Use of Polyphosphoric Acid in Asphalt Binders

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This paper was prepared by the Purified Polyphosphoric Acid (PPPA) Subcommittee, a subcommittee of the Phosphate Forum of the Americas (PFA). PFA provides a forum for information exchange on scientific and technical matters relating to inorganic phosphate products. Members of the PPPA Subcommittee are ICL Performance Products, LP and Innophos, Inc., companies that make purified polyphosphoric acid, which is used as an asphalt binder modifier for asphalt roads.

EXECUTIVE SUMMARY

Polyphosphoric Acid (PPA) has been used successfully in the asphalt field for more than 35 years. Extensive use of PPA either as a solo asphalt binder modifier or in combination with synthetic polymers has been practiced in North America for more than 10 years. PPA is increasingly being used worldwide to meet the high performance requirements for binders in Superpave™ applications. In fact, over the past 5 years, an estimated 3.5 to 14% of the asphalt pavement placed in the United States contained PPA. PPA modified asphalt binders have been used to pave roads all across the country under a wide variety of traffic and weather conditions. These roads are performing as expected in terms of reliability and durability.

This paper discusses the use of PPA as a modifier of asphalt binders.

1.0 INTRODUCTION

Asphalt binders are often modified by the use of additives to improve properties and meet performance requirements. Polyphosphoric acid (PPA) has been used for this purpose in North America for over thirty years[1]. It is currently estimated that up to 400 million tons of asphalt mix modified with PPA have been utilized on US highways in the past five years. This represents up to 14% per year of the asphalt pavement placed in the United States over that period.

PPA is currently used in the air-blowing oxidation process, as an additive in reactive polymer applications, and as a direct binder modifier. PPA is classified as a chemical modifier because it reacts with some of the components of asphalt[2]. The other broad category of asphalt modification is referred to as polymer modification and involves the use of specific elastomeric polymers. Both approaches are increasingly used in North America to meet the high performance requirements for binders in Superpave™ applications. In neat asphalt, PPA increases the high temperature Performance Grade (PG) rating of the asphalt binder without affecting the low temperature properties. Significant improvement in the water-sensitivity of mixes is also obtained. In polymer-modified asphalt, PPA provides these same benefits and also allows for a significant reduction in the level of polymer required to meet elastic recovery requirements.

The use of PPA in asphalt modification was first reported[1] in 1973. Earlier work dealt with the use of phosphorus pentoxide (P_2O_5) as a catalyst in the air-blown oxidation of asphalt[3,4]. Significant research on the use of PPA with polymers to modify asphalts, conducted since the late 1990s, is illustrated in several patents[5-8].

Considerable interest continues in understanding how PPA interacts with binders and developing technology to optimize its performance. There are a large number of recent papers and presentations[9-35].

2.0 THE EFFECT OF PPA IN ASPHALT

Asphalt 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[2]. The asphaltenes consist of complex polyaromatic compounds aggregated together showing a lamellar structure. The polarity of each component of the asphaltene controls the degree of association, mainly through hydrogen bonding[36].

Typically, the addition of PPA to asphalt (0.2 to 1.5%) increases the asphaltene content and concurrently reduces resin concentration[2, 16, 37]. As opposed to a typical asphalt oxidation process, the increase of asphaltene is not related to oxidation of the asphalt[12, 30], but to an increase of the polarity of the asphaltene-PPA-resin complex.

The reactions between the asphaltene component and PPA are not yet completely understood due to the extreme complexity of the asphaltene composition. However, it has been reported that asphaltene phosphorylation may occur[2], but this appears to be asphalt dependant[30]. Also, the PPA acidity definitely contributes tremendously to the asphaltene structure reorganization[2]. The exact nature chemical reactions are still under investigation using model compounds[28].

The PPA modified asphaltene significantly affects the rheology of the asphalt binder giving the PPA modified binder the capacity to resist higher temperatures and stress level conditions more than neat asphalt.

As mentioned above, the asphaltenes are aggregated though hydrogen bonding. Additional acidity brought by PPA impacts the association degree of asphaltene. The chemical reactions affect the asphaltene structure, leading to a higher degree of dispersion and thus increasing the viscosity of the asphalt.

The PPA modified binder also shows higher capability for adhesion to aggregate [17, 27].

3.0 PERFORMANCE HISTORY

Asphalt binders used in asphalt pavements should be designed to provide optimum resistance to mechanical failure and permanent deformation and achieve high durability performance within a broad range of temperature and traffic conditions. Asphalt binders produced from straight run distillation are not always suitable to fulfill these needs, therefore, asphalt modifiers may be required. Typical modifiers have been polymers, chemical additives, or a combination of the two.

Of the available chemical additives, PPA is most widely used. While recent publications[18] have raised interest in PPA usage in North America, it may not be a broadly understood technology.

The four main applications currently using PPA as an asphalt modifier are: PPA catalytic asphalt blowing, PPA asphalt modification, PPA/polymer asphalt modification and PPA/crumb rubber asphalt modification.

3.1 PPA Catalytic Asphalt Blowing

PPA was first used as a substitute for anhydrous phosphorous pentoxide as a catalytic blowing agent in the 1960s and has been used for this purpose ever since.

The first literature on PPA use as a catalytic air blowing agent is found in 1961 when a patent[38] was granted claiming the benefit of using a blend of anhydrous phosphorous pentoxide and orthophosphoric acid instead of anhydrous phosphorous pentoxide. (This mixture is equivalent to 76% P_2O_5 content which corresponds to 105% PPA.) The benefits of PPA in the air blowing process are related to the ability of PPA to modify the microstructure of asphalt resulting in less binder oxidation and thus less brittleness[38, 39].

3.2 PPA Asphalt Modification

In 1972, The Oil Shale Company (TOSCO) was the first company that cited PPA as an asphalt modifier without air blowing[1]. PPA has since been used to improve the asphalt binder grade (softening point improvement and penetration reduction) prior to the Strategic Highway Research Program (SHRP) and to improve the PG after SuperpaveTM without oxidation of the binder. Since then, PPA usage in asphalt increased sharply after the implementation of the PG grading system in the late 1990’s and is currently used extensively to improve asphalt properties.

The addition of polyphosphoric acid to neat bitumen results in the following changes: increased viscosity, higher softening point, lower penetration at room temperature, and a slight increase or no change in penetration at very low temperatures. Results from two examples are shown in Table 1. The general finding from these and several other examples is that polyphosphoric acid changes the rheology of bitumens, making them more viscous and harder at relatively high temperatures, while keeping them soft at cold temperatures.

In terms of Superpave testing, the addition of polyphosphoric acid to bitumens has a significant effect in the dynamic shear rheology parameters, with higher values for the complex modulus (G^*) and lower values for the phase angle (δ). The ratio of the two, taken as $G^*/\sin\delta$, increases with acid addition at each temperature, as shown in the example in Figure 1, indicating higher stiffness as the level of polyphosphoric acid is increased at any given temperature. In this example, the minimum original $G^*/\sin\delta$ value of 1.00 kPa required for PG rating is maintained up to 70° C for the system with 0.6% polyphosphoric acid 115 and 76° C for the system with 1.2% polyphosphoric acid 115. The PG ratings obtained for three other bitumens using different levels of polyphosphoric acid are shown in Figure 2. The data shows that polyphosphoric acid causes an increase in the high-temperature grading with no loss of the low-temperature properties. This extends the useful temperature range (UTR).

As asphalt composition has significant variability, the impact of PPA on asphalt physical properties varies accordingly. A full grade improvement requires typically 0.5 to 1.5 wt% of PPA. Where an asphalt needs to be improved less than a full grade, PPA is typically used at a rate lower than 0.5 wt%.

3.3 PPA/Polymer Modification

Asphalt modification with both PPA and polymers is widely used and has become increasingly popular as state agencies move to PG-Plus specifications for items such as elastic recovery and ductility. Among a broad range of polymers, claimed to be beneficial in combination with PPA[5-8], those preferred are the styrene-butadiene-styrene (SBS) copolymers and ethylene terpolymers (e.g., Elvaloy®), which have been used with PPA since the late 1990's.

Table 1. Conventional Properties of Bitumens Modified with Polyphosphoric Acid

Bitumen	Viscosity Abs @ 60 C (M Pa s)	Softening Point (°C)	Penetration (dmm)		Approximate ASTM D3381 Viscosity Grade Classification	Approximate ASTM 946 Penetration Grade Classification
			25° C	4° C		
A Neat	285	52	51	24	AC-30	40-50
A + 0.50% Polyacid 105	697	58	46	26	AC-70	40-50
B Neat	261	48	84	31	AC-30	85-100
B + 0.50% Polyacid 105	566	55	72	35	AC-50	60-70
Polyacid = Polyphosphoric Acid						

Figure 1. Dynamic Shear Rheology of Bitumens with Polyphosphoric Acid.

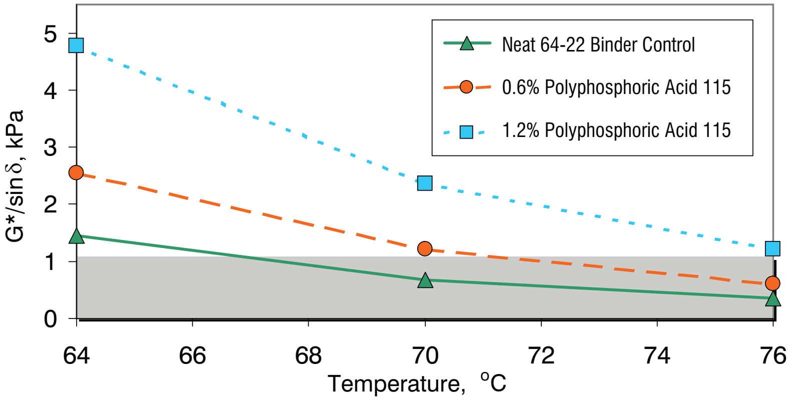
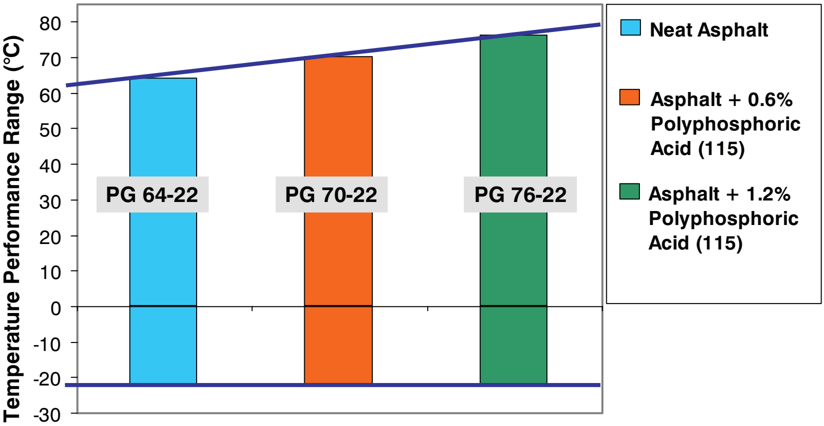


Figure 2. Bitumen Performance Grade (PG) changes with the use of polyphosphoric acid



The major benefit of this particular combination is that PPA and polymers in asphalt achieve optimum binder performance. PPA improves adhesion that may negate the need for antistrips. Viscosity of the polymer/PPA modified binder is more manageable, with respect to the current Superpave™ requirements and especially after storage. This results in ease of pumping and allows for lower operating temperatures. Lower temperatures ultimately reduce emissions from asphalt operations. Asphalt binder elasticity, thermal cracking resistance, and permanent deformation resistance improvement are also optimized in the synergistic combination of PPA and select polymers. The overall cost of using modified asphalt binders is reduced by use of less total modifier, possible elimination of antistrips, and energy savings from reduced operating temperatures.

Research using PPA with both major types of polymer systems, SBS and ethylene terpolymers, strongly indicates that the combination of PPA and polymers creates formulations that are superior to those achievable with either polymer modifier by itself.

The work with SBS, using the new Multiple Stress Creep Recovery (MSCR) grading approach[31, 32], conducted by the Federal Highway Administration, is summarized in Table 2.

As these tests show, the use of PPA in combination with SBS polymer increases the useful temperature range by approximately 4.5 degrees C, nearly doubles the J_{nr} performance, and increases the % recovery by approximately 20 to 25%. Further, there is little or no effect on Elastic Recovery. This level of performance appears to be only achievable when using a combination of PPA and SBS and not with either alone.

Table 2. Multiple Stress Creep Recovery (MSCR) and Elastic Recovery of Binder with Polymer

Continuous Grade	Polymer	PPA, wt%	Test Temp., °C	MSCR J_{nr} * (3.2kPa)	MSCR % Recovery (3.2kPa)	Elastic Recovery, %
76.6-25.2	76.6-25.2 (from concentrate)	0	70	0.118	40.3	86
			76	0.235	37.0	
81.6-24.5	4% SBS (from concentrate)	0.50	70	0.067	52.0	83
			76	0.138	42.5	

* J_{nr} is non-recoverable compliance, the new test proposed by the FHWA to replace $G^*/\sin\delta$ to measure high temperature performance

Using PPA in combination with Elvaloy® reduces the reaction time from 1 day to hours, lowers the reaction temperature from 385°F to 330°F, and results in a cost savings by reducing the amount of Elvaloy® RET required. What is not so generally known is that the properties of the final product are greatly improved as well, as shown on Table 3.

Table 3. Use of PPA in Combination with Elvaloy[40]

	Pass/Fail Temperature		BBR		SHRP Temperature Spread (°C)
	Unaged (°C)	RTFO (°C)	s-value T, °C @ <300 MPa	m-value T, °C @ >0.300	
Base AC	55.3	56.3	-23.4	-22.7	88.0
+Elvaloy® AM	64.0	65.3	-21.6	-22.0	95.6
+Elvaloy® AM & PPA	71.1	74.1	-23.4	-23.5	104.5

3.4 PPA/Crumb Rubber Modification

Since 2003, the beneficial effect of PPA in crumb rubber modified asphalt has been recognized. The addition of PPA to crumb rubber modified asphalt allows for the desired crumb rubber modification without some of the typical negatives associated with higher dosage crumb rubber modification. PPA improves the PG grading, viscosity, storage stability, and the elastic recovery of crumb rubber modified asphalt with typical process conditions of modified asphalt. This allows for high performance crumb rubber modified asphalt utilizing less rubber. Ultimately, less binder is needed in the mix versus pure crumb rubber modification. Typical PPA levels of 0.5% - 1.0% in combination with 5 - 8% rubber produce results similar to those of polymer or the PPA/polymer combination[9]. Cost savings in modification are achieved by reduced binder requirement and lower operating temperatures.

4.0 PPA MODIFIED BINDER IMPROVEMENT AND MIXTURE PERFORMANCE

PPA has been used for many years to improve binding and mixture performance. Improved properties of the asphalt binder have been confirmed to improve the asphalt mix properties by reducing the rutting phenomena[11], as well as maintaining improved thermal and fatigue cracking resistance[29]. Field tests reinforce these laboratory observations. Multiple sections of the National Center for Asphalt Technology (NCAT) test track[26] have been constructed with PPA modified asphalt combined with SBS, along with amine and lime anti-strip agents. These sections demonstrate excellent performance with respect to rutting, fatigue resistance, and resistance to moisture damage (stripping). Another field test is underway at the MnRoad test track[33,41] and will be monitored over the next five years. In addition, an Asphalt Institute Task Group is collecting data on the field performance of PPA modified pavements.

PPA has been used successfully in the asphalt field for more than 35 years. Extensive use of PPA either as a solo asphalt binder modifier or in combination with synthetic polymers has been practiced for more than 10 years across North America. This use has grown extensively as the industry has grown more confident in the use, application, and performance of PPA as an asphalt binder modifier.

4.1 Moisture Resistance

Resistance to moisture damage is a key aspect of good pavement design. When water finds its way to the binder-aggregate interface it can lead to poor *adhesion* of the binder to the aggregate. The presence of moisture within the binder itself can lead to poor *cohesion* of the asphalt cement itself. With time, both mechanisms will most likely cause pavement failure. Moisture sensitivity is dependent upon many factors, including the source of binder and aggregate, the presence of additives, and the compaction methods and conditions. When used properly and within a typical range, PPA modified binders show good moisture resistance. If an anti-strip agent is used, it should be compatible with PPA, for example a phosphate ester[18].

Various standard tests are used by industry and government to measure the effect of water on pavement performance. This includes the Texas Boil Test, a basic screening test to insure that there is reasonable adhesion between the binder and the aggregate after exposure to water. Another test, the Lottman T-283 test, measures the tensile strength of a compacted asphalt mixture before and after conditioning under water. A third test, the Hamburg Loaded Wheel test, evaluates the susceptibility of a compacted road specimen to both the loss of adhesiveness and the onset of rutting, or permanent deformation. These tests have all been used to evaluate the performance of pavements made with binders modified with PPA and some of the findings are reported here[24].

4.1.1 Texas Boil Test

The estimated percent adhesion of several binders to Lithonia granite, a moisture-sensitive aggregate, was evaluated using the Texas Boil Test. Mixtures of aggregate and binder were boiled in water for ten minutes, after which the percent adhesion was determined by visual inspection. The use of PPA results in a dramatic increase in adhesion in all cases, bringing the adhesion values from a 25-45 percent range to a 60-80 percent range. Studies involving binders, granite aggregate and commercial amine based anti-stripping agents and lime are shown in Figure 3. The results indicate good adhesion levels, compared to the control asphalt C, which suffered extensive stripping.

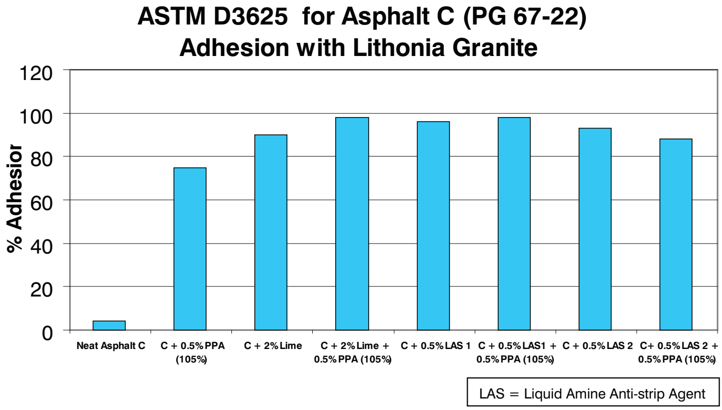


Figure 3. Adhesion of Asphalt Binder to Lithonia Granite

4.1.2 Lottman Test

The Lottman test measures the tensile strength of a compacted sample before and after saturation with water, following a freeze-thaw cycle and subsequent immersion under water for a specified period of time. Results are expressed as the ratio of tensile strength (TSR) before and after treatment. Figure 4 shows that treatment of a representative binder with PPA leads to an increase in TSR for mixtures with granite or limestone aggregates. Figure 5 shows good results using PPA together with amine anti-strip agents.

In addition, there have been many presentations and publications lending support to moisture sensitivity improvement with use of the proper amount of PPA[10, 15]. In many cases an anti stripping agent is not required, depending on the type of binder. If an anti-strip agent is needed, it is recommended that a suitable choice be made from compatible anti-stripping agents and proper testing with all components of the pavement be undertaken.

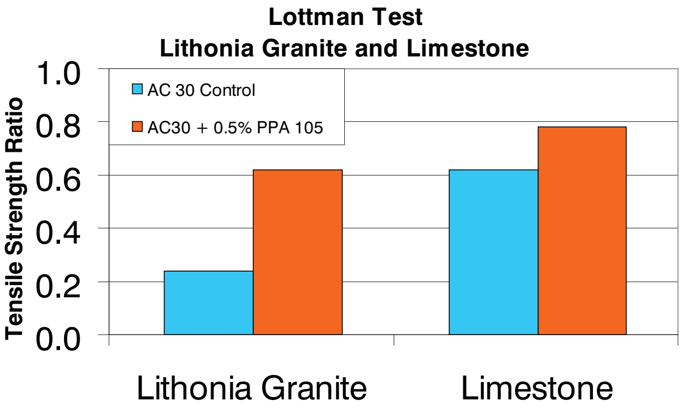


Figure 4. Lottman Test Results of Binder with Lithonia Granite and Limestone

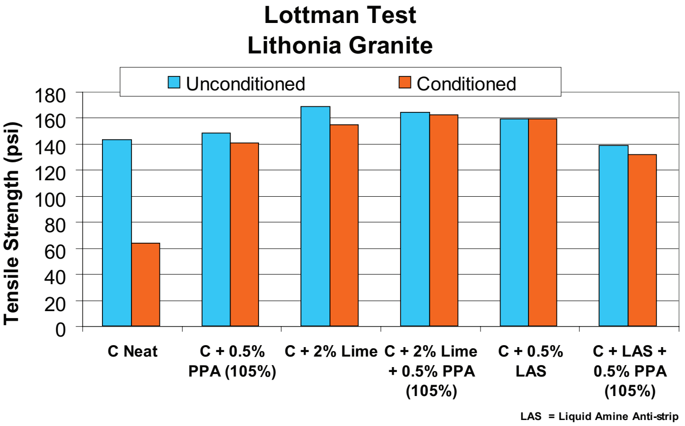


Figure 5. Lottman Test Results of Binder with Lime and a Liquid Anti-Strip Agent

4.1.3 Hamburg Loaded Wheel Test

The Hamburg Loaded Wheel Test is the most severe of the moisture sensitivity tests. The test is conducted under water at 50 degrees C using a loaded wheel and the extent of rutting is measured in millimeters. Figure 6 shows the results of a representative binder with and without PPA and various anti-strip agents. In most cases, rutting of 12.5 mm or more is considered failing. All of the systems containing PPA compared favorably to the control.

For aggregates, such as granite and porphyry based materials, the use of PPA generally provides resistance to stripping. For other aggregates, such as limestone, the performance is more binder dependent and a compatible anti-stripping agent may be required.

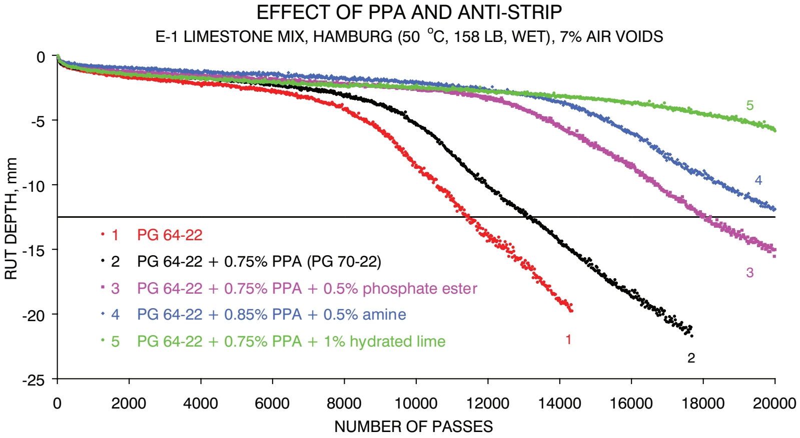


Figure 6. Hamburg Wheel Test with Lime and Liquid Anti-Strip Agents

4.2 AGING OF PPA MODIFIED ASPHALT CEMENT

The properties and performance of all asphalt cements will change with time. This “aging” process is mostly related to changes taking place at the molecular level, which includes oxidation, reactions between asphalt molecules, and volatilization. Short-term aging occurs during processing at the terminal and the hot-mix facilities and is a consequence of the relatively high process temperatures. Long-term aging occurs after the pavement has been laid down and results from the combination of several environmental factors, including: exposure to air, water, sunlight and cycles of extreme high and low temperatures. The most obvious manifestation of asphalt aging is an increase in hardening, where the asphalt becomes stiff and brittle and, ultimately, leads to road failure.

The use of PPA in asphalt cements does not accelerate asphalt aging and there is evidence that in many cases it actually slows it down[12, 14, 35]. This is demonstrated from both simulation and field studies using a variety of crudes. One study using RCAT (Rotating Cylinder Aging Test) evaluations demonstrates that PPA does not lead to increased asphalt oxidation and actually improves aging performance at both high and low temperatures[12, 14].

Simulated terminal storage testing shows no negative impact of PPA in binder properties at high temperatures. The percent change of G*/Sinδ after storage at 350 °F for seven days is actually lower for the system containing PPA, as shown in Table 4.

	Neat Binder	Binder + 0.5% PPA 115
G*/Sinδ, kPa Initial	1.21	1.94
G*/Sinδ, kPa After 7 Days@ 350 oF	1.88	2.31
Percent Change	+55%	+19%

Table 4. Changes in Binder Stiffness After Simulated Terminal Storage

The effect of aging in low temperature performance is demonstrated from extended oxidative aging tests using the pressure-aging vessel (PAV). The results clearly demonstrate superior low temperature performance for PPA-modified binders[24], as reflected in the creep stiffness and direct tension measurements after 20 and 30 hours of oxidation, Figure 7.

5.0 CHEMISTRY

Polyphosphoric acid (PPA) is a clear, viscous inorganic compound consisting of monomers, dimers, trimers, and higher condensed species[42, 43] of composition $H(PO_3H)_nOH$. Polyphosphoric acid is generally considered milder than other inorganic acids. The chemical and physical properties of PPA are shown on Table 5.

It is important to differentiate PPA from its monomeric form, orthophosphoric acid. Orthophosphoric acid is generally called “phosphoric acid.” Commercially available grades of orthophosphoric acid contain 5 to 65% water, which will lead to foaming when added to hot mix asphalt. Orthophosphoric acid, therefore, is NOT recommended for use in this application. PPA contains no free water and IS recommended for use with asphalt. NOTE: Certain non asphalt industry segments use the term “PPA” when referring to purified phosphoric acid. Be sure that PPA used in asphalt is polyphosphoric acid.

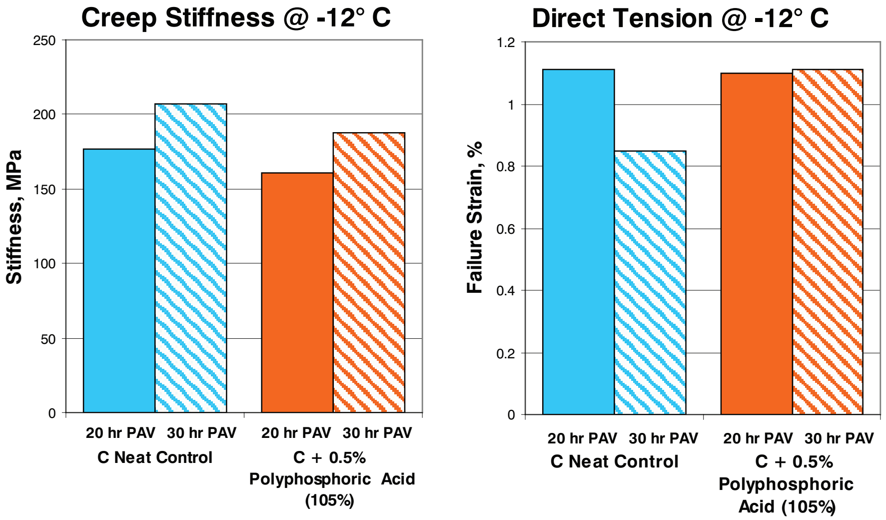
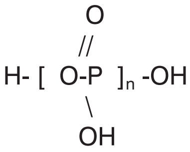


Figure 7. Low-Temperature Performance Following PAV Aging

PPA is formed by condensing orthophosphoric acid to eliminate water between two or more molecules. For example, if two molecules of orthophosphoric acid are heated to remove one molecule of water, then PPA is formed.

H_3PO_4 ---- heat ----> $H_4P_2O_7 + H_2O$

PPA consists of linear molecules of various chain lengths and NO FREE WATER. PPA includes the molecules orthophosphoric acid (H_3PO_4), pyrophosphoric acid ($H_4P_2O_7$), triphophoric acid ($H_5P_3O_{10}$), tetraphosphoric acid ($H_6P_4O_{13}$), and higher condensed species with the general formula:



$$\mathrm{H\text{-}\,[\;O\text{-}\underset{\substack{\backslash\\ OH}}{\overset{\substack{O\\ //}}{P}}\;]_n\,\text{-}OH}$$

Typical commercial concentrations of PPA are 105% and 115%, based on equivalent

Table 5. Chemical and Physical Properties of Polyphosphoric Acid

	Polyphosphoric Acid (105)	Polyphosphoric Acid (115)
Chemical Properties		
Formula	$H(PO_3H)_nOH$	$H(PO_3H)_nOH$
Equivalent H_3PO_4 (%)	105	115
P_2O_5 (%)	76.1	83.3
P_2O_5, distribution as:		
Orthophosphoric acid	49	5
Pyrophosphoric acid	42	16
Triphosphoric acid	8	17
Tetraphosphoric acid	1	16
Higher polymer acid	0	46
pH (1% solution)	1.7	1.7
Physical Properties		
Density @ 25° C, lb/gal	16.0	17.0
Specific Gravity (@25.5° C/15.5° C), g/cc	1.94	2.06
Viscosity @25° C (k Pa s = centipoise)	800	28,000
Viscosity @ 100°C (k Pa s)	36	510
Solubility in Water (%)	Infinite	Infinite
Freezing Point °F (°C)	61 (16)	---------
Boiling Point °F (°C)	572 (300)	1022 (550)

H_3PO_4 content, as shown in Table 5. In general, favorable results can be achieved in asphalt with both 105% PPA and 115% PPA, but 105% PPA is easier to handle.

6.0 STORAGE AND HANDLING

For information on storage and handling of PPA, please refer to the Material Safety Data Sheets (MSDS) for which links are provided below:

http://www.icl-pplp.com/page.aspx?id=180
http://www.innophos.com/msdslib.asp?sort=1

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