EFFECT OF ACCELERATED WEATHERING ON POLYPHOSPHORIC ACID MODIFIED BINDER

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ABSTRACT

Polyphosphoric acid modified asphalts are increasingly being used in hot mix asphalt to meet the higher pavement performances requirements. Despite the extensive studies that have been performed on PPA modified asphalts, there is very limited information which has been published regarding the effects of weathering on PPA modified hot mix asphalt. The longer term performance of PPA modified asphalt mixtures has not been fully comprehended by existing laboratory tests conditions. Furthermore there has not been a satisfactory method to weather pavements which simulates what happens in the field. The use of the Accelerated Pavement Weathering System (APWS) has been proposed to simulate the temperatures, moisture and UV radiation a pavement would be exposed to in thefield. The purpose of this study was to investigate the effect of water, temperature, and UV exposure over time on various hot mix asphalt mixtures modified with Polyphosphoric acid using the Accelerated Pavement Weathering System (APWS) device. The hot mix asphalt mixtures were prepared with various concentrations of polyphosphoric acid and polymer and were submitted to cycles 9 minutes of water spray every hour during 3000 hours at 140F (60C) while exposed to UVA and UVB. The water percolated through the asphalt slabs was collected and analyzed for their phosphorus content and pH. The mix performances were measures via the APA before and after the aging and binders were subsequently recovered and performance graded according AASHTO M320 after aging.

Keywords: acid polyphosphoric, weatherometer, aging, UV, asphalt

1. INTRODUCTION

Asphalt pavements are exposed overtime to moisture, high temperature and UV rays. The simulation of those conditions all combined on large size sample at the laboratory scale has been unpractical until recently. The Asphalt Pavement Weathering System (APWS), recently developed by PRI Asphalt Technologies, Inc., is a translation of the weathering test (ASTM D 4798) used for asphalt roofing shingles. It consists of cyclic exposure to light and water spray. The APWS is designed to accommodate full depth pavement specimens and to simulate natural pavement weathering [PRI internal reference]. Thus asphalt pavements are exposed to cycles of water and UV exposure at high temperature simulating the overall conditions experienced by an asphalt mix over time.

Over the past 10 years, the usage of Polyphosphoric acid (PPA) as a modifier or co-modified in asphalt has grown tremendously. The addition of PPA typically increases the stiffness of the asphalt binder at high temperature without affecting its properties at lower temperature, increasing therefore the useful interval temperature (UTI) of the binder. It is used either as a solo modifier or in conjunction with various polymers – reactive terpolymer, styrene-butadiene-styrene or crumb rubber. From the mechanism to the road performances, many aspects of PPA modified asphalt have been investigated [1-6]. However, still some questions remains on the impact of PPA concentration on asphalt mix performance. Particularly the question of the effect of its concentration has not been fully addressed yet. In other words what is the concentration of PPA where possible side effects could outweighs the benefits of this technology.

As PPA is a polar compound, ones may anticipate that as a certain concentration the PPA would leached out from the asphalt mix and therefore the deformation and moisture resistance of the mix might be affected.

This paper will present the impact of combined moisture with UV radiation and temperature on asphalt and asphalt mix performance with an increasing concentration of PPA. Additionally, the leached water was collected and analyzed for pH and phosphorous content over time.

2. MATERIALS

The asphalt binders were formulated according to the table 1 below. The asphalt source was from BP Whiting refinery. The source of polyphosphoric acid was from INNOPHOS, INNOVALT N200 and INNOVALT XL200 [7,8.9]. The addition of PPA into the neat asphalt increased the Performance Grade (PG) by one grade (6^{o}C) with 1% and up to almost 3 grades (18^{o}C) with 2% added.

Table 1 : Test results on asphalt binder. *as recovered (asphalt binders were graded according to the PG grading AASSHTO M320).

Reference	Description	PG (°C)	
		Before RTFO	**After RTFO**
1053-001-05	PG 64-22	66.2	68.3
1053-001-15	Neat + 1% N-200	72.8	74.4
1053-001-20	Neat + 1.5% N-200	77.1	77.3
1053-001-25	Neat + 2% N-200	81.0	82.7
1053-001-25	Neat + 2%SBS + 0.1%S + 0.5%XL200	NA	72.6*

A SUPERPAVE^{TM} 12.5 mm mix design with Trap Rock aggregate, granitic gneiss from northern New Jersey was used for this project. The aggregate was obtained from Trap Rock Industries (New Jersey)**.** The aggregate mineralogy was a combination of pyroxene granite containing bands of magnetite and oligoclase gneiss containing amphibolites. The asphalt binder content was 5.0% by weight of mixture. The % Air Voids was 7 +/- 1% and the gradation is reported Table 2 below.

Table 2: Aggregate Gradation (% Passing) of Blend Components and Final Job Mix Formula

US Customary	Metric	Trap Rock 8 - 26%	Trap Rock 12.5 - 38%	Trap Rock 10 - 29%	Trap Rock SD - 7%	Combined Gradation
3/4"	19 mm	100.0	100.0	100.0	100.0	100.0
1/2"	12.5 mm	82.7	100.0	100.0	100.0	95.5
3/8"	9.5 mm	51.9	96.3	100.0	100.0	86.1
N0. 4	4.75 mm	11.2	36.2	98.4	98.3	52.1
N0. 8	2.36 mm	5.0	10.9	69.2	94.9	32.2
N0. 16	1.18 mm	4.1	6.7	47.0	85.7	23.2
N0. 30	600 μm	3.7	5.5	34.8	67.3	17.8
N0. 50	300 μm	3.3	4.8	25.7	30.6	12.3
N0. 100	150 μm	2.7	4.1	18.1	5.1	7.9
N0. 200	75 μm	2.0	3.3	12.6	1.4	5.5

The mixing, compaction, curing, and beam preparation procedures adopted are similar to what occurs during the mixing and placement of hot mix asphalt. A detailed slab preparation procedure reported table 4 below was developed to obtain a nominal 90 mm thick finished beam.

Table 3 : Slab preparation steps

Step	Operation
1	Dry aggregate from four different stockpiles overnight in a forced-circulation oven at 115°C.
2	Batch the aggregate in 15,000 grams lots. Mix aggregate gradations according to the JMF (30,000 grams/slab).
3	Mix the aggregate and asphalt in a Hobart mixing device for 60 – 90 seconds at a mixing temperature between 152°C and 158°C.
4	Transfer the asphalt mixture to trays and cure in a forced-circulation oven at 135°C for 4 hours. The asphalt mixture was manually mixed every hour during this process. This aging procedure is consistent with AASHTO R 30 for the preparation of mixtures for mechanical testing
5	The asphalt mixture was then heated to the desired compaction temperature in a forced-circulation oven for 30 minutes
6	The asphalt mixture was then placed in the PMW Slab Compactor (Figure 2) and compacted for approximately 5 minutes to obtain the required density and % Air Voids. The PMW Slab Compacter was manufactured by Precision Machine and Welding Company. Once this was completed then a 90 mm slab at the required density was produced

Once the slabs were prepared, then samples were cut for the APA testing and the binder extracted according to ASTM D2172A with Toluene. The asphalt binder was subsequently recovered using ASTM D 5404 – Rotovapor and re-graded according to the AASHTO M320 standard. The rutting after 8000 passes was measured before after exposure in the APWS. The results are reported in Table 4.

Table 4 : Recovered Binder Performance Grade and APA Rut Depth, 0 hours APWS

Sample ID	Original Binder PG	Recovered Binder "Continuous Grade"	APA Rut Depth (mm) @ 64°C
#1053-001-05	PG 64-22	69.5-26.2	3.9
#1053-001-15	PG 70-22	72.9-24.1	1.9
#1053-001-20	PG 76-22	75.2-24.7	2.4
#1053-001-25	PG 82-22	81.0-23.5	1.9
#1057-017-05	PG 70-22	72.6-25.3	2.5

The recovered binders had very similar properties prior to being used for the mix production. The modified asphalts showed a lower rut depth than the neat asphalt at 64°C.

Table 5 : Multiple Stress and Creep Recovery results for the recovered binder at time 0hours (AASHTO M320 table 3).

Sample	Description	Jnr @ 100Pa	Jnr @ 3200 Pa	% Recovery @ 100Pa	% Recovery @ 3200Pa
#1053-001-05	PG 64-22	2.05	2.26	1.9	0.0
#1053-001-15	Neat + 1% N-200	1.16	1.32	8.9	1.5
#1053-001-20	Neat + 1.5% N-200	0.72	0.86	18.7	7.7
#1053-001-25	Neat + 2% N-200	0.26	0.31	37.7	27.0
#1057-017-05	Neat + 2%SBS + 0.1%S + 0.5%XL200	0.97	1.18	26.2	15.1

The 1053-001-05 compared to the 1057-17-05 exhibits a lower J_{nr} at the same PG grade and a lower percentage recovery (cf. table 5). The presence of polymer in the sample 1057-17-05 produced a higher recovery. The sample containing the highest amount of PPA shows the lowest J_{nr} and the highest percentage recovery. This sample also displayed the highest grade with a "Continuous Grade" of 81.0-23.5.

3. METHODOLOGY

The APWS protocol was established to stimulate the methodology used according to the Xenon Arc Weathering protocols (ASTM D 4798). The target temperature of the chamber was set at 140°F (60°C) and adjusted slightly to account for the external ambient temperature. One cycle (hour) consists of 51 minutes under UVA and UVB radiation with no water spray and 9 minutes with UV radiation and water spray. The amount of water per hour was 29 liters, therefore after 3000 hours, the total amount of water the slabs were exposed to was 87,000 liters. Figure 4 (in annex) displays the temperature profile based on the thermocouples located approximately 30 mm below the top surface of each slab. The slabs were placed in stainless steel trays which contained a steel wire mesh on the bottom to allow for the free flow of run off during the spray portion of the cycle (Figure5 in annex). Each slab also had a catch basin where the run-off could be collected on a periodic based for further evaluations. All the slabs were run in the Accelerated Pavement Weathering System for a period of 3,000 hours at an average chamber temperature of 135°F +/- 5F. The samples were rotated in the chamber every 250 hours to account for local variations in chamber temperature. Run-off from the slabs was collected at predefined intervals and analyzed for pH and phosphorus content.

The slabs were removed from the APWS after 3,000 hours (cf Figure 6 in annex) and further testing was performed on both the mixture and the recovered asphalt binders. The average rut depth was measured with the Asphalt Pavement Analyzer at 64°C after 8000 cycles. The top 19 mm of each slab was then removed and the binder recovered for further testing. To evaluate whether the APA rut performance a 5 mm rut depth criteria was used. The 5 mm rut depth has been proposed by a number of researchers/state agencies as a means of ranking the rutting resistance of asphalt mixes compacted to 7% air voids: < 5mm = high Rut Resistance; >5mm = Low rut Resistance [10-12].

The leached water was collected over time and the pH as well as the phosphorus content was measured. The phosphorus content was measured by Inductive Couple Plasma technique which involve a the vaporization of the sample at high temperature in a flame generated by a plasma of Argon. The emitted light specific to phosphorus element was then collected and compared to a standard of a known concentration.

4. RESULTS

a. The binder:

The physical properties of each binder were compared after 3000 hours of aging (Table 6). The high temperature grade of each binder increased with various types after aging. The high temperature increased linearly versus the amount of PPA added however the lower end temperature variations were independent to the amount of PPA added and were relatively small in most cases. The neat asphalt exhibited a more sensitive reaction to the aging process in particular its high temperature grade increased of about 10°C while the lower temperature grade was slightly reduced. The formulation involving polymer showed the highest variation at high and low temperature.

Table 6 : Comparison Between Different Binders at time 3000hrs

Sample ID	Description	Original Binder Continuous PG	Recovered Binder"Continuous Grade"	High-Temp Diff. (°C)	Low-Temp Diff.(°C) w/o PAV
#1053-001-05	PG 64-22	69.5-26.2	79.7-25.1	10.2	1.1
#1053-001-15	Neat + 1% N-200	72.9-24.1	78.7-24.3	5.8	0.2
#1053-001-20	Neat + 1.5% N-200	75.2-24.7	81.5-24.2	6.3	0.5
#1053-001-25	Neat + 2% N-200	81.0-23.5	88.5-23.0	7.5	0.5
#1057-017-05	Neat + 2%SBS + 0.1%S + 0.5%XL200	72.6-25.3	85.3-23.3	12.7	2.0

Table 7 : Multiple Stress and Creep Recovery results for the recovered binder after 3000hours.

Sample	Description	Jnr @ 100 Pa	Jnr @ 3200 Pa	% Recovery @ 100Pa	% Recovery @ 3200Pa
#1053-001-05	PG 64-22	0.37	0.41	16.4	12.0
#1053-001-15	Neat + 1% N-200	0.40	0.44	18.0	12.7
#1053-001-20	Neat + 1.5% N-200	0.24	0.26	24.6	20.5
#1053-001-25	Neat + 2% N-200	0.07	0.77	45.8	43.6
#1057-017-05	Neat + 2%SBS + 0.1%S + 0.5%XL200	0.16	0.16	37.9	33.2

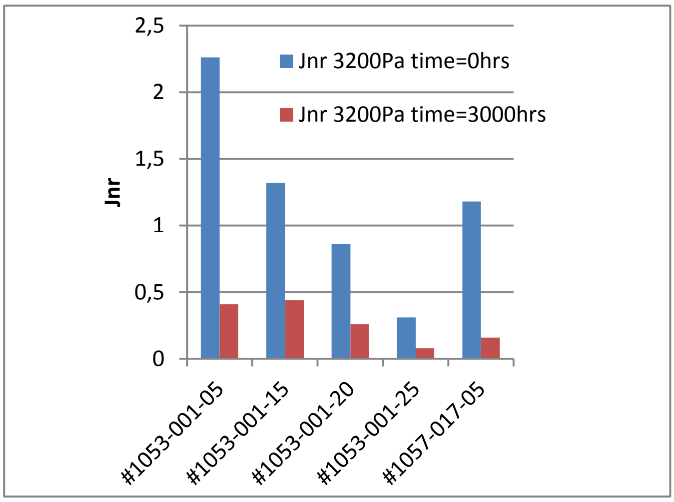

Figure 1 : Jnr at 3200Pa at time 0hrs and 3000hrs

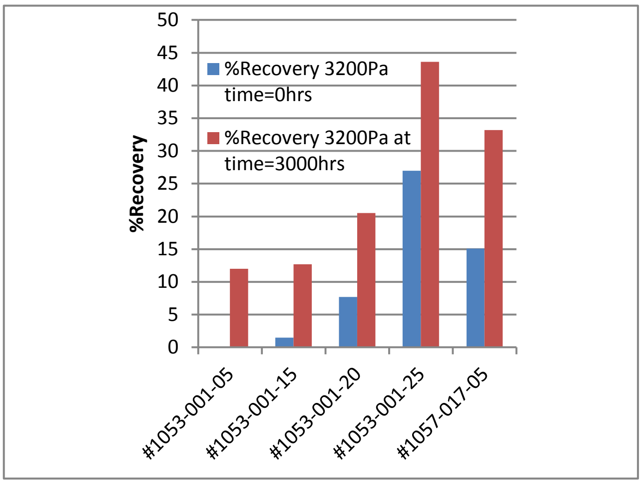

Figure 2 : Percentage recovery at 3200Pa at time 0hrs and 3000hrs

The Table 7 and Table 8 report a summary of the asphalt mix characteristics before and after 3000 hours in the APWS.

b. The asphalt mix:

Surprisingly, the air voids increased after 3,000 hours of exposure and could be related to the unconfined sate of the slabs and their ability to expand during the process. Secondly all rut depths are kept under 5 mm and therefore would be considered acceptable rutting resistance. The neat asphalt mix as well as the polymer modified asphalt with PPA had a reduced rut depth after 3000 hours. The 3 others sample had slightly higher rut depths after aging, still below the 5 mm limit.

Table 8: Mixture Properties and Asphalt Pavement Analyzer Results – Initial

Properties	Test Method	Mix ID/ Results									
		Mix 001-05		Mix 001-15		Mix 001-20		Mix 001-25		Mix 1057-017-05	
		1	2	1	2	1	2	1	2	1	2
Bulk Specific Gravity	ASTM D 2726	2.508	2.488	2.515	2.486	2.489	2.496	2.503	2.480	2.485	2.512
Air Voids, %	ASTM D 3202	6.9	7.7	6.7	7.8	7.6	7.4	7.1	8.0	7.8	6.8
Average Air Voids, %	Calculation	7.3		7.3		7.5		7.6		7.3	
Test Temperature, °C	--	64									
Average Rut Depth, mm	AASHTO TP 63	**3.9**		**1.9**		**2.4**		**1.9**		**2.5**	

Table 9: Mixture Properties and Asphalt Pavement Analyzer Results – 3000 hours in APWS

Properties	Test Method	Mix ID/ Results									
		Mix 001-05		Mix 001-15		Mix 001-20		Mix 001-25		Mix 1057-017-05	
		1	2	1	2	1	2	1	2	1	2
Bulk Specific Gravity	ASTM D 2726	2.484	2.462	2.473	2.423	2.467	2.466	2.489	2.466	2.459	2.494
Air Voids, %	ASTM D 3202	7.8	8.6	8.2	10.1	8.5	8.5	7.6	8.5	8.8	7.5
Average Air Voids, %	Calculation	8.2		9.2		8.5		8.1		8.1	
Test Temperature, °C	--	64									
Average Rut Depth, mm	AASHTO TP 63	**2.5**		**3.9**		**3.0**		**3.5**		**1.8**	

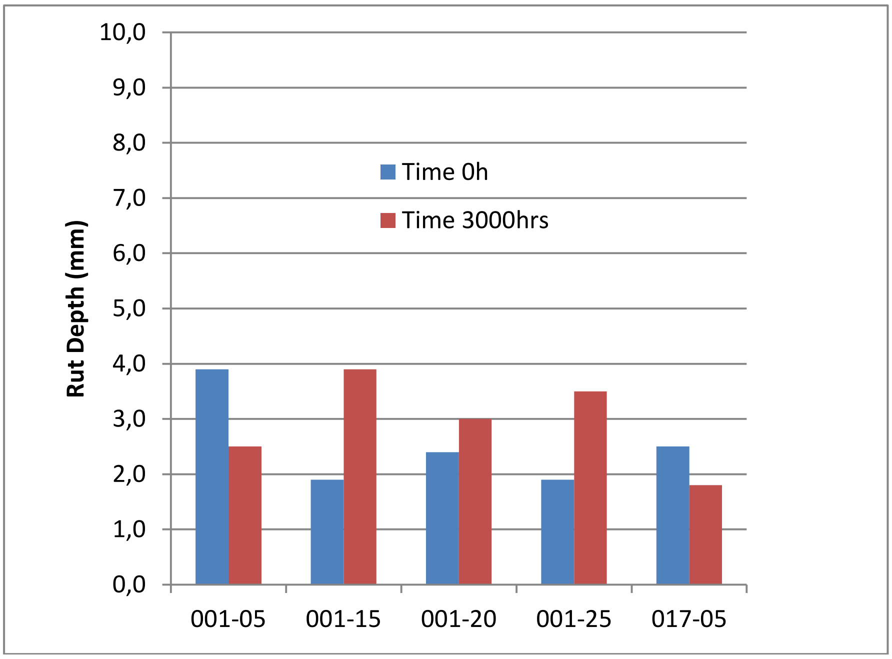

Figure 3 : Rut depth at time 0hrs and 3000hrs

In addition, the binder contents were measured through the mix thickness from the top t 20 mm to the center of the mix (20 to 45 mm). The results are reported Table 10. Except for the sample 1053-001-15 (asphalt modified with 1%PPA), the other samples did not show any significant changes in the binder content. The sample mix 1053-001-15 exhibited the highest air void increase as well.

Table 10 : Binder content of the top and middle layer of asphalt mixes, measured by ASTM D2172 method.

Properties	Layer	Mix 001-05	Mix 001-15	Mix 001-20	Mix 0011-25	Mix 017-05
Binder Content (%)	Top	5.2	4.9	5.1	5.1	5.1
	Middle	5.2	5.3	5.2	5.1	5.1

c. Characteristics of the leached water

The leached water was collected periodically and the results are reported Table 11 below. The pH stayed constant during the 3,000 hours being slightly acidic to neutral. The phosphorus could not be detected even at 2%PPA content for the sample 1057-017-05.

Table 11 : pH and phosphorus content of run-off water collected after 3000hrs.

Sample	Description	pH	Phosphorus content (µg/g of sample)
#1053-001-05	PG 64-22	6.86	< 1
#1053-001-15	Neat + 1% N-200	6.85	< 1
#1053-001-20	Neat + 1.5% N-200	6.94	< 1
#1053-001-25	Neat + 2% N-200	6.92	< 1
#1057-017-05	Neat + 2%SBS + 0.1%S + 0.5%XL200	6.92	< 1

5. DISCUSSION

The binders containing polyphosphoric acid showed much lower aging as measure by the high temperature limiting grade than the control which is consistent with previous work on the aging behavior of PPA modified asphalt [13,14]. The polymer modified asphalt combining PPA and SBS showed the highest aging susceptibility, in particular at high temperature grade and the lowest rut depth after 3000 hours.

In addition, the water collected overtime did not show the presence of any phosphorus even when 2% PPA was used in the binder, which again confirmed some of the previous work [reference] . All binders after aging exhibit less than 5 mm rut depth which is considered acceptable rutting resistance. No trends versus the amount of PPA used in the binder were identified over time, UV and moisture exposure. The air void increases were independent to the asphalt mix nature and could be related to the expansion of the slab under heat and potentially the increased absorption of water over time. Indeed as the binder aged, the oxidation mechanisms tend to produces species, especially under UV radiation, that are prone to increase the water absorption of the asphalt [15]. It appears that the concentration of PPA had no impact on this phenomenon. The mechanism of PPA protecting against the aging process is unclear. Previous research suggested [References] that the addition of PPA to asphalt reduces the formation of carbonyl and sulfoxide functionality and yet those species are the product of reaction of the oxygen to the asphalt and responsible for the stiffness increases over time. It has been proposed by G. Orange et al. that the addition of PPA leads to a higher degree of dispersion of the asphaltene solvated by resins. We could hypothesize that the resins, typically described as pre-asphaletene compounds, engaged with the PPA-asphaltene clusters would be therefore less available to react with the oxygen dissolved in the asphalt.

Finally the binder content of the first 20mm of the specimens were not affected over time for all sample except the 1053-001-15 who exhibited the highest air void increase.

6. CONCLUSION

The exposure to natural elements over time of asphalt pavement modified with an increasing content of polyphosphoric acid as well as a combination of PPA and polymer were investigate during this study. It has been shown that as anticipated, the stiffness increases proportionally to the PPA concentration on the original binder. Beside, prior to be aged, the asphalt mix produced with the neat asphalt exhibits a higher rutting than the 4 other modified ones. This difference is somehow reduced after aging. In addition, it has been noticed as well a significant air void increase over time, which appears to be independent from the nature of the binder and most likely related to the non confinement of the asphalt mix sample. Nevertheless, the effect being somehow similar for all mixes studied, the increase of air void is worsening the aging condition equally for all samples. Overall all asphalt mixes would consider highly resistant to rutting with less than 5mm rut depth after 8000 cycles.

After aging, the PPA modified asphalt recovered binder exhibit a lower stiffness increase than the neat asphalt binder which is consistent with previous research work [13]. Thus, even though submitted to extremely difficult conditions, high amount of PPA were not leached out of the mix and the recovered binder exhibit reduced aged characteristics. Finally the addition of high amount of PPA is not showing negative impact of asphalt mix integrity and performance over time.

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Annex

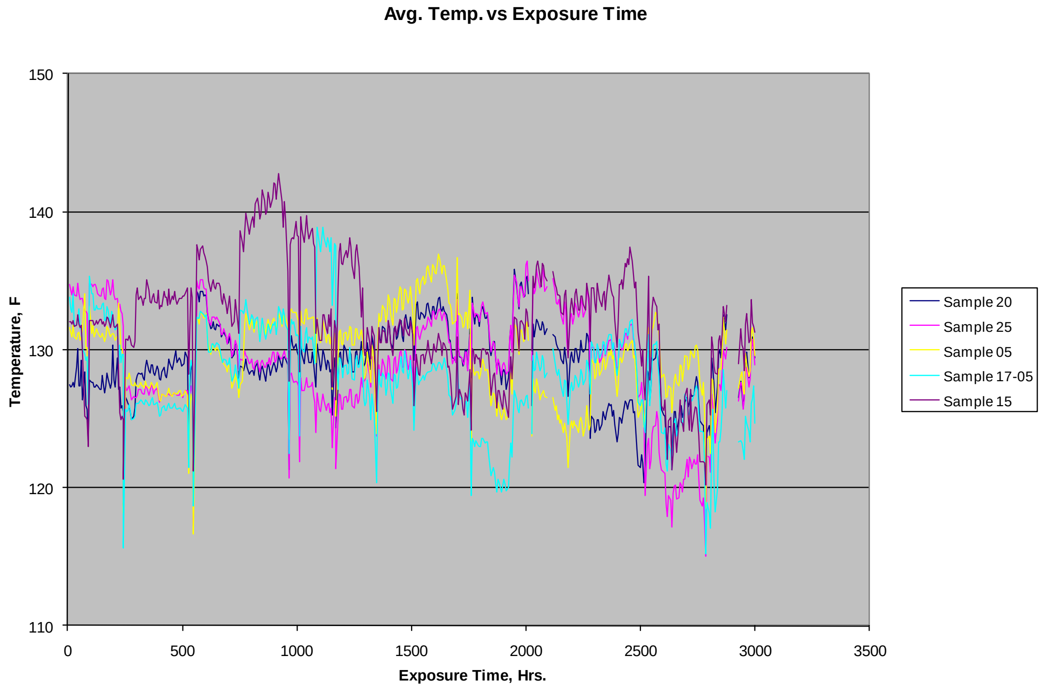

Figure 4 : Surface Temperature (^{o}F) Profile for each sample versus Exposure Time (Hours)

Figure 5: Collection Trays used for each slab in the APWS

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<tr><td>Slab 001-05 after 3000 hours in APWS</td><td>Slab 001-15 after 3,000 hours in the APWS</td></tr>
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<tr><td>Slab 001-20 after 3,000 hours in the APWS</td><td>Slab 001-25 after 3,000 hours in APWS</td></tr>
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<tr><td>Slab 017-05 after 3,000 hours in APWS</td><td></td></tr>
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Figure 6: Collection Slabs after 3000 hours in APWS

REFERENCES

1. "Effect of Polyphosphoric Acid on Aging Behaviour of Bituminous Binder", Asphalt Institute IS-220, 2005
2. " Chemical Modification of Bitumen Through polyphorphosic acid : properties – microsctucture relationship", G. Orange, JV Martin et al, Eurobitume 2004
3. "Binder Modified with a combination of polyphosphoric acid and styrene-butadiene-styrene block co-polymer : The NCAT Test track experience over the past 6 years", Baumgardner, JV Martin , R. B. Powell, P.E., P. Turner,. Eurobitume 2008
4. "Polyphosphoric Acid Modified Asphalt: Proposed Mechanisms, ", Baumgardner, G., Masson, J-F., Hardee, J., Menapace, A., Journal, Association of Asphalt Paving Technologists, 74, 283-285 (2005).
5. "Asphalt Chemically Modified with Polyphosphoric Acid: Influence on Aggregate-Binder Adhesion and Mix Moisture Resistance," Martin, J-V., Orange, G., Presentation, Petersen Asphalt Research Conference, Western Research Institute, Cheyenne, WY (2005).
6. "Use of Polyphosphoric Acid in Asphalt," Baumgardner, G., Presentation, Pavement Performance Prediction Symposium, Western Research Institute/Federal Highway Administration, Cheyenne, WY (2005).
7. "Method for preparing reinforced multigrade bitumen/polymer and use of the resulting compositions for producing bitumen/polymer binders for surface coatings", Planche, J-P., US5880185
8. " Use of inorganic acids with crosslinking agents in polymer modified asphalts", Buras, P., US7495045
9. "Method for preparing an improved bitumen by addition of polyphosphoric acid and a cross-linkable polymer", Martin J-V, US7985787
10. Development of a Rutting Criteria for Use in the Asphalt Pavement Analyzer for New Jersey, Bennert, T., A. Maher, and I. Marukic, FHWA-NJ-2003-02, 2003, 33 pp.
11. Evaluation of the Asphalt Pavement Analyzer for HMA Mix Design,Kandhal, P. and R. Mallick, NCAT Report No. 99-4, 1999, 34pp.
12. "Asphalt Pavement Analyser (APA) evaluation", Eugene Skok, Eddie Johnson, Amir Turk, Report MN/RC 2003-02
13. "Effect of Polyphosphoric Acid on Aging Behaviour of Bituminous Binder", Petersern Conference, 2004, JV Martin, G Orange, B Marcant
14. " Phosphoric Modified Asphalt", T. Arnold, FHWA AMAP 02/2007.
15. " Bituminous Materials:Asphalts, Tars, and Pitches", A. Hoiberg. Volume II:Asphalts Part one.