

Benefits and limits of PPA modification

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Abstract

Since its industrial introduction at the end of the 20th century, modification of bitumen with Polyphosphoric acid has always been a source of controversy. Special handling of the product and incompatibility with some antistripping agents or crosslinkers have led to multiple discussions and some mistakes in use. Through a decade of intensive use, US has gained tremendous experience about this technology, its advantages and its limits. Based on literature review, recent data and common practice, and in the light of the on-going refining changes, we intend to present an updated status about the use of this technology in the four different applications : - PG bump - Combination with polymer - Combination with crumb rubber - Oxidation additive

1. BACKGROUND

1.1. Intellectual Property

Although the use of acid during oxidation of bitumen was patented as early as 1936 [1], it is only 40 years later that straight modification of bitumen with polyphosphoric acid (PPA) was patented [2]. Since that time, a large number of patents were issued about the use of PPA in bitumen, even recently.

1.2. Effect on bitumen

When used as a solo modifier, PPA stiffens bitumen, while maintaining or sometimes lowering the cold temperature properties. The temperature service conditions of the binder are thus increased. This is accompanied by a significant increase of binder viscosity, and a slight decrease of binder complex modulus. Moisture resistance can be increased in limited cases like granite based aggregates [3], and fatigue resistance may improve for moderate PPA concentration [4]. No storage stability issues are encountered [5].

The effect is largely dependent on the composition of the bitumen. T. Arnold's measurements [6] seem to indicate that reactivity of PPA is increased in the presence of a high asphaltene content in first rank and a high aromatic content in second rank. G. Baumgardner [7] studied 7 different bitumen and found a correlation between the maltene solvency and the impact of PPA.

When used as blowing agent, PPA acts like flux oil, making it possible to obtain a high softening point and limit the impact on penetration [8].

1.3. Mechanisms

Giavarini et al. were the first to suggest a reaction of PPA with asphaltenes [9]. Through NMR ³¹P and NMR ¹³C of extracted asphaltenes, Orange et al [10] proposed a mechanism of neutralisation of polar interactions between the stacked asphaltene molecules, either by protonation or esterification, leading to a de-agglomeration of the asphaltenes and the formation of phosphate esters in situ. J-F. Masson confirmed this potential mechanism from theoretical point of view [11]. Baumgardner et al. went further with Atomic Force Microscopy of bitumen and Gel permeation chromatography of asphaltene fractions [12]. They demonstrated that pending the type of bitumen, PPA impacts either the dispersed phase or the continuous phase, and they suggested several mechanisms to explain this behaviour on the microstructure of bitumen.

In Polymer Modification, some authors suggest that PPA has a synergistic or catalytic effect on polymer. Giavarini et al. for example demonstrated that the addition of PPA to Polypropylene modified bitumen was changing the bitumen structure from sol to gel and thus improving storage stability [13]. PG studies [14] and fluorescence microscopy tests [15] showed that SBS was better dispersed in the presence of PPA and suggested kind of crosslinking effect. Colloidal changes were observed upon addition of PPA to SBS modified bitumen [16]. Yaodong [17] attributes them to the contribution of PPA to the change from sol to sol-gel structure.

With Reactive Elastomeric Terpolymer, PPA has a strong catalytic effect [18].

It was shown that combination of crumb rubber and PPA present higher characteristics than the addition of the independent effects of rubber and PPA which could be due to some interaction between the two modifiers [19].

2. CONTROVERSIES AND SUCCESSES

2.1. Use

PPA is employed in the US since the 1970s. Its use increased dramatically upon implementation of the Superpave PG grading in the mid 1990s. This technology is indeed cheaper than polymers for the stiffening of bitumen. In 2010, Fee et al. estimated that 400 million tons involving PPA were paved the last 5 years, representing 14% of the total asphalt laid on US highways [20].

It is likely that such massive volume generated some misuse leading to failures. Indeed, like any modification technology, PPA presents technical limits. It was especially demonstrated that PPA does not improve significantly the elastic recovery [21, 22]. It may also deteriorate moisture resistance when employed at concentrations of 1.5% or more [23]. Nowadays, implementation of the PG Plus specification helps certainly to employ the technology properly, not only in US, but also all the countries which have adopted this specification.

In Europe, acid is among the technologies available to manufacture multigrade bitumens since the 1990s [24]. Following the generalised use in the US, the technology was successfully implemented in some PmB and RmB manufacturing units, in combination with SBS and crumb rubber. Today, the evolutions in bitumen quality are likely

to open more opportunities for modification with PPA at low dosage, in order to adjust bitumen consistency in penetration/softening point ratio.

2.2. Controversies

First major controversy about PPA technology started in the early 2000s in the US. Premature transverse cracking of I-80 in Nebraska was observed on PPA catalysed Elvaloy modified bitumen sections compared to SBS modified sections (186 cracks/mile vs. 6) [25]. This led to extensive speculations about PPA causing premature oxidation of binder. Indeed, since PPA is employed as a blowing additive for bitumen oxidation, this was making perfect sense. However, Reinke [3] clearly demonstrated that the cracking sections were likely caused by a higher air void content in most of the Elvaloy sections, and the PPA was not to blame. Glaser et al. definitely demonstrated that PPA is not inducing premature oxidation of the binder [26].

In 2007, a series of flushing appeared in New York state on fresh pavements and was attributed to PPA. Several years later, a study demonstrated that PPA was not present in all the sections that failed. In addition, other causes were identified like inappropriate PG specification in some cases, and low air voids in other cases [27].

Presence of phosphorus in binder is not automatically linked to the use of PPA. Analysing data from 20 job sites in Ontario Canada, Soleimani et al. [28] found zinc in the worst performing contracts and attributed this presence to the use of Re-Engineered Oil Bottoms (REOB) containing zinc dithiophosphate.

2.3. Lab testing

Checking potential degradation of the binder modified with PPA in real conditions requires special attention. Indeed, Reinke et al. [29] established that some phosphorus (and potentially acid) may stay with the aggregate during binder extraction from the asphalt, resulting in artificial binder stiffness reduction. This phenomenon is dependent upon the type of aggregate and the solvent used, and toluene is highly recommended to avoid artefacts [30].

The main relevant concern is the potential neutralisation of PPA by limestone aggregates, and lime or amine antistripping agents. Such partial reversion of the reaction between bitumen and PPA translates into loss of modification [31] meaning increased rutting, and/or removal of the necessary antistripping leading to higher moisture damage [32]. Extensive testing was carried out using Tensile Strength Ratio, wheel-tracking tests [3, 33], and more recently Surface Free Energy method [34, 35, 36]. From these studies, it seems that generally lime treated aggregates do not show any reaction with PPA. In the case of PPA concentration higher than 1%, limestone aggregates and liquid amines (for aggregates other than granite) generally interact negatively with PPA.

2.4. Successful field tests

The Asphalt Institute gathered field tests results all over the United States, in Arizona, Colorado, Louisiana, Maine, Michigan, New Hampshire, Pennsylvania [37]. They showed that PPA modified asphalt pavement were performing similarly to those without PPA. Unfortunately, due to incomplete data, they were not able to identify the conditions where PPA can bring performance advantage.

NCAT performed test tracks of SBS/PPA modified binders from 2003 [38]. Rutting and fatigue were low, and no moisture damage was noticed.

MnROAD performed a 7 years field testing from 2007 [39]. PPA and SBS/PPA modified bitumens were compared to SBS and Elvaloy modified binder. Again, rutting and cracking were found similar to standard PmB.

3. PG BUMP

The table and graph below present some data measured in our lab on a standard Shell French bitumen.

Table 1. Effect of PPA on bitumen, EU and US standards

	Standard	50/70 base bitumen	50/70 + 1.3% PPA 105
EU specifications			
Ring & Ball (°C)	EN 1427	49	58.6
Penetration (1/10 mm)	EN 1427	56	40
Fraas (°C)	EN 12593	-12	-19
Complex Modulus (MPa)	EN 14770	19.5	16.1

Flash point COC (°C)	AASHTO T48	334	338
Viscosity Dyn. 135°C (mPa.s)	AASHTO T316	391	791
US specifications			
PG Grade		64-16	70-22
High Temperature PG	ASTM D7643	66.4	74.9
Low Temperature PG	ASTM D7643	-21.7	-22

As expected, increase of Ring & Ball and high temperature PG are obtained. Fraas is significantly reduced, although low temperature PG is almost constant.

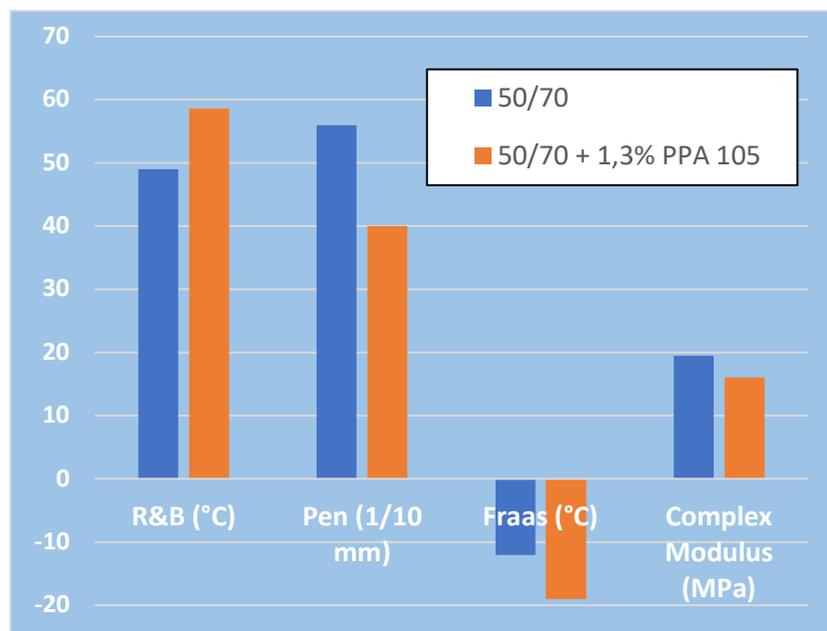


Figure 1: Impact of PPA on bitumen, EU standard

PPA brings stiffening benefit to a majority of streams blended as bitumen in a refinery [40]. The magnitude of the effect is strongly dependent upon the composition of bitumen. From a manufacturing point of view, this means that for a fixed recipe (concentration) of PPA, fluctuating performance of PPA modified bitumen may be obtained if the bitumen source is fluctuating, or if the composition of a single source of bitumen is fluctuating. In other words, operators that do not know or control their source of bitumen may face quality issues with PPA as single modifier.

Nowadays, most refineries, especially in Europe, are facing challenges that may impact the composition of the bitumen they produce. For example, crude sources of various origins may be employed for cost optimisation. Also, the new IMO regulation on bunker sulphur content early 2020 may cause significant levels of visbreaking residue into some bitumen blends. Now, it was demonstrated that PPA can crystallize in the presence of visbreaking residue, leading to an effect on bitumen which is exactly the opposite to what is expected [41].

In any case, employing PPA as solo modifier requires special care. We recommend a maximum concentration of 1.5%, control of bitumen source, and in-depth lab formulation study to check potential incompatibility with limestone aggregates, lime or other antistripping agents.

4. POLYMER MODIFICATION

The combination of elastomer and PPA is probably the largest application. In a majority of cases, PPA can replace part of the polymer and the corresponding Polymer Modified Bitumen (PmB) still reach the specifications [42, 43]. The main benefit is reduction of raw material costs.

The formulation strategy is described in Figure 2. It is based on the following principle: gain of softening point is cheaper with PPA than with SBS.

Since PPA has limited impact on elastic recovery, the 1st step is to establish the minimum amount of SBS required to reach the elastic recovery specification (blue line). In our example, the minimum is 3% SBS. At this stage, if softening point specification is reached, then there is no interest in using PPA.

If it is not the case (like in our example), then step 2 is to establish the concentration of SBS required to reach the ring & ball specification (dark green line). In our example, this is 4.2%.
 Last, step 3 is to identify which concentration of PPA is needed with the minimum amount of SBS (3%) to reach the softening point specification. In our example, this is 3.4%.
 Evaluation of raw material costs between both formulations (step 2 and step 3) makes it possible to determine if the combination of SBS and PPA is a cheaper formulation than SBS alone.

EU standards were employed for this description, but US standards can be similarly employed as well.

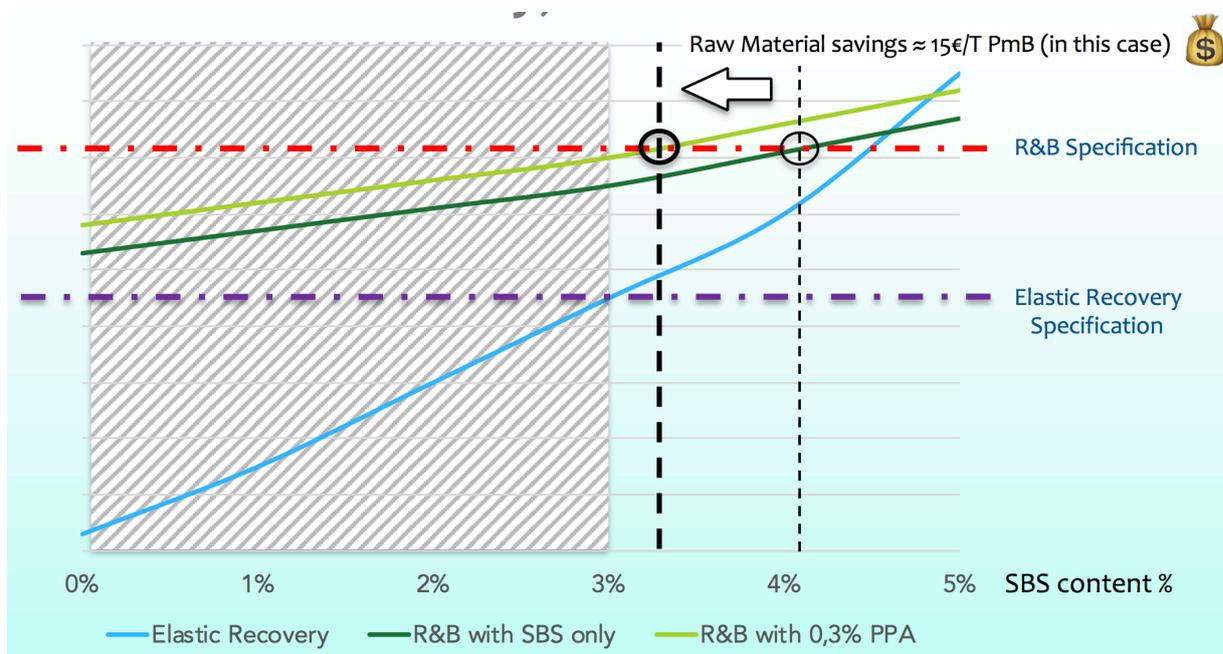


Figure 2: PmB Formulation Strategy with PPA

From the low temperature performance side, SBS/PPA modified bitumen is not negatively impacted when moderate amount of PPA is employed. It is either similar to SBS alone [44], or improved in some cases [45].

For this application, we recommend not to exceed 0.5% PPA. In such conditions, interaction with other components of the asphalt is limited, but shall be checked through lab investigation.

5. PPA HANDLING

PPA is a liquid product with very high viscosity at low temperature [46]. The most popular grade 105% H3PO4 is even crystallizing around room temperature. In these conditions, proper industrial handling at the various stages of the process is key in order to avoid issues during production.

5.1. Feeding of PPA

PPA exhibits high heat loss, which leads quickly to high viscosity and even crystallization that may plug the feeding line. Short feed lines, insulation or even line tracing are alternatives to keep this phenomenon under control.

5.2. Injection of PPA into bitumen

A poor mixing of PPA with bitumen may involve local excessive modification (with gelification or crystallization risks) and no modification at all in the vast majority of the binder.

There are basically 2 ways for batch addition of PPA to bitumen (Figure 3).

For injection on the top, we recommend a good stirrer insuring both shear at the level of addition of PPA and circulation of the binder.

In-line injection in the circulation loop requires high turbulence in the pipe, and proper rate of addition of PPA in order not to exceed locally the final concentration targeted for the modified bitumen.

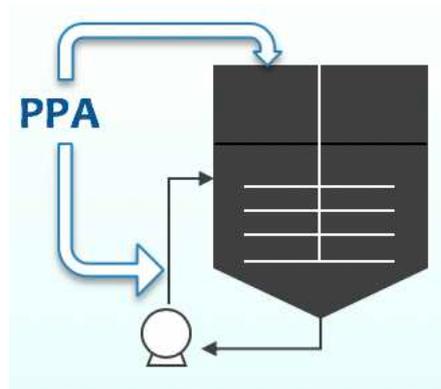


Figure 3: Addition of PPA to bitumen

In both cases, PPA injection outlet shall be away from the tank or pipe walls to avoid accumulation on the surfaces and potential corrosion due to high local concentration of PPA. When mixed in bitumen, PPA does not increase corrosion when concentration stays below 2%.

6. CONCLUSION

PPA is one of the technologies available for bitumen modification, either by itself or in combination with other modification technologies (elastomers, reactive terpolymers, crumb rubber). It is probably one of the most cost competitive way to increase service temperature of bitumen.

Strategies for formulation of PmB and RmB are presented in this paper and can be used as guidelines at the lab.

Potential incompatibility with other components of the asphalt requires in-depth laboratory formulation at binder and asphalt levels, especially for high concentrations (0.5% or more).

Like any modification technology, PPA modification is binder composition dependent. With the on-going changes in refineries, it is highly advisable to know or measure the fluctuations of the bitumen source so as to adapt the formulation if necessary.

Last but not least, proper industrial handling of PPA is necessary to insure the best performance of the technology.

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