.137
	AGED BASE BITUMEN 5.0% STEROL					
0	108.2	100.4	-25.02	-22.42	-2.60	2.303
20	116.8	108.9	-22.04	-17.30	-4.74	2.513
40	123.5	115.6	-20.69	-13.44	-7.25	2.727
60	130.8	122.6	-19.70	-11.17	-8.54	2.832
	AGED BASE BITUMEN 7.5% STEROL					
0	101.6	94.3	-24.25	-22.48	-1.77	2.098
20	112.4	104.7	-22.20	-19.77	-2.43	2.336
40	119.1	111.2	-20.10	-15.43	-4.67	2.497
60	125.5	117.1	-20.70	-13.99	-6.71	2.686
	AGED BASE BITUMEN 10.0% STEROL					
0	98	90.7	-25.05	-24.50	-0.55	2.012
20	107.8	99.3	-22.96	-21.35	-1.61	2.210
40	114.9	106.8	-21.69	-18.73	-2.95	2.323
60	119.2	111.4	-20.32	-16.26	-4.06	2.484
	AGED BASE BITUMEN 12.5% STEROL					
0	94.5	87.2	-23.46	-24.04	0.59	1.895
20	103.3	95.4	-22.85	-22.25	-0.60	2.007
40	110	102.4	-18.95	-17.24	-1.71	2.184
60	114.2	105.8	-18.75	-16.04	-2.71	2.276

Inspection of the data in Table 2 shows that at the lowest dosage level of 0.5% sterol there is a reduction in the high temperature PG grade due to sterol addition. As the dosage increases the high temperature PG grade is reduced. $T_{S\text{-}}$

$_{CRITICAL}$ is only moderately impacted by sterol due to aging, while $T_{m\text{-}CRITICAL}$ is substantially decreased compared to the zero-sterol control. All blends except for the unaged 12.5% sterol blend are m-controlled, however inspection of $T_{m\text{-}CRITICAL}$ data for each dosage level shows lower $T_{m\text{-}CRITICAL}$ values at each aging condition. The improvement of ΔT_c at each dosage level and conditioning time provides a means of quantifying the ability of sterol to retard the rate at which $T_{m\text{-}CRITICAL}$ is degraded due to aging. ΔT_c increases when $T_{m\text{-}CRITICAL}$ becomes more negative which means sterol has a marked, beneficial effect on the relaxation properties of the aged bitumen. The ability of sterol to retard the increase in $T_{m\text{-}CRITICAL}$ results in improved relaxation properties with increased sterol dosage and this leads to lower R-values because the cross over modulus remains higher compared to no or low sterol loadings. A few plots are provided to demonstrate the more meaningful impacts.

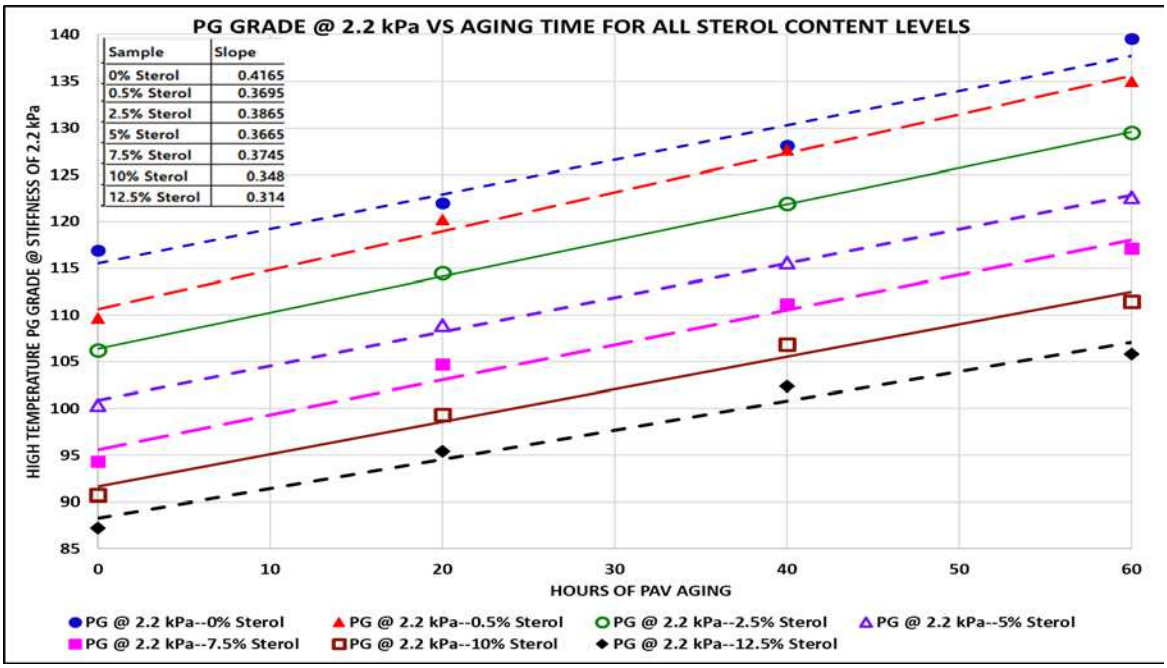

Figure 1: PG Grade @ 2.2 kPa versus PAV aging time in hours for all sterol content dosages

Figure 2: $T_{m\text{-}CRITICAL}$ plot versus PAV aging time in hours for all sterol content dosages

High temperature grade is reduced due to sterol loading; the reduction increases with dosage (Figure 1). Sterol does not prevent bitumen aging, but it reduces the rate of aging as evidenced by the diminishing slopes of the aging trends. At 5% dosage and above the rate of aging is lower than at the 2.5% dosage and lower.

Figure 2 shows $T_{m\text{-CRITICAL}}$ is substantially impacted by sterol dosage. At 0.5% sterol the rate of aging is similar to the rate of aging of the untreated aged base bitumen. As dosages increase the rate of aging decreases as evidenced by the decreasing slopes of the trendlines; there is a noticeable change from 0.5% to 2.5% sterol and again to 5% sterol. The most significant age retarding dosages are 2.5% to 7.5% with only modest improvement at 10% and 12.5%. This data should not be taken to imply that those higher dosages would never be impactful for all bitumen materials. Our research has shown that the more aging susceptible bitumen is more effect a higher sterol dosage has on retarding $T_{m\text{-CRITICAL}}$ aging. Aging was terminated at 60 hours, in part because we had found in previous work that 40 hours of PAV aging represented more than eight years of field aging in south east Minnesota (Reinke G. H., 2016). Had aging time been increased to 80 or 100 hours of PAV aging 10% and 12.5% sterol data would have differentiated themselves just as 2.5%, 5% and 7.5% sterol results are differentiated after 60 hours of aging even though their $T_{m\text{-CRITICAL}}$ data at zero time are similar.

3.2 Comparative analysis of sterol and bio-derived bitumen additives

Numerous bio-derived products are marketed as rejuvenators. Evaluation of all additives has not been possible, but several have been tested using the same procedure of blending recommended dosages into samples of the aged base bitumen utilized for the reported sterol data. All bio-derived additives reported in this paper have been code named and they are either seed oil or tall oil based and may have undergone chemical modification. All were obtained from the vendors with little specificity as to composition.

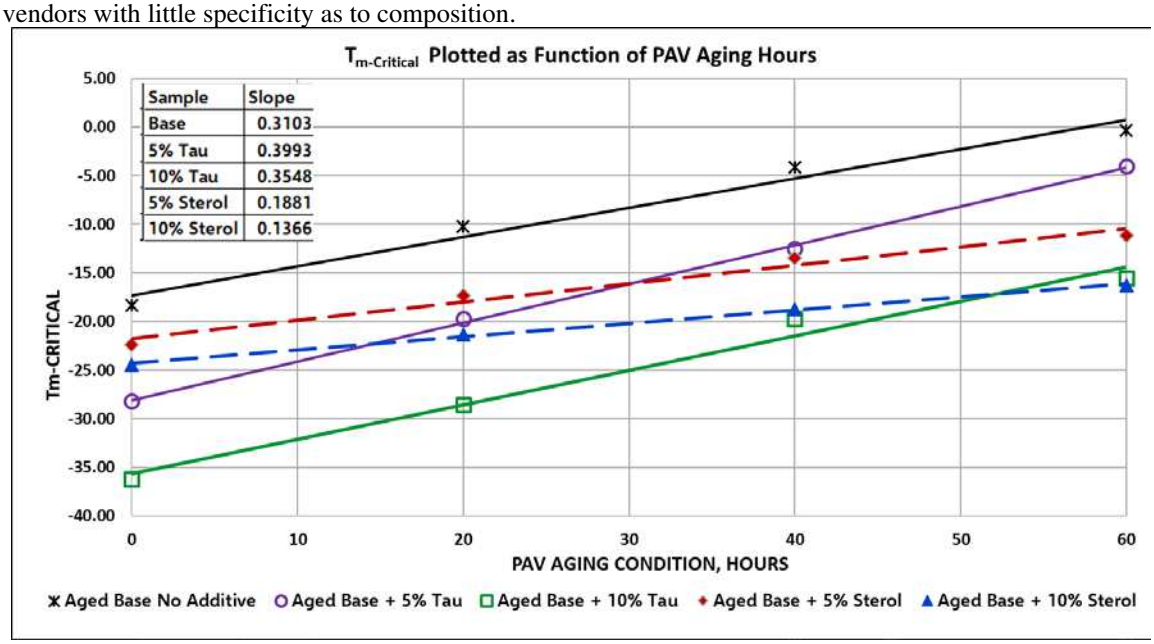

Figure 3: $T_{m\text{-CRITICAL}}$ plot as function of PAV aging condition in hours for sterol and bio oil Tau

$T_{m\text{-CRITICAL}}$ data in Figure 3 shows the bio oil labelled as "Tau" reduces $T_{m\text{-CRITICAL}}$ of the aged bitumen by 10°C for 5% and 18°C for 10% dosages. The comparative data also shows when this aged material is subjected to further aging the rate of aging based on the slopes of the data is higher than the aging of the base bitumen with no additive. This might be expected since the base material is an aged bitumen, however the sterol blends show a flatter aging rate. The 10% Tau blend also ages at a slightly more rapid rate than does the 5% Tau blend whereas the 10% sterol blend aging rate is lower than the 5% sterol blend. Beneficial rejuvenators should not age worse at higher dosage levels.

Figure 4 shows results for additional bio oils compared to sterol. The product labelled Sigma ages very rapidly, with 5% dosage being the same as the base bitumen with no additive after 60 hours of aging. The 10% Sigma and 10% Zeta have the same starting $T_{m\text{-CRITICAL}}$ value at zero time, but the Sigma blend exhibits a higher slope than the Zeta blend. The 4% Gamma blend has the lowest slope of all bio oils, but is also the lowest dosage. Although Gamma has a lower $T_{m\text{-CRITICAL}}$ value at zero time compared to 5% sterol after 20 hours of PAV aging the data are the same and beyond 20 hours the Gamma blend continues to age more rapidly than the 5% sterol.

The previous data has shown sterol possesses the ability to reduce the rate of further aging when combined with an aged bitumen. Sterol is not a softening additive and the reduction in high temperature and $T_{m\text{-CRITICAL}}$ and subsequent re-aging is, we hypothesize, due to sterol's ability to disrupt the asphaltene aggregation that occur due to aging. Sterol retards the aging of bitumen based on its ability to alter detrimental changes in the physical and compositional properties of the bitumen into which it is added. Data supporting these concepts will be discussed in another section.

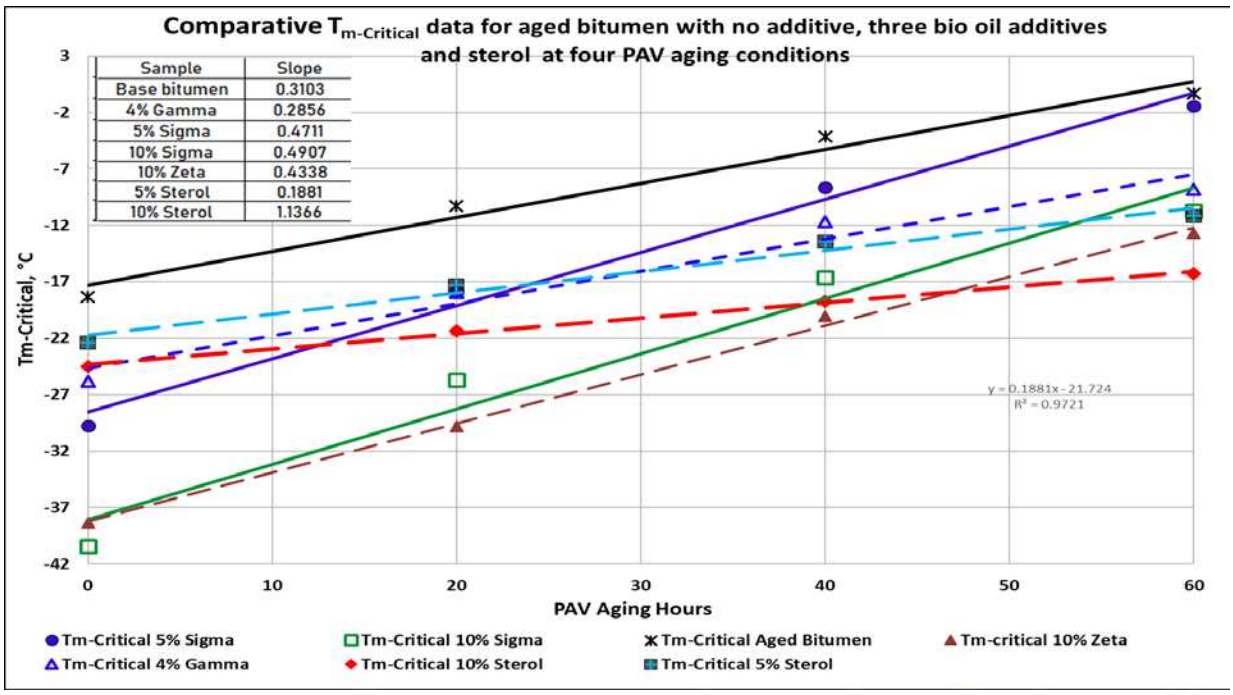

Figure 4: $T_{m\text{-}CRITICAL}$ as function of PAV aging condition for sterol and bio oils Sigma, Zeta and Gamma

Figure 5 provides some data to demonstrate this point. The 5% Zeta and 4% Gamma blends' data have been discussed; in Figure 5 data is presented with those same blends also containing 7.5% sterol. Sterol further reduces $T_{m\text{-}CRITICAL}$ of these blends as would be expected, but the sterol presence also alters the age retarding characteristics of the bio oil containing bitumen. Comparison of the slopes of the blends with sterol shows that slopes have been substantially reduced from blends without sterol.

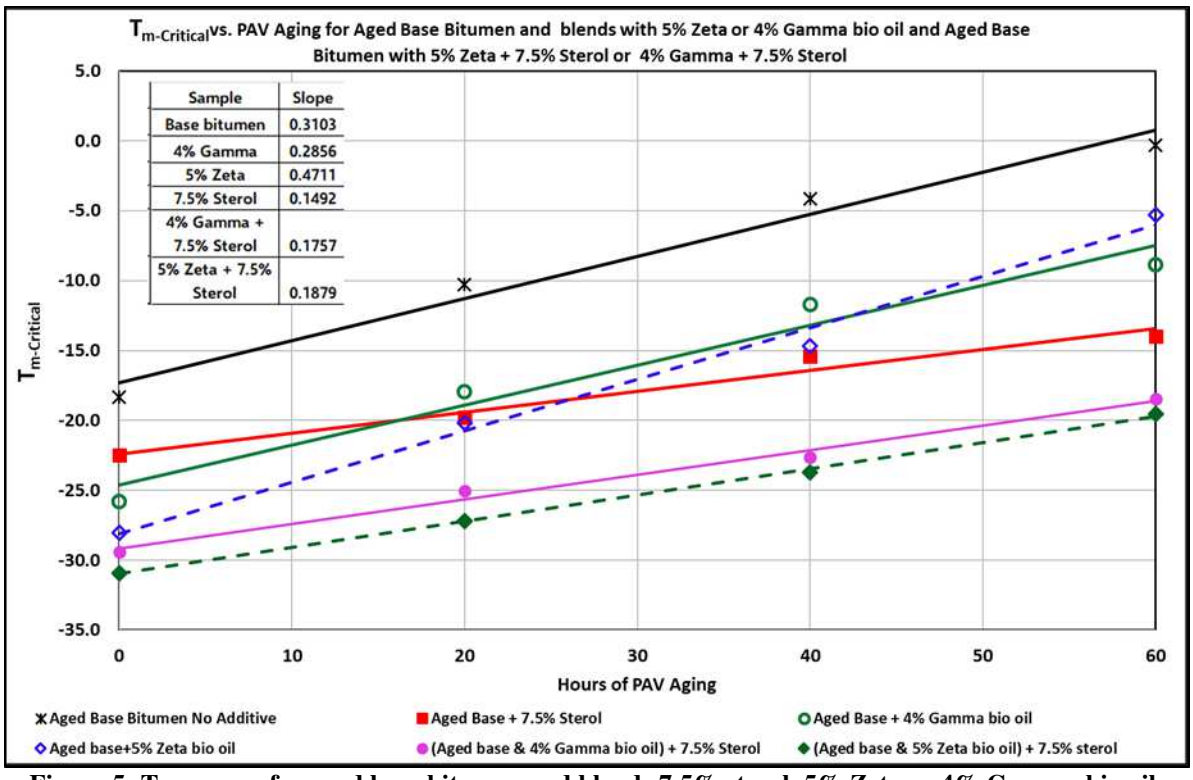

Figure 5: $T_{m\text{-}CRITICAL}$ for aged base bitumen and blends 7.5% sterol, 5% Zeta or 4% Gamma bio oils and those same blends with 7.5% Sterol

The slope for 5% Zeta only blend reduced from 0.4711 to 0.1879 for 5% Zeta plus 7.5% sterol. The presence of sterol cannot completely mitigate the poor aging characteristics of the Zeta additive, but it does provide a beneficial improvement to the age retarding of both Zeta and Gamma blends. This data does not suggest that 7.5% sterol is the desired dose to improve the poor aging properties of a bio oil. A lower dose of sterol in these blends would

have imparted less reduction in age retardation and a higher dose would have resulted in better performance. There is definite synergy between softening additives that can impart good starting properties and the use of sterol to conserve those beneficial properties when aging occurs. The optimum level of sterol and of softening additive would need to be determined based on properties of the starting materials.

3.3 Impact of asphaltene and carbonyl changes resulting from additive type, amount and aging time

Table 3. Asphaltene and carbonyl ratio for seven sterol levels and four aging times

	Asphaltenes					Carbonyl Ratio			
%Sterol	0 age	PAV 20	PAV 40	PAV 60	%Sterol	0 age	PAV 20	PAV 40	PAV 60
0	32.4	35.0	38.2	40.1	0	0.157	0.187	0.228	0.232
0.5	32.6	34.4	36.8	40.3	0.5	0.159	0.188	0.213	0.236
2.5	30.9	34.0	35.7	37.8	2.5	0.160	0.189	0.217	0.225
5	30.9	33.4	34.3	36.6	5	0.157	0.183	0.210	0.232
7.5	28.6	31.3	34.2	36.0	7.5	0.149	0.187	0.208	0.229
10	28.2	30.8	33.4	36.1	10	0.146	0.173	0.213	0.228
12.5	27.0	29.8	31.7	34.9	12.5	0.146	0.175	0.205	0.220

Table 3 lists asphaltene and carbonyl ratio data for the sterol blends in aged bitumen at four aging times. The reduction in asphaltenes and carbonyl at zero aging must be considered as a dilution of the existing properties of the bitumen. Subsequent aging for each dosage shows, as expected, increase in both asphaltenes and carbonyls. Examination of the PAV columns for asphaltenes and carbonyls shows decreasing levels of both these products of aging. Whether these decreases are just the dilution effect being carried forward is a question to be answered by evaluating a physical property impacted by asphaltene or carbonyl increases due to aging.

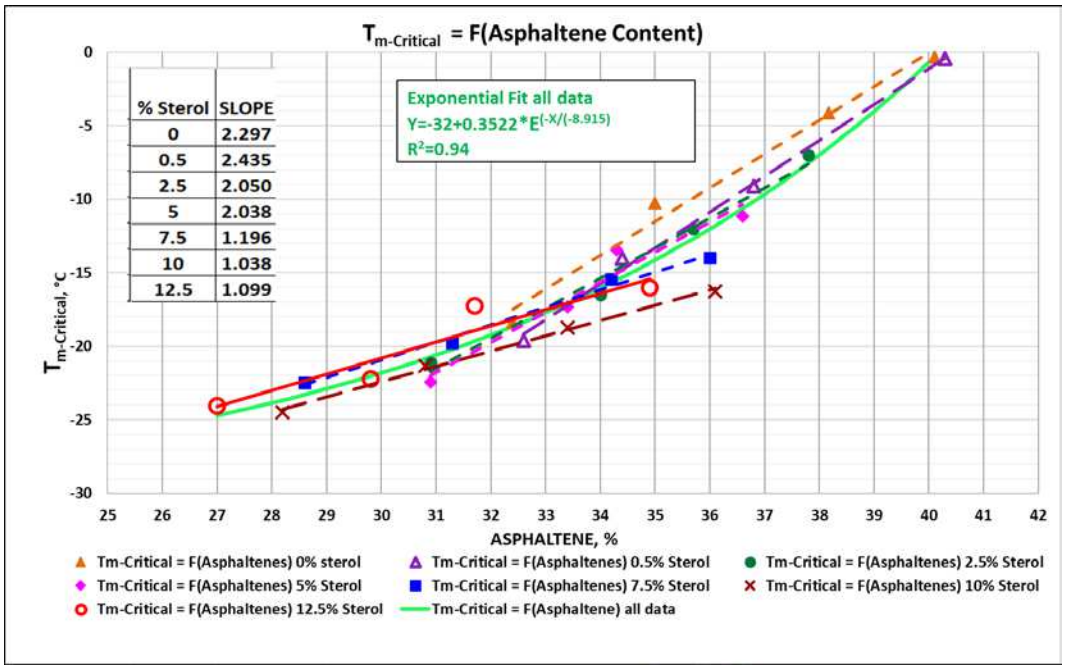

Figure 6: Plot of $T_{m\text{-}CRITICAL}$ as a function of asphaltenes at seven sterol dosages over seven aging conditions

Figure 6 plots the asphaltene data from Table 3. The slopes for individual dosage levels at four aging times are shown in the insert. The expectation was that the data would move to the lower right side of the plot in an approximately parallel fashion relative to the zero sterol at zero aging time. The 0.5% sterol dosage followed that pattern, but subsequent sterol dosages behaved in an unexpected fashion. Although the plot is busy with overlapping data the precise point of Figure 6 is that these data are behaving more as a single material than seven different samples. The slopes of $T_{m\text{-}CRITICAL}$ as a function of asphaltene content flatten with increasing sterol content while at the same time decreasing the overall range of asphaltenes from the unaged to the PAV 60 condition. Examination of the total data gave the appearance of not seven different sets of data but a single set of data describing the aging behaviour of sterol concentration with respect to aging. When an exponential function was fit

to the total data a smooth function resulted with a R^2 of 0.92. This was the first definitive indication that sterol was impacting the internal structure of the bitumen and provided an explanation as to why aged sterol blends exhibited age retarding functionality

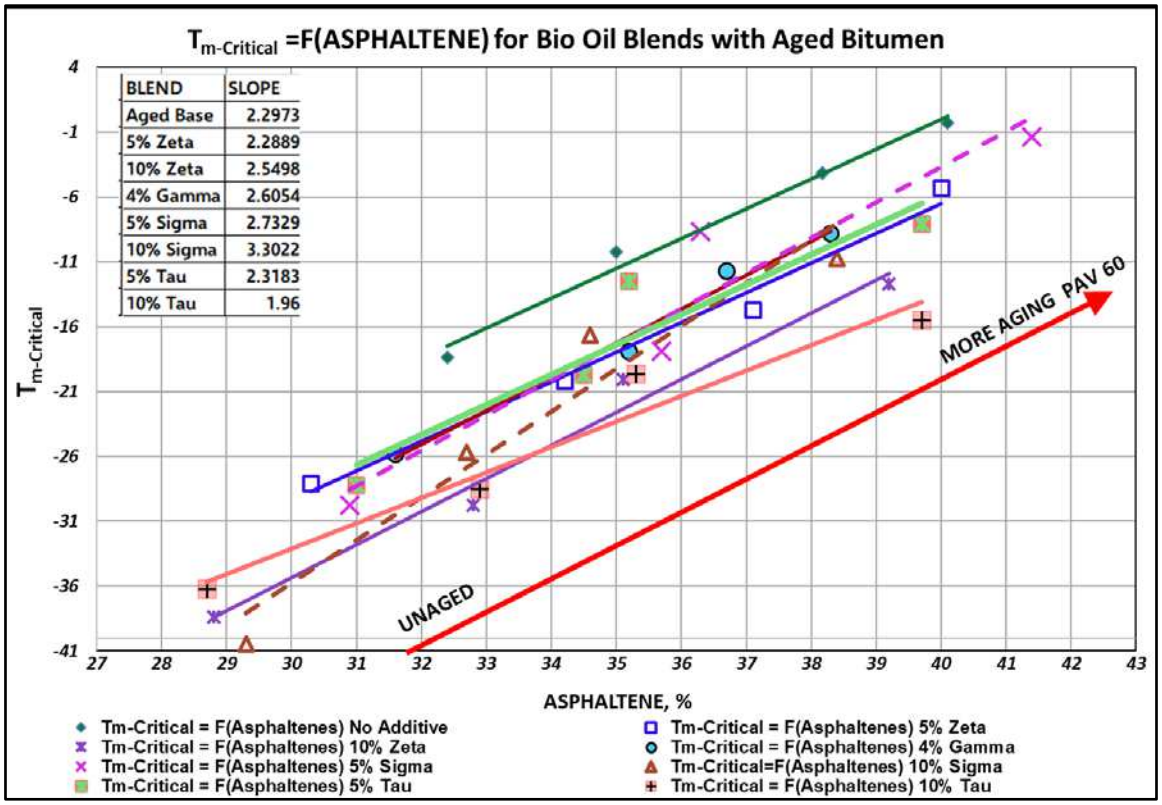

Figure 7: Plot of $T_{m\text{-}CRITICAL}$ as a function of asphaltenes for four bio oils at two dosage levels

To further explore this theory asphaltene data for bio oil blends produced with the same aged bitumen source were obtained. $T_{m\text{-}CRITICAL}$ was plotted as a function of asphaltene content for several of the bio oil blends. The results of those data are plotted in Figure 7. In contrast to the behaviour observed for the sterol blends in Figure 6, the data for many of the blends presented in Figure 7 overlap exhibiting little differentiation. The slope data shows little differentiation from that of the aged base bitumen indicating asphaltene aging rate comparable to the base bitumen. Except for the 10% Tau sample all blends had slopes higher than the base bitumen which means those blends had an increased rate of asphaltene growth with aging. All blends exhibited decreases in asphaltenes at zero time indicative of a dilution effect. The three 10% blends had asphaltene levels at zero time 3.5% to 4% lower in asphaltenes (a dilution effect) than the base bitumen, but after 60 hours of aging were only 0.5% to 1% lower. The 5% blends after 60 hours of aging had asphaltenes matching the base bitumen. The data in Figure 7 is indicative of softening (as evidenced by a nearly parallel shift from aged base bitumen to lower $T_{m\text{-}CRITICAL}$ values) and dilution (a diagonal shift to the lower left towards lower levels of asphaltenes relative to the aged base bitumen initially, but not a rejuvenating effect on the aged bitumen into which it was blended because of reduction in sustainability.

Trends in carbonyl ratio data also demonstrate the age retarding effect of sterol relative to bio oil modified bitumen. Figure 8 plots the carbonyl ratio for the seven sterol blends at all aging times with the aged base bitumen of this study. As with the asphaltene data there is little change at 0.5% sterol loading. As the sterol dosage increases the slopes of $T_{m\text{-}CRITICAL}$ as a function of carbonyl ratio rotate to lower values. At 5% sterol and greater the initial carbonyl values begin to decrease; again, this is believed to be a dilution effect. However, the rate of carbonyl increase would not be a dilution effect. If the sterol addition was a dilution effect the slopes relative to the untreated base bitumen should be similar and they are not. Carbonyl growth is a result of bitumen aging and the sterol in a dose response mechanism is disrupting the rate at which carbonyls increase due to aging. In comparison data in Figure 9 shows carbonyl data for 5% and 10% Zeta and 5% and 10% sterol and the aged bitumen. Note that the range over which the carbonyl ratio was determined for these two sets of data are different. Data in Figure 8 were obtained using a base line region of 1740 to 1517 cm^{-1} and a carbonyl region of 1721 to 1676 cm^{-1}, which is typical for bitumen. For the data in Figure 9 an expanded carbonyl region was used because the Zeta additive, being bio-derived, contained carbonyl chemistry which had to be considered but not included as resulting from aging. Therefore, the aged base bitumen and sterol samples were reanalysed over the same wave numbers as the Zeta blends. The carbonyl baseline was 1800 to 15141 cm^{-1} and the carbonyl data determined over the range of 1755 to 1676 cm^{-1}. This explains the

higher carbonyl ratios for the base bitumen and the sterol samples in Figure 9, but this approach does not disadvantage the Zeta blends

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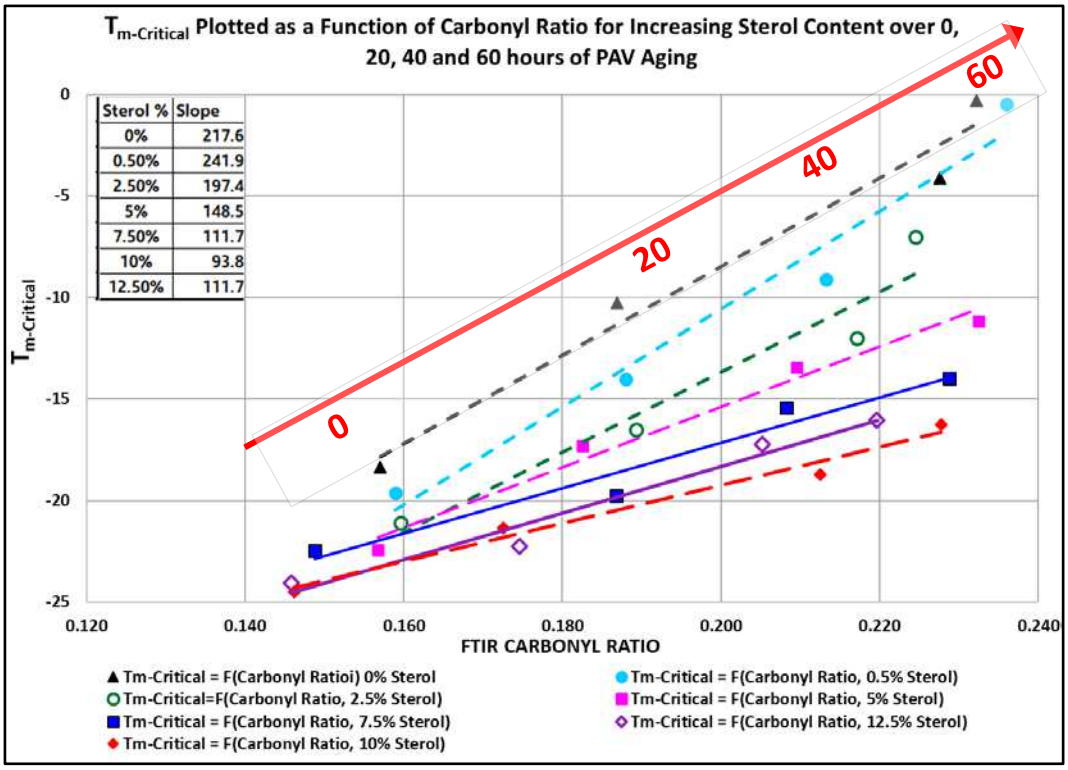
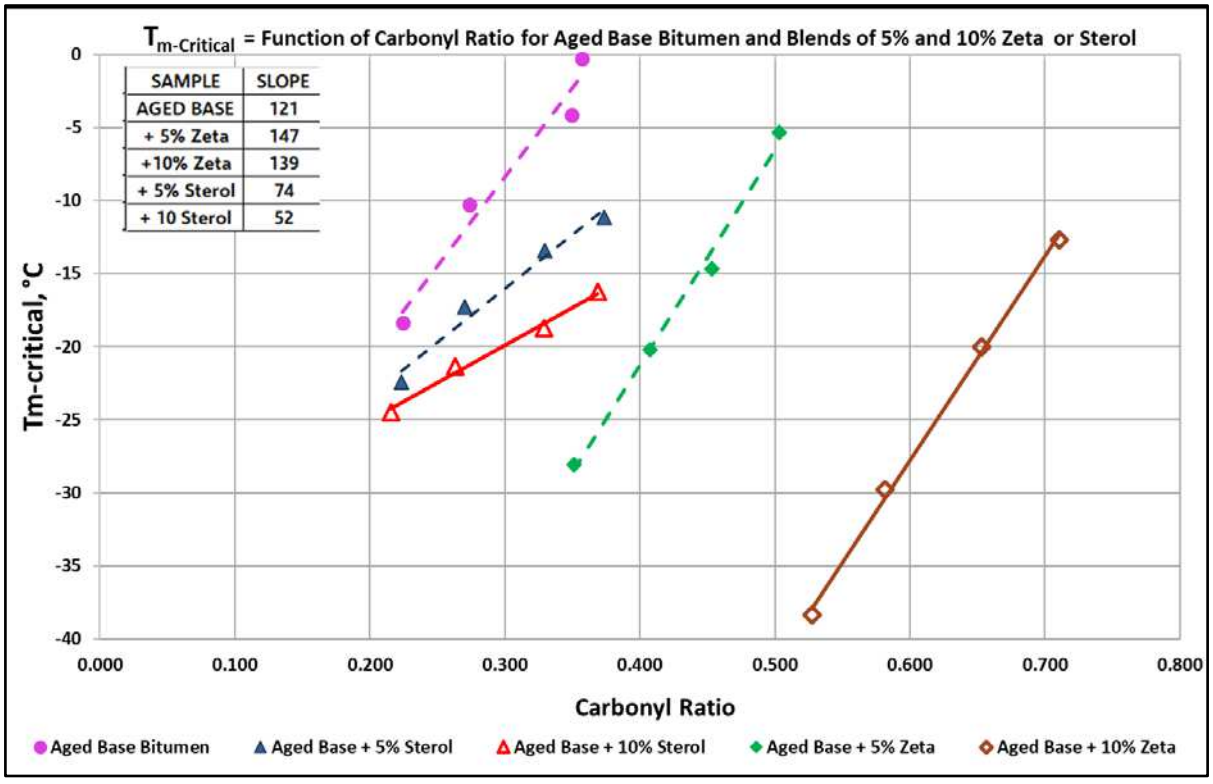


Figure 8: Plot of $T_{m\text{-}CRITICAL}$ as a function of carbonyl ratio at seven sterol dosage levels and four aging times



dFigure 9: $T_{m\text{-}CRITICAL}$ as a function of carbonyl ratio for aged base bitumen and blends with 5% and 10% Zeta and 5% and 10% Sterol

The Zeta data in Figure 9 shows a definite increase in carbonyl ratio, most of which is due to the carbonyl containing molecules in the product which is not particularly concerning. Consistent with the asphaltene data a dilution effect is shown by the shift to lower $T_{m\text{-}CRITICAL}$ values for the Zeta oil blends. The increase in $T_{m\text{-}CRITICAL}$ for the Zeta blends due to aging occurs at a rate comparable to the aged bitumen as shown by the slope values. The

sterol samples show a dilution effect of 5°C to 7°C decrease in $T_{m\text{-}CRITICAL}$ at zero aging time but also exhibit a reduced rate of aging relative to the original base bitumen and the Zeta blends.

3.4 Comparative analysis of R-Value data for bio-derived oil and sterol blends

According to Mogawer, et al (Mogawer, 2015) a bitumen rejuvenating effect results when an additive is able to improve the rheological index or R-Value when added to a bitumen. Utilizing a constant glassy modulus of 1E9 Pascals an improvement in R-Value requires that the crossover modulus of the bitumen increases. For the crossover modulus to increase the bitumen must relax more rapidly (i.e. at a higher frequency on the mastercurve) than a comparable bitumen with a lower crossover modulus. When the bitumen crossover modulus increases $T_{m\text{-}CRITICAL}$ for that bitumen decreases to lower temperatures. Therefore, the relationship between $T_{m\text{-}CRITICAL}$ and R-Value will be an indicator as to whether anything that could be considered a rejuvenating effect has occurred. Figure 10 plots R-Value data for four different bio-derived oils and sterol at 5% and 10% dosage rates as a function of $T_{m\text{-}CRITICAL}$ in comparison to the aged base bitumen used to produce all blends. The plot for the aged base bitumen has been extended to lower $T_{m\text{-}CRITICAL}$ values to show all the bio-derived oil samples are in a region where R-Values trend higher than the base bitumen. The Tau oil data plots closer to the base bitumen, but the 10% bio oil data always plots at higher R-Values than the 5% bio oil data for each pair of samples. This implies that using more of the bio oil will ultimately result in higher R-Values for any given $T_{m\text{-}CRITICAL}$ temperature. Sterol data plots below the base bitumen.

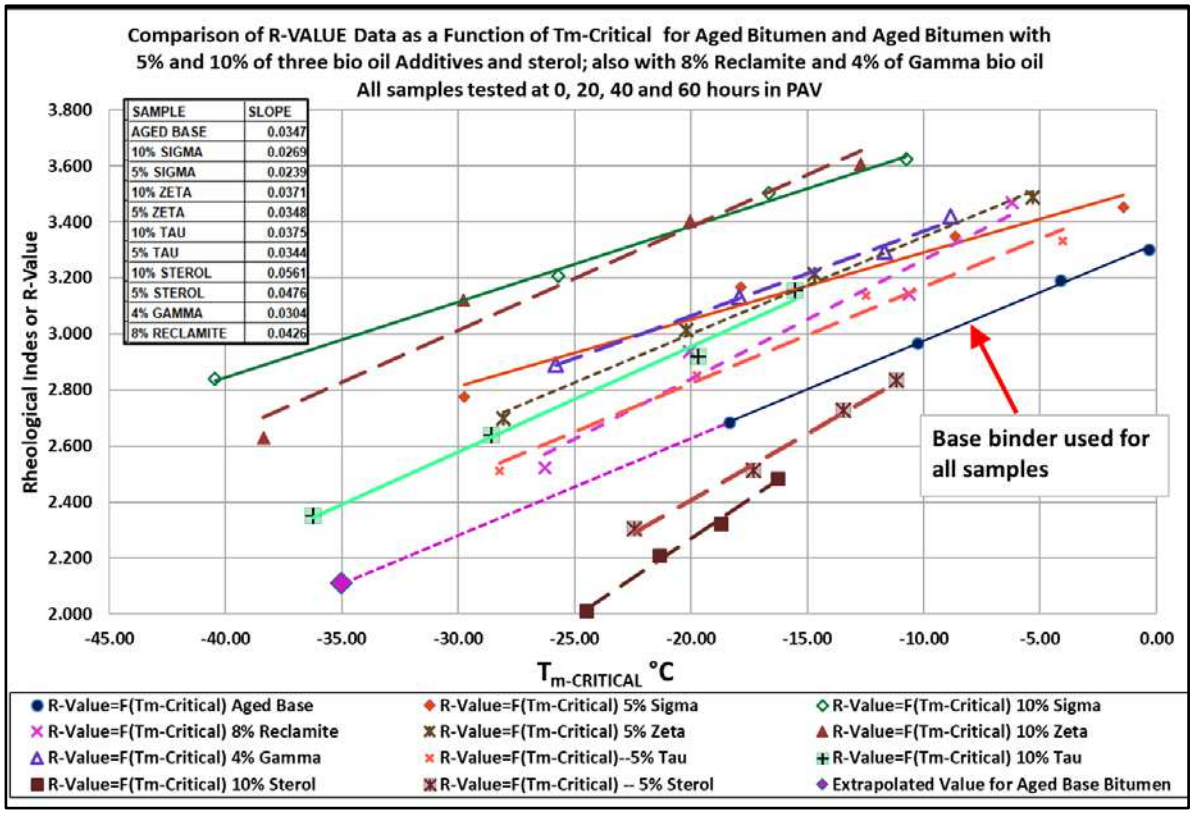


Figure 10: R-Value plotted as a function of $T_{m\text{-}CRITICAL}$ for bio-derived oils, Reclamite and sterol blends in aged bitumen base at four aging conditions

It is doubtful that any additive can truly rejuvenate (as in reverse aging) aged bitumen. The carbonyl data for sterol blends in Figures 8 and 9 and the carbonyl data in Table 3 show carbonyl levels for all blends at each aging time to be similar within a narrow range implying that the increase in carbonyls with aging is ongoing. The difference in bitumen properties is not a function of rejuvenation but rather a function of disrupting how those carbonyls structure in the bitumen to affect relaxation. Similar comments apply to asphaltenes. Asphaltenes continue to increase with aging (Figure 2 and Table 3) but their rate of increase is reduced, and this results in better low temperature properties. It is within the mechanism of sterol's interaction in the bitumen that reduces this rate of increase. The Atomic Force Microscopy data which follows provides additional support for this interpretation.

3.5 Atomic Force Microscopy (AFM) evaluation of sterol contain aged bitumen blends

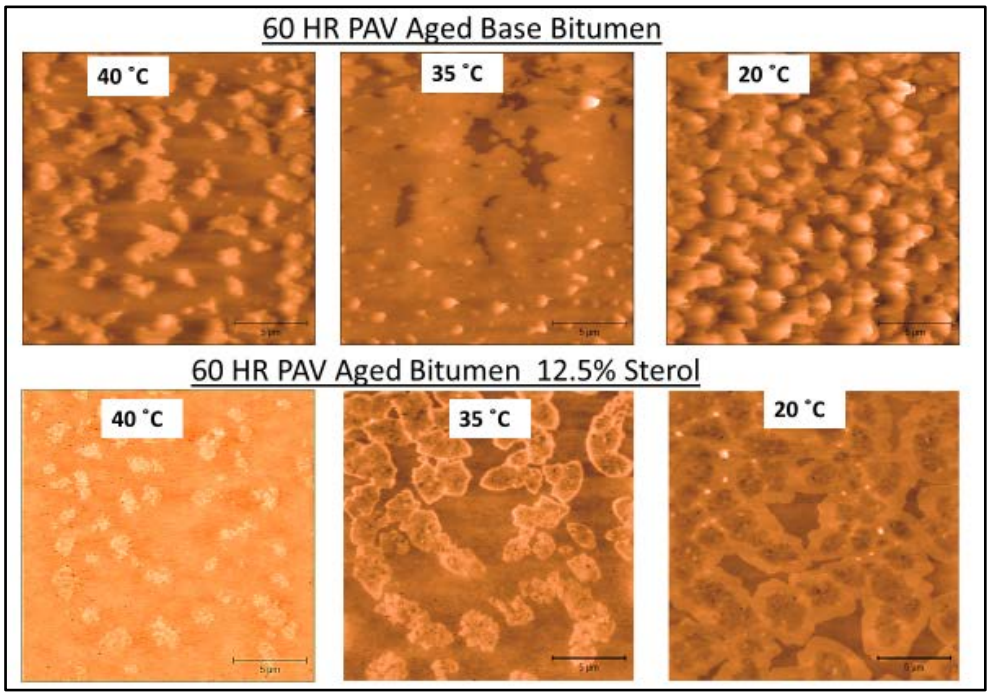


Figure 11: Morphological evolution of surface structure for zero sterol and 12.5% sterol

Atomic Force Microscopy was utilized evaluate differences between surface properties of aged base bitumen after 60 hours of PAV aging for no sterol, 7.5% sterol and 12.5% sterol. Because of sample stiffness test samples were deposited at 135°C on 20mm AFM pucks at 10 µm thickness, annealed for 5 minutes and cooled to the starting imaging temperature of 50°C. Imaging was conducted at intervals of 5˚C from 50˚C to 20˚C. An Agilent 5500 AFM using Mikromasch NSC15 cantilevers was used to perform non-contact imaging, using acoustic AC mode to yield topographic and phase images. At 50°C the image showed no structuring of the bitumen samples. Figure 11 shows the scans at 40°C, 35°C and 20°C for zero sterol and 12.5% sterol after 60 hours of PAV aging. Each image is 20 µm by 20 µm.

To analyse the surface structural changes in these samples with cooling 20 line-profiles were taken across the surface of structures protruding from the surfaces at each temperature. Using this data an average height at each temperature for the untreated, 7.5% and 12.5% sterol samples were determined. Also determined was the RMS roughness (Figure 12) over total surface area of the scans which are 512 by 512 pixels. The average heights for these samples at 20°C are 15.8 nm for 0% sterol, 14.4 nm for 7.5% sterol and 3.6 nm for 12.5% sterol. Reduced heights and roughness is indicative of fewer defects.

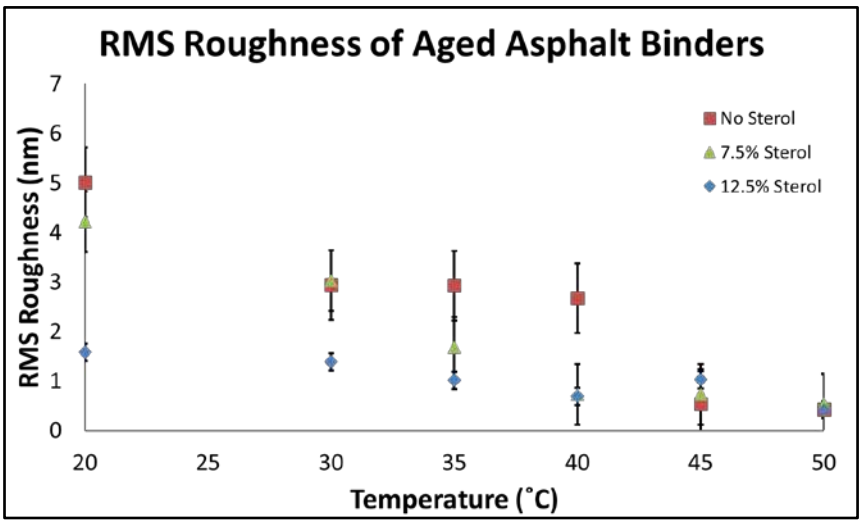


Figure 12: Surface roughness for 60-hour PAV samples of zero, 7.5% and 12.5% sterol

The data and images show that the presence of sterol, even at the most aged condition is able to retard or disrupt the development of surface defects in a dose responsive fashion. Plots of asphaltenes and carbonyl ratio for 0%,7.5% and 12.5% sterol taken from Table 3 are plotted in Figure 13. Asphaltenes and carbonyls are not temperature

dependent, but the plots show that at 20°C the change in roughness is minimal between 0% and 7.5% and at 40°C the change between 12.5% and 7.5% is minimal. This reflects that as temperature decreases the surface defects, expressed as RMS roughness have a temperature dependency. Once again these are the most aged samples and less temperature dependency would be expected at the shorter aging conditions.

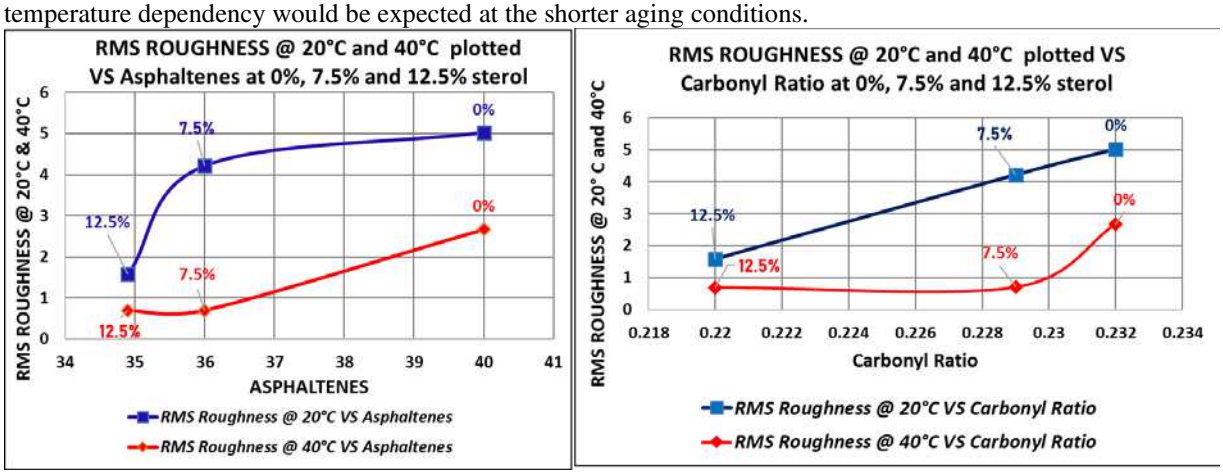


Figure 13: Plots of RMS roughness for 0%, 7.5% and 12.5% sterol blends after 60 hours PAV aging

4 CONCLUSIONS

Sterol when blended into bitumen does not function as a softening additive, although some reduction in high and low temperature stiffness does occur.

The main function of sterol addition to bitumen is to alter the internal structure of the bitumen to retard the rate at which the bitumen ages.

Bitumen that ages rapidly seems to be more significantly impacted by sterol than bitumen that has good aging properties

Comparative testing of aged bitumen using sterol and several bio-derived oils shows that sterol retards the re-aging rate of the bitumen as demonstrated by

1. A decreased rate of increase in $T_{m\text{-CRITICAL}}$
2. A decreased rate of decrease in ΔT_c
3. Reduction in high temperature PG Grade
4. A dose dependent response of the above

$T_{m\text{-CRITICAL}}$ as a function of asphaltenes and carbonyl ratio for aged bitumen with seven levels of sterol showed

1. Increase in $T_{m\text{-CRITICAL}}$ is reduced with increasing dosage
2. Asphaltenes increase when aging occurs, but at a reduced rate compared to the same bitumen treated with bio-derived oils or no additive
3. Based on the AFM data of the reduction in surface roughness and heights of imperfections it appears as though sterol is disrupting the formation structures within the bitumen that result in bitumen stiffening and loss of relaxation.
4. We postulate that sterol is dispersing asphaltene aggregation and the stiffening caused by carbonyl growth. Data shows that carbonyls increase at nearly the same rate when sterol is present or not, but the low temperature relaxation properties don't reflect this growth.

Bio-derived oils serve to soften or dilute aged bitumen and thereby reduce low temperature stiffness and high temperature stiffness substantially. These changes appear to be transitory and degrade rapidly with aging

The age retarding properties provided by sterol appears, based on the data in this paper, to preserve much of the softening provided by bio oil additives.

The AFM data provides physical, structural evidence supporting the inferential results of rheological and bitumen compositional data that the internal structure of the bitumen is aging by mechanism that is different than the aging mechanism typically observed.

5 ACKNOWLEDGEMENTS

The authors wish to acknowledge the dedication and hard work of Doug Herlitzka and Mary Ryan specifically as well as the entire laboratory staff at MTE Services, Inc.

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Annex

1. UPDATED RESEARCH FINDINGS FOR STEROL TREATED BITUMEN

Subsequent to submission of the paper in 2019 our research has continued to better understand the properties of sterol enhanced bitumen. Two findings of importance will be discussed in this document.

1. The sterol that is added to bitumen and then aged is not consumed during the aging of the bitumen
2. When sterol is added to a bitumen that bitumen not only ages at a reduced rate but based on our analysis the bitumen exhibits unique and improved aging and rheological characteristics compared to the starting bitumen. The result being the sterol containing bitumen is functioning as a different bitumen.

1.1. Impact of aging on the sterol content present in bitumen

We have shown that when sterol is added to bitumen followed by aging the bitumen ages at a reduced rate, asphaltenes and carbonyls are decreased and those two species of aging increase at a reduced rate with further aging. Our normal procedure used to evaluate bitumen treated with additives is to determine rheological properties at each aging step, perform FTIR tests and Iatroscan (NTS Iatroscan® MK-6, n.d.) testing after each aging step. Prior to performing the Iatroscan FID procedure asphaltenes are separated from the bitumen sample using ASTM D 3279. Figure 1 shows Iatroscan test results for two sterol bitumen blends and the original bitumen. Analysis of Iatroscan data shows that sterols elute with the resin fraction but at a slightly shorter time and therefore show up as a separate peak.

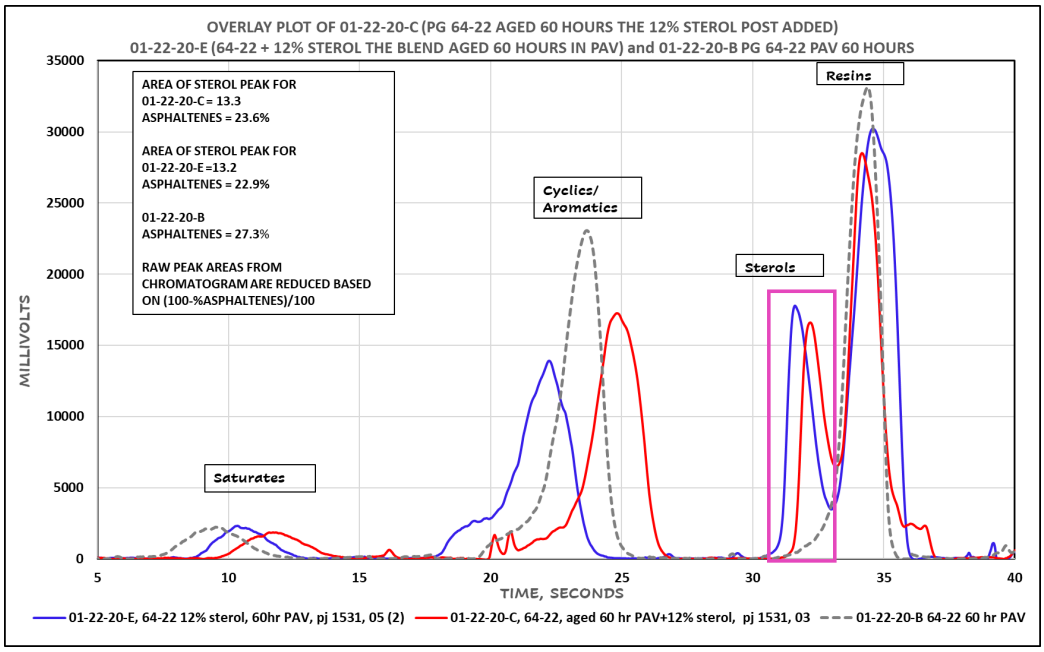

Figure 1: Overlay of Iatroscan results for 64-22 bitumen plus 12% sterol aged 60 hours in PAV and 64-22 bitumen aged for 60 hours in PAV to which 12% sterol was post-added

What is more important however, is that the area of the sterol peak does not decrease after aging of the treated bitumen. Sample 01-22-20-E is a blend of 12% sterol in PG 64-22 PAV aged for 60 hours and sample 01-22-20-C is a blend of 64-22 PAV aged for 60 hours to which 12% sterol has been post added. The PG 64-22 sample prior to aging has an asphaltene content of 13.9% and PAV aged 60 hours with no sterol (dashed data Figure 1) has 27.3% asphaltenes. The pre-blended sample of 64-22 plus 12% sterol has 23.6% asphaltenes after aging and the post-blended sample has 22.9% asphaltenes. Considering the 60-hour aged sample without sterol had 27.3% asphaltenes these data show that sterol can prevent asphaltene growth during aging and is also able to disrupt and reduce the asphaltenes that had developed during PAV aging of the original PG 64-22. Adjusting the peak areas for asphaltene concentration of each sample shows nearly identical sterol peak areas.

While Figure 1 shows the sterol peak and based on peak area suggests the sterol content is present before and after aging, it does not substantiate that the sterol is present in a viable form. Another experiment was needed to verify the efficacy of the sterol in an aged bitumen sample. Sufficient PG 58-28 was aged for 72 hours in thin films at 135°C in a forced draft oven at ambient pressure to produce approximately 1000 g of a surrogate RAP bitumen. A sample of this surrogate RAP bitumen with zero percent sterol and blends of 5% and 10% sterol in the surrogate RAP bitumen were further PAV aged for 60 hours. A 50% blend of the 10% sterol PAV 60-hour aged sample and 50% of the PAV 60-hour aged sample with no sterol was produced and tested for high PG grade, R-Value, and low temperature stiffness and relaxation PG grades, and determination of the Delta Tc (ΔTc) properties of the blends. The low temperature properties were determined using the 4 mm DSR test as developed by Western Research

Institute. R-values were determined from 4 mm mastercurve data and used one giga Pascal as the glassy modulus for all samples. Low temperature, ΔTc and R-Value results are shown in Figure 2.

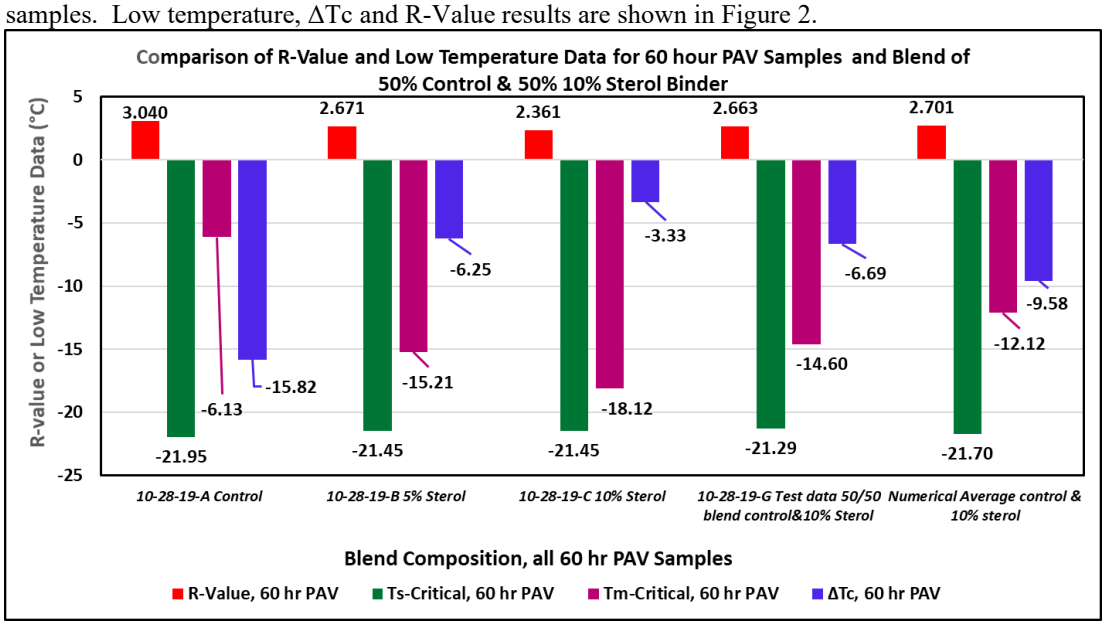

Figure 2: Comparison of R-value and low temperature property data for 50% aged binder with 10% sterol blended with aged binder Containing no sterol for 60-hour PAV samples

Figure 2 shows the 50/50 physical blend test results and the numerical average of 50% 10-28-19-A and 50% 10-28-19-C. Figure 2 shows similar results for the physical blend compared to the original 5% sterol sample (10-28-19-B). R-Value, Tm-Critical and ΔTc agree closely while the numerically averaged data is noticeably different especially for R-Value, Tm-Critical, and ΔTc. Ts-Critical generally does not change substantially with aging as is shown here.

1.2. Transformation of bitumen due to sterol modification

Figure 3 is a plot of asphaltene content for blends of 7.5% sterol in a Mayan crude PG64-22 (Pemex) and 7.5% sterol in a Canadian crude PG 64-22 (Tank 6).

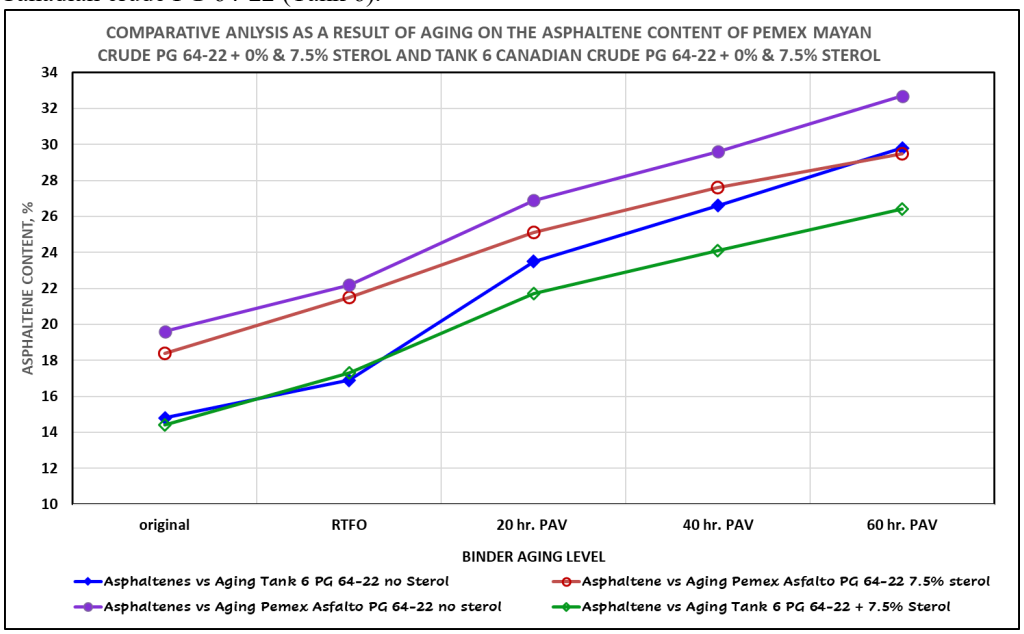

Figure 3: Comparative analysis of asphaltene content of Mayan and Canadian PG 64-22 bitumen with zero and 7.5% sterol aged to 60 hours in the PAV

The asphaltene data in this plot shows that addition of 7.5% sterol to each of these bitumen results in an altered aging profile for the bitumen beyond the RTFO aging step. Each bitumen follows an aging path indicative of a bitumen with decreased asphaltene levels. The rate at which asphaltenes increase with aging is an inherent characteristic of that bitumen. Based on the data presented in this Annex it is our conclusion that sterol treatment of bitumen results in a material that when aged can be recycled and the benefits of the original sterol additive can be reclaimed in the new pavement. Furthermore, the addition of sterol can transform a bitumen to material that has improved aging characteristics over its service life compared to the service life of the original bitumen.

7th E&E Congress
Errata for paper 320 *Use of plant derived sterols as an age retarding additive for bitumen and asphalt mixtures*

Page 6 four lines from the bottom, sentence beginning with "The slopes of $T_{m\text{-}CRITICAL}$ as a function of asphaltene content flatten with increasing sterol content while at the same time decreasing the overall range of asphaltenes from the unaged to the PAV 60 condition."

The corrected content appears below and is underlined

The underlined portion of the sentence is incorrect the corrected sentence is below
"The slopes of $T_{m\text{-}CRITICAL}$ as a function of asphaltene content flatten with increasing sterol content and while the range of sterol increase from zero to 60-hour PAV is similar for all sterol loadings the rates of asphaltene increase beginning with the decreased asphaltene levels at zero time for each sterol loading that are reduced."

On page 7 the last sentence reads "was 1800 to 15141 cm^{-1}. It should be "was 1800 to 1514 cm^{-1}.