APPLICATION OF POLYPHOSPHORIC ACID FOR HMA MODIFICATION. US AND EUROPEAN EXPERIENCE

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ABSTRACT.

Polyphosphoric acid (PPA) is widely used as bitumen modifier in the paving industry due to increasing demand for high performance binders. The use of PPA has been shown to increase bitumen high temperature stiffness, and reduce the short-term and long-term aging. To better understand the performance of PPA across wide range of binder type and sources, the effect of different asphalt sources were examined. The main purpose of the study was to determine the effect of polyphosphoric acid modification on bitumen from different geographic regions of the world with respect to the different types of specifications. The binders were evaluated with respect to the EN 12591-Specification for paving grade bitumens, AASHTO M320 (Table 1 & 2), ASTM D 946 – Penetration Graded Asphalt Binders and ASTM D 3381 – Viscosity Graded Asphalt Binders. Several chemical analysis technique like ASTM D 4124 – Component Analysis by Iatroscan and EN 12606-1 – Paraffin Content Determination were performed to relate the resulting performance to bitumen chemistry. Key areas that were examined include the effect of PPA modification on the short and long term aging properties as conditioned by the Thin Film Oven Test (TFOT) and Pressure Aging Vessel (PAV). The impact of PPA on low temperature properties was evaluated using the Bending Beam Rheometer, Direct Tension Test and Fraass Breaking Point.

Key words: polyphosphoric acid, bitumen, improved properties, low temperature performance

INTRODUCTION.

Each year a large amount of money and resources are spent to build new roads or to maintain the existing roads around the world. One of the most important and challenging tasks of the asphalt industry is to develop stronger and more durable pavements which are able to withstand high volume traffic, continuous increase in the traffic flow as well as variation in climate. Therefore, more focus has been put on research in transport related areas in the last several years, including new and improved road materials. At the moment significant research and development efforts in development of asphalt technologies take place worldwide. The main goal of many research projects is to develop more durable, safely performing and functional materials with minimal environmental impact. One of the most developed technologies is the application of modified bitumens. Modified bituminous materials can bring real benefits to highway maintenance/construction in terms of better and longer lasting roads and savings in total road life cost. Bitumen has been modified with variety of materials including polyphosphoric acid, polymers, rubber, and fibers.[1-3]

By the end of 2011, 34 Million tons of asphalt is expected to be used in North America.[4] Polyphosphoric acid (PPA) has been used for many years in North America as a bitumen modifier and meets demanding performance requirements. PPA-containing bitumen accounts for 19% of modified bitumens in the USA and this number is expected to increase to 26% by the end of 2011.[5] The application of polyphosphoric acid in bitumens was first reported in a 1973 patent assigned to Tosco-Lion[6] and its use in the US has increased steadily since that year. Today, polyphosphoric acid is used in the air-blowing process, primarily for roofing applications, as a catalyst in reactive terpolymer applications, and as a direct bitumen modifier. The latter application involves modification with polyphosphoric acid alone or in combination with elastomeric polymers.[7-19] In neat bitumen, polyphosphoric acid increases the high-temperature Performance Grade (PG) rating of the bitumen (per Superpave™ specifications in the US) while maintaining the low-temperature properties, while frequently significantly reducing the total modifier load. Significant improvements in the water sensitivity of mixes are also obtained.

The purpose of this study is to investigate of the effect of PPA on the physical and rheological properties of bitumens obtained from different parts of the world. It is widely known that the extent of bitumen reaction and modification with PPA is dependent on the chemical nature of the binder. This dependence generally varies from geographic region and crude source and it is often related to the level of asphaltenes and other components in the bitumen. Bitumen testing and grading methods also vary across the world. So the primary aims of this study is to measure and report the level of modification that can be achieved across a wide range of bitumen sources using a variety of test methods. European classification of bituminous materials is based on empirical test methods such as penetration, softening point and viscosity. In the USA a very different binder grading system was introduced by the Strategic Highway Research Program (SHRP) and it is based on the performance of the binder at difference temperatures. According to this system binder is being classified by two numbers (e.g. PG 64-28), where the first of these numbers (64) indicates binder's performance at high temperature and the second number (-28) is binder's performance at low temperature.[20] Due to fundamental differences in European and American systems of binder grading it was decided to use both systems in order to demonstrate the effect of addition of PPA and its compatibility with different types of asphalt

MATERIALS AND METHODS.

Materials. Polyphosphoric acid of 105 % concentration from ICL Performance Products LP was utilized as a modifier. Some of the key properties of polyphosphoric acid (PPA) are listed in Table 1 below. Information on bitumen products from different geographic regions of the world is presented in Table 2.

Table 1. Typical Properties of Polyphosphoric Acid [21, 22]

	Polyphosphoric Acid 105
Formula	$H_{n+2}(P_nO_{3n+1})$
P_2O_5 (%)	76.1
Equivalent H_3PO_4 (%)	105
Molecular Weight (avg, g/mol)	126
Specific Gravity (@25° C)	1.94
Viscosity @25° C (k Pa s)	800
Viscosity @ 100° C (k Pa s)	36
Freezing Point °F (°C)	84 (29)
Boiling Point °F (°C)	572 (300)
pH (1% solution)	1.7

Table 2. Bitumen sample information.

Superpave™ Classification	European Classification	Origin
PG 58-28	AC-10	Canada
PG 64-22	AC-20	Venezuela
PG 58-22	AC-10	China
PG 64-22	AC-20	Russia

Methods. The binders were evaluated with and without PPA modification with respect to the EN 12591- *Specification for paving grade bitumens* and AASHTO M320 (Table 1 & 2). Several chemical analysis techniques like ASTM D 4124 – *Component Analysis by Iatroscan* and EN 12606-1 – *Paraffin Content Determination* were performed to relate the resulting performance to asphalt binder chemistry. The effect of short and long-term aging on PPA-modified bitumens was studied by conditioning samples using TFOT and PAV. Low-temperature performance was measured by the Bending Beam Rheometer, Direct Tension Device and Fraass Breaking Point. For all lab tests the bitumen samples were heated to 275°F (135°C) and 0.5 wt% 105% PPA was added while under low shear. Concentration of PPA was chosen to be 0.5 wt% based on the weight of the binder and did not change throughout the study. The samples were then allowed to mix for additional 30 minutes under low shear. The various test methods performed on the bitumens according to US and European standards are presented in Table 3.

Table 3. Binder Test Methods.

Name of the method	US test method	European test method
Wax contents		EN 12606-1
Component analysis	ASTM D 4124	
Specific gravity	ASTM D 70	
Flash Point	ASTM D 92	EN 22592
Dynamic Viscosity	ASTM D 2171	EN12596
Kinematic Viscosity	ASTM D 2170	EN 12495
Penetration	ASTN D 5	EN 1426
Solubility in TCE	ASTM D 2042	EN 12592
Softening Point		EN 1427
Fraass Breaking Point		EN 12593
Penetration Index		Annex B EN 12591
% Mass Change after RTFO	AASHTO T 240	EN 12607-3
Dynamic Shear	AASHTO T 315	
Creep Stiffness	AASHTO T 313	
Direct Tension	AASHTO T 314	

Results and Discussions.

Bitumen is a complex mixture of hydrocarbons which can be separated into fractions of increasing polarity, namely, the saturates, aromatics, resins and asphaltenes. Figure 1 shows a variation of composition of four different bitumens used in present work.

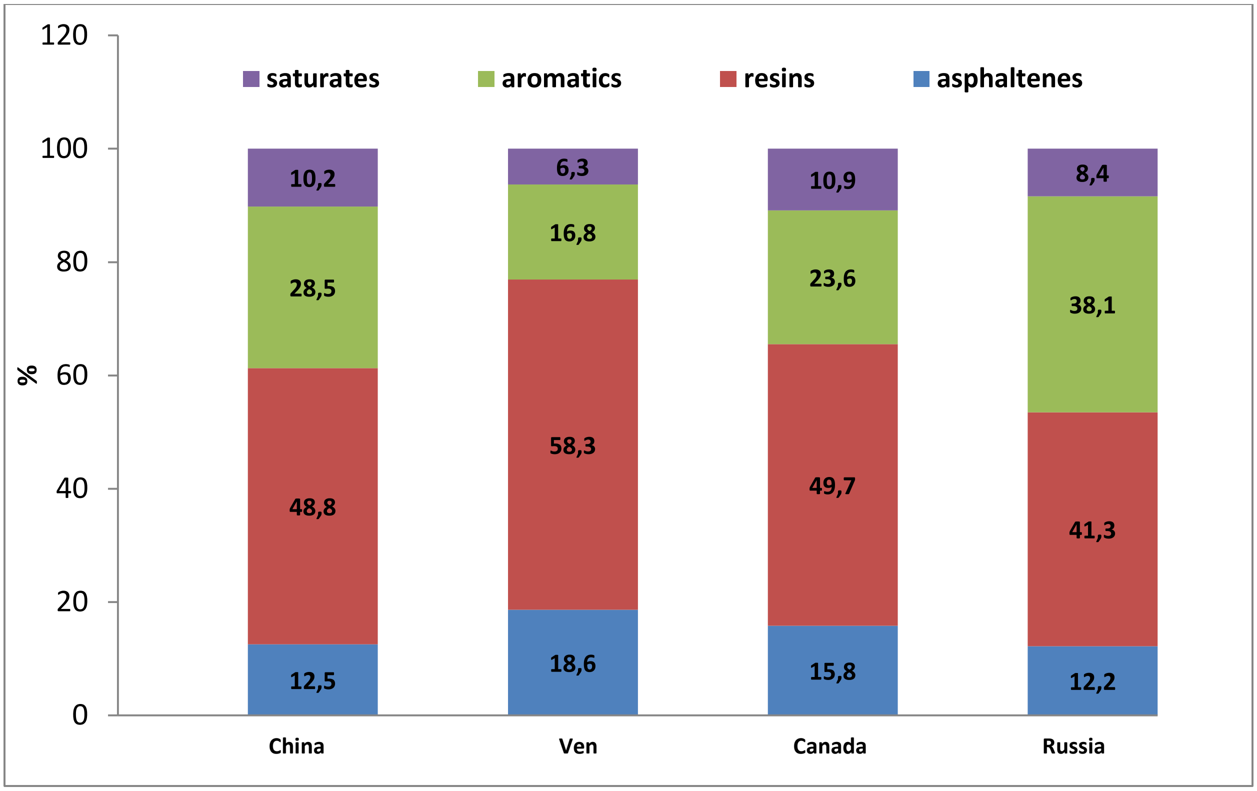

Figure 1. Dependence of the composition of bitumen on the origin.

As it is seen from Figure 1 composition of four selected asphalts varies significantly. Composition of bitumen is typically described as a colloidal substance, in which a dispersed phase, consisting of asphaltenes, is covered by a protective layer of polar resins and the continuous phase consists of a mixture of aromatic and saturate oils.[23] Previous studies show that amount of asphaltenes in bitumen sample is critical in producing PPA-modified bitumen with improved physical and rheological properties. It is believed that high dielectric constant of PPA and increased dielectric constant of heteroatomic compounds of asphaltenes would cause PPA to react with asphaltenes.[24, 25] The extent of PPA modification is loosely related to the level and exact composition of asphaltenes,[23] but this has not been clearly elucidated. The influence of the composition of asphalt has been recognized for many years, as being an important factor in controlling the performance of such material.[23] Impact of the addition of PPA on physical and rheological properties of different types of bitumen and its connection with bitumen composition will be discussed further in this paper.

Effect of Addition of PPA on Conventional Physical Properties of Bitumen.

The effect of addition of 0.5% PPA into different binders was investigated by monitoring physical properties of the binders before and after modification with PPA. Dynamic viscosity, penetration and softening point were determined according to *Specification for paving grade bitumens* EN 12591.

Table 4 shows a comparison of physical properties of the original asphalts and those asphalts modified with PPA. As indicated in Table 4, upon addition of PPA dynamic viscosity measured at 60 °C increases for all tested bitumen samples. For the Canadian sample addition of PPA allowed to meet the product specification above required minimum of 145 Pa s.

The results of the penetration test measured at 25 °C are shown in Table 4 and indicate a decrease in penetration with addition of PPA for all types of bitumens. Furthermore, bitumens from all regions were found to have penetration values higher than specified by standard. Upon addition of small amounts of PPA it was possible to bring penetration value within the range specified by the standard. A lower penetration value means higher resistance to deformation in the road pavement. Therefore, addition of PPA changes the rheology of bitumens, making them more viscous and harder at relatively high temperatures. It is worth mentioning that penetration at lower temperatures (i.e. 4°C) generally goes up upon addition of PPA, [26] which is consistent with other observations showing no loss of properties at low temperatures.

Table 4. Variation of Conventional Physical Properties of Bitumens.

	Test method/ specifications	China		Venezuela		Canada		Russia	
		No PPA	PPA	No PPA	PPA	No PPA	PPA	No PPA	PPA
Dynamic viscosity, Pa s @ 60 °C	EN 12596 145 min	170	280	349	907	93.7	191	3,027	4,734
Penetration, dmm (100g, 5 sec.) @ 25 °C	EN 1426 50-70	71	55	71	57	112	87	75	61
Softening Point, °C	EN 1427 46-53	49	53	53	59	51.5	51	46.1	51.5

The percentage of retained penetration indicates aging of bitumen and it is measured by penetration before and after the Thin Film Oven Test (TFOT) according to EN 1426 test procedure, where %retained penetration = penetration after TFOT x(100)/penetration before TFOT. Table 5 shows variation of retained penetration value upon addition of PPA for Chinese bitumen. Similar dependencies were obtained for Venezuelan, Canadian and Russian bitumens.

Table 5. Results on Penetration Calculated for Chinese Bitumen.

	Specifications	No PPA	With 0.5% PPA
Penetration before TFOT, dmm		71	55
Penetration after TFOT, dmm		48	45
Retained penetration, %	50 min	67.6	82

As seen from Table 5 increase in retained penetration from 67.6% to 82% was observed for Chinese bitumen. For Venezuelan, Canadian and Russian bitumens values of retained penetration upon addition of PPA were found to be 84%, 75% and 70.5%, respectively. Increased value of retained penetration is an indication of lower susceptibility of bitumen to short term aging. Therefore, the data suggest that modification of different types of bitumens with PPA leads to improved resistance to aging. High percentage of retained penetration may also suggest increased stiffness and good rutting resistance. So addition of PPA consistently results in smaller loss in penetration with aging, which is indicative of reduced aging.

Results of Softening Point tests are shown in Table 4. From Table 4, it can be seen that the softening point value for PPA-modified bitumen increases upon addition of PPA, with the exception of Canadian bitumen whose softening point remained essentially unchanged. The same effect has been found across bitumen from other regions, namely South Korea [27] and Taiwan. [1]

Effect of Addition of PPA on Superpave™ Binder Parameters.

Superpave™ binder tests are designed to study and quantify asphalt binder performance at three stages: original, after mixing and construction and after in-service aging.[20] Dynamic Shear Rheometer (DSR) was used to determine complex modulus (G*) and phase angle (δ) values for all binders with and without PPA. Complex modulus (G*) is a response of the binder to shear strain and it is calculated as the ratio of total shear stress to total shear strain. Phase angle (δ) is a measure of elasticity of the material and can be defined as time lag between applied strain and resulting stress. The ratio of complex modulus and phase angle (G*/sinδ), referred to as the stiffness, is determined by individual contributions of viscous and elastic components. The DSR data for binders (both neat and PPA-modified) taken at 70 °C are shown on Figure 2. Black dotted line indicates lower limit of specification for DSR value. DSR values for all samples were found to be lower than specified value prior to modification with PPA. Addition of 0.5 wt% of PPA leads to increase in stiffness for all of the samples. Furthermore, for Venezuelan and Russian samples the small quantity of PPA used in this study was found to be sufficient to achieve specified DSR value. For Chinese and Canadian asphalt slightly higher concentration of PPA would be required in order to meet the PG specifications requirements. Relative increase in stiffness is directly related to the asphaltene contents and type of the asphaltenes. It asphaltenes contain a lot of oxygen-containing groups, higher reactivity towards PPA and therefore, higher stiffness values are expected.

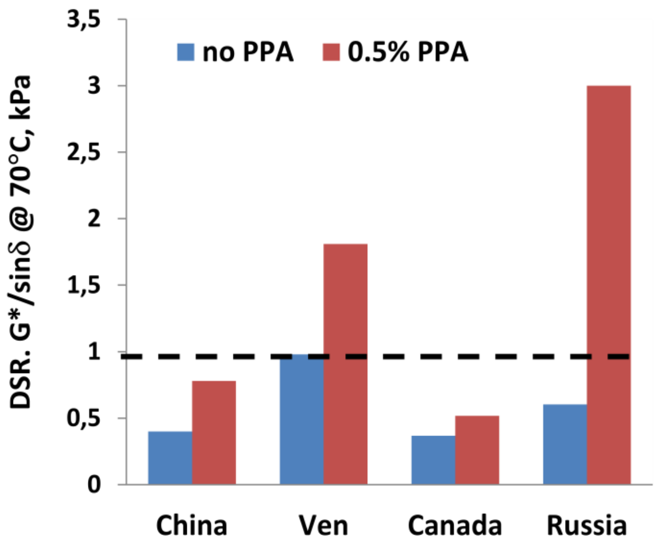

Figure 2. Variation of DSR values as a function of addition of PPA for different bitumens.

DSR measurements were also performed for PAV aged samples. As it was stated earlier PAV is used to simulate in-service aging of bitumen. The results also include determination of values of G* and δ, however, results are presented as product of multiplication of G* and sin δ (G* x sin δ) and used to evaluate the resistance to fatigue cracking. The higher value indicates that binder will be more prone to fatigue cracking. This portion of the specification is under much debate and generally agreed that it is not the appropriate measure for fatigue related distresses.[29] Figure 3 shows dependencies of fatigue values for PAV aged samples on addition of PPA. Black dotted line indicates the highest allowed value for fatigue. As it is seen from the Figure addition of PPA either decreases the measured value, as it is observed for Chinese and Venezuelan bitumen, or has no effect, as it can be observed for Canadian and Russian bitumens. If it is desirable to achieve asphalt binder which is less susceptible for long term aging (in the case of Chinese and Venezuelan bitumens) higher concentration of PPA may be chosen.

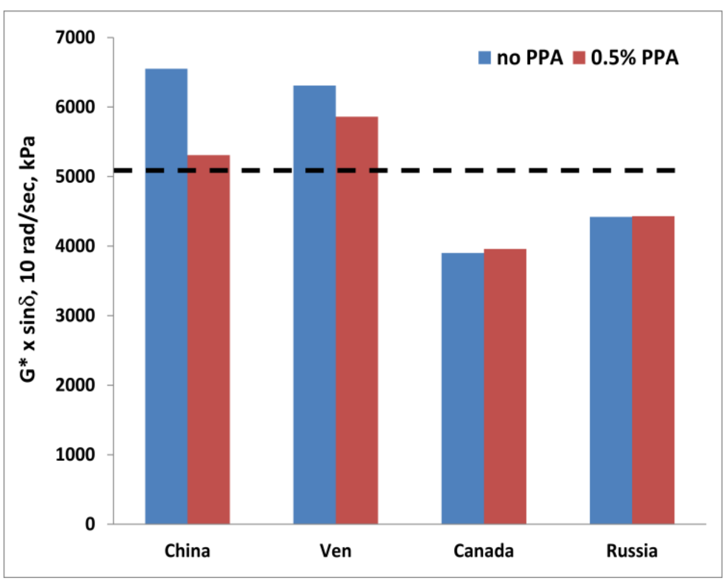

Figure 3. Effect of long-term aging on DSR data for PPA-modified bitumens.

Low temperature performance of PPA-modified asphalt.

Low temperature performance of bitumens was investigated according to European and PG specifications. According to European specifications Fraass breaking point was used to study the influence of PPA on bitumens, whereas bending beam rheometer (BBR) was used to determine creep stiffness and investigate the same effect according to PG specifications. Results of Fraass breaking point and creep stiffness, determined at -18°C neat and PPA-modified bitumens are presented in Tables 7 and 8.

According to data presented in Table 7 for Fraass breaking point addition of PPA leads to slight decrease of Fraass breaking point for Venezuelan and Canadian bitumens. For Chinese and Russian bitumens slight increase in Fraass breaking point was observed. All of the changes observed in Fraass breaking point are within the tests experimental error and therefore, it can be concluded that no significant effect was observed.

Table 7. Variation of Fraass breaking point of PPA-modified bitumens.

Country	Fraass breaking point, °C	
	No PPA	PPA
China	-8.5	-6
Venezuela	-9	-10
Canada	-13	-16.5
Russia	-11	-10

BBR was used to evaluate strength properties of the asphalt modified with PPA under constant load. Table 8 shows variation of creep stiffness value measured at -18°C for unmodified and PPA-modified bitumens. One of the outputs of BBR measurements is the value of creep stiffness, which is the measure of stress at a defined load and time during the Bending Beam testing. Typically the value of creep stiffness should not exceed 300 MPa, and lowers value are associated with better performance of the asphalt binders. According to Table 8 addition of PPA decrease creep stiffness values for Chinese, Venezuelan and Russian asphalt, which indicates that samples modified with PPA will be able to withstand higher stress. Sample of Canadian bitumen shows slight increase in creep stiffness value upon addition of PPA but it remains within specifications. All changes in creep stiffness are quite small and consistent with the earlier observation that PPA addition has little effect on low temperature performance.

Table 8. Dependence of creep stiffness value on addition of PPA for various bitumens.

Country	specification	Creep stiffness, MPa, @-18 °C	
		No PPA	PPA
China	300 max	357	328
Venezuela	300 max	299	286
Canada	300 max	214	224
Russia	300 max	221	217

CONCLUSIONS.

The effects of the addition of PPA to bitumens obtained from different geographic regions of the world was investigated. The binders were evaluated with respect to European and US specifications. In particular, the composition of the different bitumens, conventional physical properties, and the Superpave™ binder parameters were evaluated. On the basis of the performed experiment the following conclusions can be drawn:

- Composition of bitumens obtained from different geographic regions of the world varies significantly. This variation in the composition leads to significant difference in physical and rheological properties.
- Addition of small amount of PPA changes the rheology of bitumens, making them more viscous and stiffer at relatively high temperatures.
- Addition of PPA significantly improves penetration values for all types of bitumens. Upon addition of small amount of PPA it was possible to bring penetration within the specification values.
- Stiffer binder can be produced upon modification with PPA. Higher stiffness value means higher resistance to deformation in the road pavement and therefore relatively lower rutting.
- PPA-modified binders are less susceptible to long-term aging.
- Low temperature performance was improved for most binders.
- Level of PPA-modification must be individually selected for different bitumens due to large differences in composition.

Improvements in penetration grade as well as in PG grade were obtained upon addition of 0.5 wt% of 105% PPA. Studies done elsewhere[12] demonstrate that additional PG grade improvements are possible using higher levels of polyphosphoric acid. The findings from the moisture-sensitivity studies [12] (Texas boil test, Lottman assessment, Hamburg wheel test) all demonstrate polyphosphoric acid improve properties on its own or in combination with lime or liquid anti-strip agents. The best moisture-sensitivity results throughout were obtained for a combination of polyphosphoric acid and lime.

The bitumens studied were sourced from different producing regions and represent a wide range of compositions. In this study it was found that composition of bitumen varies significantly from region to region, however, the general finding is that polyphosphoric acid changes the rheology of bitumens, making them more viscous and harder at relatively high temperatures. These results are consistent with the results reported earlier for different types of bitumens. [12, 15, 28, 30]

In terms of the mechanism by which polyphosphoric acid interacts with asphalt to improve its rheology and overall properties, this is still under investigation by various methods.[15] One theory that has been put forward suggests that polyphosphoric acid reacts with various organic functional groups in asphalt,[22] breaking up asphaltene agglomerates and allowing the individual asphaltene units to form a better dispersion in the maltene phase. The dispersed individual asphaltene units are relatively more effective in forming long-range networks and in turn contribute to elastic behavior, Figure 4.

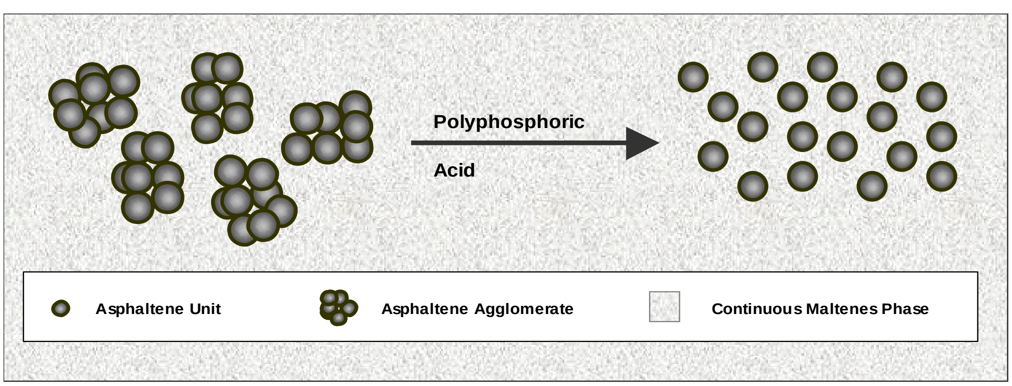

Figure 4. Possible Mode of Action of Polyphosphoric Acid in Asphalt Modification

Data obtained in the present work are supported by practical application of PPA for bitumen modification. Polyphosphoric acid has been used successfully in the United States for many years to modify asphalt pavements. [31-33] This includes modification with PPA alone and co-modification with polymers. One very good documentation of pavement performance is from the NCAT (National Center for Asphalt Technology) test track at Auburn University in Alabama.[34] The test track allows accelerated performance monitoring by continuously driving a test vehicle around the track. Each track section sees the same load, use, and environmental conditions. So performance comparisons can be made between sections. Eighteen track sections with bitumen co-modified with PPA and SBS polymer were tested from 2000 to 2002. After 2 years (10 million ESAL), there was no significant rutting, no moisture damage, and no fatigue cracking.[32, 33] An additional 19 test sections with bitumen co-modified with PPA and SBS were tested from 2003 to 2005. Again, there was no significant rutting, nor moisture damage and no fatigue cracking. [31, 32] The highway performance of PPA modified bitumen showed similar performance.[31]

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DISCLAIMER

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