Effect of polyphosphoric acid on aging kinetics of bituminous binders

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ABSTRACT

Polyphosphoric acid (PPA) is widely used asphalt modifier to improve the properties of neat asphalt binders when added at low concentrations. Since PPA acts to stiffen the binder, there has been a concern that PPA also accelerates oxidative aging of asphalt. The purpose of this study was to evaluate the effect of PPA on the aging kinetics of asphalt binder. We used extended PAV aging at various times followed by determination of carbonyl contents and PG grade after each aging period. PAV material containing the binder modified with 1% PPA was investigated by DSR and BBR and showed that such binder has wider Effective Temperature Range, compared to control without PPA. The binder with 1% PPA exhibits improved high temperature stiffness. After 60 hours of PAV aging, the low temperature properties of the PPA modified binder are comparable to those of the original, unaged binder. The control binder without PPA exhibited expected changes due to oxidative aging, proportionate to PAV exposure time. The rate of carbonyl formation was approximately 12% slower for PPA-containing binder than the control without PPA. These improvements strongly suggest that the use of PPA improves a binder's resistance to oxidative aging. Bitumen recovered from compacted mixes containing 35% of recycled asphalt pavement (RAP) and PPA-modified binder also show lower stiffness for PPA-containing binders. This suggests that PPA-modified binders may provide anti-aging benefit and reduce the need for rejuvenating agent in the RAP mixes.

Keywords: Additives, Ageing, Chemical properties, Rheology

1. INTRODUCTION

Polyphosphoric acid (PPA) has been used for many years in North America as a bitumen modifier to meet demanding performance requirements. The application of polyphosphoric acid in bitumens was first reported in a 1973 patent assigned to Tosco-Lion [1] and its use in the US has increased steadily since that year. Today, polyphosphoric acid is a widely accepted modifier which is used as a direct bitumen modifier or together with elastomeric polymers [2-11]. PPA is also used as a reactant in air-blowing oxidation processes or as a catalyst in reactive terpolymer applications. In neat bitumen, polyphosphoric acid increases the high-temperature Performance Grade (PG) rating of the bitumen while maintaining the low-temperature properties. Significant improvements in the water-sensitivity of mixes are also obtained. The effect of PPA modification was found to be highly dependent on the chemistry of the binders. Previous studies show that a minimum level of asphaltenes is required for producing PPA-modified bitumen with improved physical and rheological properties [10].

One of the major problems of the modern paving industry is aging of the bituminous material. Aging of the bitumen binder is always related to the formation of a hard and brittle structure which starts during the production of bitumen and asphalt mixes and continues throughout the lifecycle of the pavement. Aging typically produces oxidized bitumens which are characterized by very high asphaltene content [12]. By extension, there is a perception in the paving community that the increase in stiffness of the bituminous binder provided by PPA and the resulting increase of the asphaltene content is associated with faster oxidation and, therefore, faster aging of the bitumen.

The main objective of the present work was to determine if PPA contributes to the bitumen oxidation process. In particular, we studied the effect several contributing factors such as additional aging of the binder in PAV, air-blowing followed by aging in PAV, and the presence of recycled (aged) material on the chemical and rheological characteristics of PPA-modified bitumens.

2. EXPERIMENTAL

2.1. Materials.

Polyphosphoric acid of 105 % or 115% concentrations from ICL Performance Products LP was utilized as a bitumen modifier. Paving bitumens from BP, and Venezuelan, Eastern Canadian and Western Canadian fluxes were used in the present study. The PPA is a polymer of orthophosphoric acid (H_3PO_4). The basic compounds of PPA are phosphorus pentoxide (P_2O_5) and orthophosphoric acid. PPA is available in various grades the naming of which can be confusing as the percentage can exceed 100%. Concentrations of PPA are calculated from the weight ratio P_2O_5/ H_3PO_4. For example, one hundred percent phosphoric acid contains 72.4% P_2O_5 as calculated from the formula weight ratio P_2O_5/H_3PO_4. The ratio of these P2O5 contents provides a relative phosphoric acid content, which is 76.1%/72.4% = 105% for 105% PPA and 83.3%/72.4% = 115% for 115% PPA, respectively.

2.2. Methods.

For all lab tests involving modification with PPA the bitumen samples were heated to 135°C and PPA was added while mixing for 30 minutes under low shear. Neat and PPA-modified binders were evaluated with respect AASHTO M320 (Table 1 & 2). Chemical analyses according to ASTM D 4124 – Component Analysis by Iatroscan were performed to relate the resulting performance to asphalt binder chemistry. The effect of long-term aging on PPA-modified bitumens was studied by conditioning in PAV for various times at 100 °C and 300 psi according to ASTM D 6521. Oxygen content was determined using UOP method 649-74. The method is based on pyrolysis-gas chromatographic technique and determines total oxygen content of organic compounds.

Air-blowing was performed using a small scale blowstill (4,000 g batches). Neat or PPA-modified binder was heated to 260 °C, air flow rate was kept at 2.0 L/min, while high shear agitation was used to disperse air bubbles. Air-blowing was performed until target softening point of 98.9-101.7 °C was reached.

To investigate the effect of PPA on the performance of the asphalt mix containing recycled asphalt pavement (RAP) the PG 58-28 binder was blended with 0.6 wt% 105% PPA for 30 minutes at 160 °C under low shear. Two SUPERPAVE™ mix designs were then constructed with a blend of trap rock and 35% RAP to generate samples for the performance test. Resilient Modulus and Indirect Tension were tested at 25 °C while Hamburg Test was performed at 50 °C according to AASHTO T307, T322, and T324.

3. RESULTS AND DISCUSSION

3.1. Anti-aging properties of PPA (paving asphalt).

We investigated and compared the characteristics of aged neat and PPA-modified binders. The oxidative aging approach using extended PAV procedure was used to produce aged binder. Physical and performance properties, as well as composition of such binders were determined. Figure 1 shows a variation of true grade as a function of PAV exposure time for neat and PPA-modified binders.

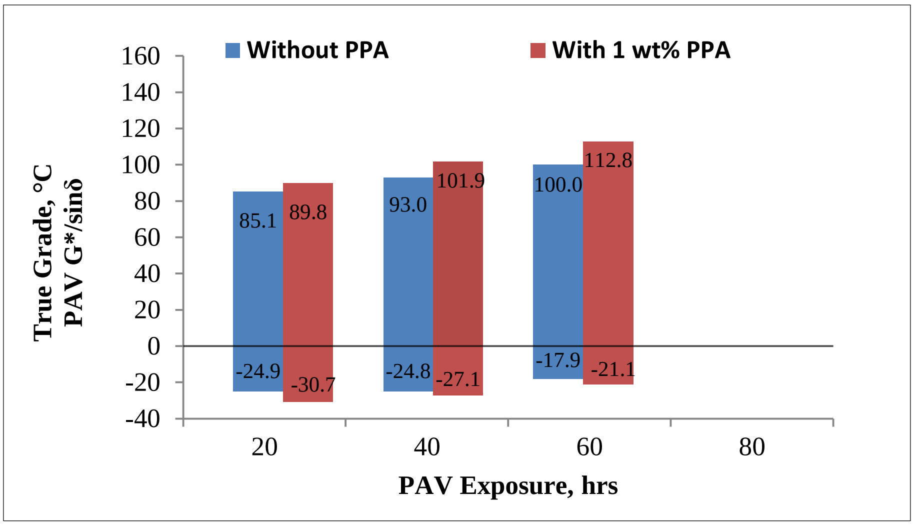

Figure 1. Variation of true grade as a function of PAV exposure time for neat and PPA-modified binders.

As it is seen from Figure 1, both neat and PPA-modified binders show increase in high temperature DSR values and a slight decreased in low temperature grade obtained from BBR testing as aging progresses from 20 to 60 hours. However, in every aging point PPA-modified binder shows better low temperature performance than the unmodified binder and as a result of this a wider effective temperature range (ETR). These data suggest that PPA-modified binder will exhibit less cracking at low temperature which may improve the service life of the pavement.

Oxidative aging is one of the major factors affecting bitumen durability. Reaction of bitumen with atmospheric oxygen leads to hardening and embrittlement of the binders which ultimately leads to quick deterioration of the road [13, 14] Typical aged binder is characterized by high carbonyl and oxygen contents, and high concentration of asphaltenes. Here we investigated the effect of the presence of PPA in the binder on these parameters. Table 1 shows the data for carbonyl index, oxygen content and concentration of asphaltenes for neat and PPA-modified binders as a function of PAV aging time. The carbonyl index is calculated from the adsorption bands of C=O groups from FTIR spectra and it is defined as a ratio of peak area of carbonyl band at 1700 cm^{-1} to the total area of all peaks in the range of 2000 to 600 cm^{-1}.

Table 1. Variation of carbonyl, oxygen and asphaltene contents as a function of PAV aging time

	Oxygen Content, %		Carbonyl Index		Asphaltenes, %	
PAV aging time, h	Neat binder	Binder + 1% PPA	Neat binder	Binder + 1% PPA	Neat binder	Binder + 1% PPA
0	0.63	0.63	0	0	13	17.1
20	1.20	0.88	208	171	21.5	24.8
40	1.58	1.06	305	263	25.5	27.6
60	1.73	1.51	433	338	26.6	29.8
80	2.39	2.01	533	483	30.1	30.5

As it is seen from Table 1, and as expected, PAV aging of both neat (unmodified) and PPA-modified binders leads to an increase of all three parameters. However, for PPA-modified binders the oxygen content and carbonyl index were found to be smaller than for the neat binders. This indicates slower oxygen uptake and, therefore, slower aging of PPA-containing binders.

At the same time, the amount of asphaltenes was found to be higher in PPA-modified binders. Asphaltenes are highly reactive polar aromatic compounds which consist primarily of carbon, hydrogen, nitrogen and oxygen. When the neat bitumen undergoes normal air oxidation more than three quarters of the oxidation takes place with molecules from the polar aromatics fraction which leads to an increase in asphaltenes content.

When PPA is present in the binders there are two effects which may take place simultaneously. It is well known that PPA provides a dispersing effect to the asphaltenes [15] creating an asphaltenes network in the maltene phase. To understand how PPA reduces oxidation, we know that PPA chemically reacts with oxygen-reactive polar aromatics compounds present in the asphaltene molecules producing new “asphaltene”-like compounds. Formation of such compounds prevents their further reaction with oxygen and, therefore, further oxidation. This hypothesis is also supported by lower oxygen and carbonyl compounds contents found in PPA-modified binders. Similar anti-aging effect of PPA on bitumen was earlier observed by various researchers [16, 17].

3.2. Anti-aging properties of PPA-modified roofing binders

Air-blowing is a well-known procedure used to produce oxidized bitumen. Oxidized bitumens are used almost entirely for industrial applications, like roofing, paving, flooring mastics, pipe coatings, and paints. In the US such oxidized bitumens are mostly used to produce roofing bitumen, however, in the EU oxidation is used for production of both roofing and paving binder. Typical air-blowing procedure involves the bubbling of hot air through a column with hot bitumen until the desired softening point is reached. The resulting binder typically has higher stiffness and a higher concentration of asphaltenes.

Air-blowing is a time and energy-consuming process. Therefore, the application of catalysts/accelerators is gaining more widespread use as a way to produce high quality binders. Several technologies exist for catalyzing the air-blowing process. These include the application of PPA or ferric chloride ($FeCl_3$) for bitumen modification. PPA is a typical accelerator used during the air-blowing process known for its ability to decrease air-blowing time and also positively affect the final properties of the bitumen. The goal of this part of the investigation was to demonstrate the effect of PAV aging and PPA modification on the resulting properties of the oxidized binders. Table 2 summarizes the data for three different neat and PPA-modified bituminous binders which were subjected for oxidation with hot air.

Table 2. Variation of the properties of neat and oxidized PPA-modified binders

	Venezuelan		Eastern Candian		Western Canadian	
Base asphalt, %	100	99.7	100	99.7	100	99.7
PPA (115%), %	0.0	0.3	0.0	0.3	0.0	0.3
Properties before air blowing						
Softening point, °C	37	42	40	41	42	41
Penetration @ 25 °C, dmm	93	74	89	90	74	81
Properties after air blowing (target softening point 100 °C)						
Oxidation time, hrs	2.8	2.6	3.3	2.9	5.7	2.3
Final Softenning Point, °C	102	99	100.5	100	100	99
Penetration @ 25 C, dmm	15	22	14	17	12	16

The air-blowing procedure can be considered an aging procedure itself, which typically produces binder characterized by high stiffness, reflected in low penetration and target high softening point. Table 2 demonstrates that in the absence of PPA all three binders show a substantial decrease in penetration after air-blowing. But in all cases penetration was found to be relatively higher for the PPA-modified binders. The data imply that despite of the harsh oxidation conditions introduced by air-blowing, PPA does not contribute to the aging of the binders. Instead, PPA brings some anti-aging benefits which result in softer binders.

The aforementioned binders were further subjected to aging in pressure aged vessel (PAV) for 15 and 25 hours at 100 °C and 300 psi. The values of creep stiffness and m-value were determined binders and summarized in Figures 2 and 3 for Western Canadian binder as an example, but the same trend was observed for all three binders.

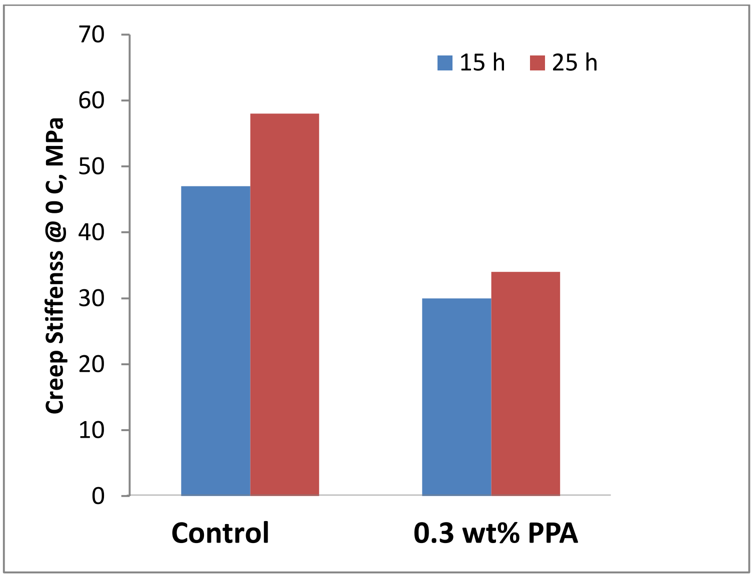

Figure 2. Variation of creep stiffness for PAV-aged oxidized Western Canadian binder

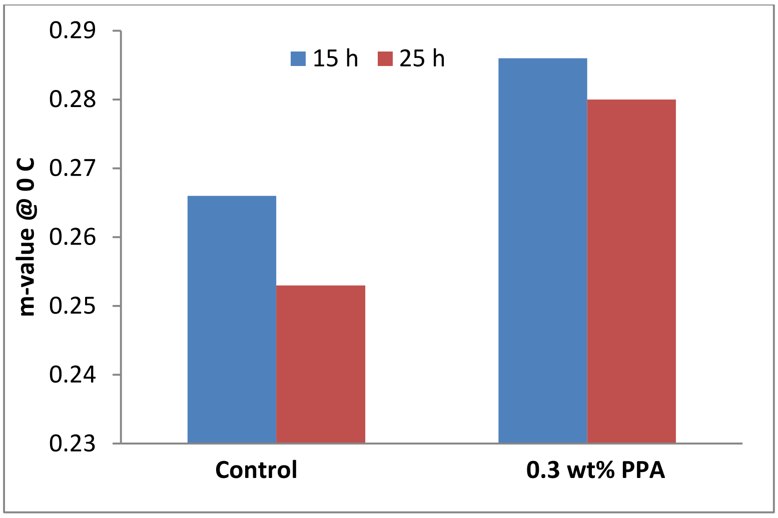

Figure 3. Variation of m-value for PAV-aged oxidized Western Canadian binder

The value of creep stiffness is typically a measure of the thermal stresses in the bituminous binder resulting from thermal contraction [16]. Higher number would indicate stiffer binder and higher susceptibility for cracking. The m-value is an indication of relaxation processes in the bituminous binder. A higher m-value is desirable; it indicates faster relaxation of the binder after applied stress. Figures 2 and 3 show that for PPA-containing binders the value of creep stiffness was found to be lower, whereas the m-value was found to be lower than that once found for controls. This indicates that modification of the binders with PPA does not contribute to aging of the bituminous binders. On the contrary, the data with PPA-modified binders demonstrate higher flexibility and lower stiffness at 0°C.

Bitumen components (saturates, asphaltenes, resins, and aromatics, aka SARA) and the concentration of carbonyl compounds were determined for air-blown (oxidized) bitumens in the presence and in the absence of PPA. Table 3 shows the variation of the bitumen components for Eastern Canadian flux with addition of PPA before and after airblowing.

Table 3. Variation of bitumen components for neat and PPA-modified Eastern Canadian binders

	Before air-blowing		After air-blowing	
	Control	Flux+0.6% PPA(105%)	Control	Flux+0.6% PPA(105%)
asphaltenes	14.1	17.8	34.0	32.2
polar aromatics	41.6	41.1	35.1	29.8
naphthene aromatics	37.7	34.8	24.3	32.1
saturates	6.6	6.0	6.6	5.9

As it is seen from Table 4 addition of PPA to the flux prior airblowing slightly increases the asphaltene content. This phenomenon was observed previously and could be possibly due to a dispersion effect provided by PPA. Air-blowing is bitumen aging procedure which involves the treatment of bitumen with hot air for extended period of time. As a result of this procedure the concentration of asphaltenes typically increases. The concentration of asphaltenes in the PPA-modified samples was found to be lower than the concentration of asphaltenes in control sample. This indicates that PPA provides an anti-aging effect and actually may slow down aging of bituminous binders.

The effect of additional PAV aging for 20 and 40 hours on the rheology and carbonyl contents of such binders was also investigated. Figure 4 shows a dependence of the percent of carbonyl content increase on the aging regime for bitumen samples.

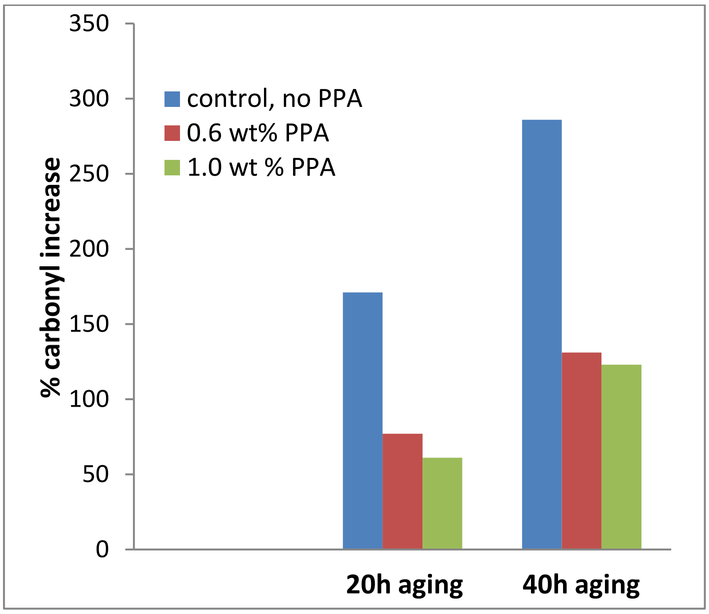

Figure 4. Percent of carbonyl increase as a function of aging regiment for Eastern Canadian flux.

As it is seen from Figure 4, the percent increase of carbonyl reaches 170% and 286% for a control sample aged for 20 and 40 hours, respectively. When the bitumen samples contained 0.6 wt% PPA the increase in % carbonyl content was found to be smaller, 77% and 131% for 20 and 40h aged samples. For the sample containing 1 wt% PPA this effect was found to be even more pronounced. Oxidative aging is an irreversible chemical reaction between the components of bitumen and oxygen, therefore, the amount of carbonyl compounds determined in the aged bitumen is a good indication of the aging process. Figure 4 shows that addition of 1 wt% of PPA to oxidized bitumen leads to the smallest % increase of the carbonyl compounds. Similar dependences were observed for all other fluxes.

Rheological properties of the PAV aged PPA-modified oxidized bitumen were also investigated. Table 4 shows a summary of the rheological properties for these binders.

Table 4. The effect of PAV aging on rheological properties of PPA-modified oxidized binders.

	Control, no PPA	0.6 wt% PPA	1.0 wt% PPA
Air Blown Binder			
Penetration, @ 25 °C, dmm	14	20	20
DSR, kPA (G*) @ 100 °C	7.16	7.83	8.38
Creep Stiffness, Mpa @ 0 °C	46	30	36
PAV (300 psi, 20h, 100 °C)			
Penetration, dmm	9	12	12
DSR, kPA (G*) @ 100 °C	36.7	40.3	46.9
Creep Stiffness, Mpa @ 0 °C	77	57	59
PAV (300 psi, 40h, 100 °C)			
Penetration, dmm	7	10	11
DSR, kPA (G*) @ 100 °C	99	78.8	72.3
Creep Stiffness, Mpa @ 0 °C	95	78	79

Table 4 shows that addition of PPA has a great effect on rheological properties of the binders reflected in change of DSR and creep stiffness values. In particular, the increase in DSR and creep stiffness values were found to be the highest for control sample indicating that additional aging of the air-blown bitumen leads to formation of stiff binders. Application of such binder in road construction will have a negative effect on the performance of the road. Addition of PPA leads to smaller increase in DSR and creep stiffness indicating improvements in resistance to oxidative aging.

3.3. The application of PPA in bitumens containing recycled materials (RAP)

Recycled or reclaimed asphalt pavement (RAP) is the term used to describe materials containing asphalt and aggregates that are generated when existing asphalt pavements are removed during construction or resurfacing [17]. The material is generally crushed and screened to a consistent quality and used together with new aggregate in new pavements. The recycling of asphalt pavements this way is commonplace in the US and other countries, resulting in benefits in terms of both the environment and the materials cost. Typically 10 – 25 % RAP is used as part of the asphalt mix, but higher levels are sometimes used. Due to the presence of severely aged materials, RAP-modified pavement tends to show relatively high fatigue, which may lead to cracking, higher susceptibility to rutting and decreased performance at low temperatures. Typically the application of RAP also requires incorporation of oils and rejuvenating agents. We evaluated the effect of PPA in systems containing 35% RAP and trap rock aggregate in a 19 mm Superpave^{TM} mix design. The RAP was obtained from a local source in the state of Florida in the US. 5.0 wt% of the bituminous binder was used in the mixes and this was either a PG 58-22 asphalt binder used as-is, or the same binder after it was treated with 0.6% PPA. The sample were subjected to a series of performance tests including Resilient Modulus, Indirect Tension, and Hamburg Tests. The results are summarized in Table 5.

Table 5: Results for Resilient Modulus, Indirect Tensile Strength and Hamburg of RAP Mixes

Mix ID	Average resilient modulus @ 25 °C, ksi	Average tensile strength, psi	Hamburg test @ 50°C, after 20K cycles, mm
PG 58-22	8,710	275.0	7.98
PG 58-22 + PPA	7,842	263.7	4.83

Table 5 shows the results of tests in the compacted mixes. Both samples display much higher Resilient Modulus and Indirect Tensile Strengths than normal pavement samples. The sample from the PPA-modified binder, shows a relatively lower increase in both parameters and also a significantly lower level of deformation in the Hamburg test. Clearly, modification with PPA has led to a RAP-based pavement with superior rut resistance and better fatigue and low temperature performance without the need to add other recycling agents. These data suggest that the application of PPA-modified binders may provide some benefits and reduce the need of rejuvenating agents in the RAP mixes.

4. CONCLUSIONS

The effect of PPA modification on aging of various binders was investigated. In particular, we were interested in the aging of PPA-modified binders obtained via regular distillation process and also binders obtained via air-blowing (oxidation) process. On the basis of the data obtained from SARA analysis for PPA-modified aged bitumens we can conclude that modification of bitumen with PPA results in an increase in the aspaltenes content. However, the presence of PPA does not promote oxidation; on the contrary, it seems that the presence of PPA slows the oxidation process down. The data for carbonyl and oxygen content demonstrate that the amount of oxygen in the PAV-aged samples also decreases for PPA-modified bitumens compared to the binders without PPA. Oxidized bitumens also show a reduced aging affect upon modification with PPA. This was demonstrated by low temperature performance data obtained from BBR testing. The data demonstrate that oxidized PPA-modified bitumens are characterized by lower stiffness and higher m-value compared to unmodified binder. This indicates that PPA-modified binders will show higher flexibility and lower susceptibility to cracking at low temperature. The performance data for RAP-containing PPA-modified asphalt mixes showed that the application of PPA-modified binders may provide some anti-aging benefits and reduce the need of rejuvenating agents in the RAP mixes

5. ACKNOWLEDGEMENTS

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REFERENCES

[1] U.S. Patent 3,751,278 to Tosco-Lion, Inc Alexander SH. (1973).

[2] "Polyphosphoric Acid in Asphalt Modification," Falkiewicz M, Grzybowski K. Presented at the 41st Petersen Asphalt Research Conference - Symposium on Prediction of Pavement Performance, Cheyenne, WY, June 2004.

[3] "Asphalt Modification With Polyphosphoric Acid," Maldonado R, Falkiewiz M, Bazi G, Grzybowski K. Presented at the 51st Annual Conference of the Canadian Technical Asphalt Association, November 2006.

[4] "Polyphosphoric Acid in Roofing" Maldonado R, Falkiewicz M. Presented at Asphalt Institute Spring Meeting, Washington, DC, April 2006.

[5] "Asphalt Modification With Polyphosphoric Acid" Maldonado R. Presented at 5th Asphalt Congress of the Mexican Asphalt Association, Cancun, Mexico, August 2007.

[6] "The Reaction Between PPA and Bitumen" Masson JF, Gagne M, Robertson G, Baumgardner G, Falkiewicz M, Maldonado R. Presented at the 44th Petersen Asphalt Research Conference, Laramie, WY, July 2007.

[7] "Moisture Sensitivity of Acid Modified Asphalt & Mixtures With and Without Anti-Stripping Agents" Reinke G. , Presented at the Rocky Mountain Asphalt Users/Producers Group Meeting, March 2004.

[8] "Effect of Polyphosphoric Acid on Aging Behaviour of Bituminous Binder" Martin JV, Orange G., Presented at the Petersen Conference 2004.

[9] "Rutting and Moisture Resistance of Asphalt Mixers Containing Polyphosphoric Modified Asphalt" Baumgardner G, Presented at the Rocky Mountains Users/Producers Group Meeting, March 2004.

[10] "Polyphosphoric Acid Modified Asphalt: Proposed Mechanisms" Baumgardner G, Masson JF, Hardee J, Menapace A. Journal of the Association of Asphalt Paving Technologists, 74, p. 283-285, 2005.

[11] "Polyphosphoric Acid Modification of Asphalt", Asphalt Institute, Lexington, KY USA Publication IS-220, 2005

[12] “Relating asphalt aging and durability to its compositional changes” Tuffour Y. A., Ishai I., Craus J. AAPT, V.58, p.163-181, 1989

[13] “Developing an aging model to evaluate engineering properties of asphalt paving binders”, Chen, J. S., and Huang, L. S., Materials and Structures Constructions, vol. 33, pp 559-565, 2000

[14] “Asphaltenes and Asphalts” Petersen C. 2. in Developments in Petroleum Science 40B, Chapter 14, 2000

[15] “Polyphosphoric Acid Modified Asphalt Binders –Industry Perspective; Usage, Why, How” Baumgardner G. L., , Paragon Technical Services, Inc., 2009

[16] “Effect of PPA on Aging Characteristics of PG 64-22 Asphalt Binders” N. Ramasamy M.S. Thesis University of North Texas, 2010

[17] “A New Technology of Recycling 100 % Reclaimed Asphalt Pavements” Do H. J., Park J. Y. Journal of Testing and Evaluation **37** (5), p. 479-482, 2009