The Use of Phosphoric Acid as a Modifier for Hot Mix Asphalt

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ABSTRACT
The use of phosphoric acid (PPA) to stiffen paving asphalt has become quite ubiquitous. Recently, several premature paving failures have been attributed to its usage, however much of this has been based on incomplete information or speculation. Subsequently this has created uncertainty regarding hidden pitfalls surrounding its use. The primary concerns are the effect of different grades of phosphoric acid, the reactivity of asphalts from different sources and whether PPA accelerates aging, or increases the moisture sensitivity of binders.

This paper discusses research conducted to address many of these issues. Data are presented to show the effect of increasing levels of acid modification on moisture sensitivity. Both the absorption of moisture into the binder and mastic samples as well as the leaching of phosphoric acid from gyratory specimens were examined. The latter findings suggest that high levels of acid modification are a potential source of groundwater pollution.

Preconceived notions about the use of phosphoric acid with alkaline antistrip additives are also addressed. Use with antistrip additives is perfectly feasible if the proper screening tests are conducted before use.

Background:
Phosphoric acid has been used to stiffen paving asphalt for many years. Experienced industry practitioners have found that the addition of small amounts (ca 0.5%) of polyphosphoric acid (PPA) to polymer-modified binders improved both their handling and performance. When used with SBS polymers it enables suppliers to achieve higher Superpave Performance Grades while improving the mixing and compaction characteristics. With ethylene terpolymers, it catalyzes the reactivity of the glycidyl methacrylate groups. Both types of polymer-modified binders have shown the addition of PPA to increase rut resistance of the binder. More recently, the increasing popularity of PPA has led to its use as a partial replacement for polymer modification.

Exacerbated by several apocryphal reports on highway failures attributed to the use of phosphoric acid, the unknowns associated with its use have raised questions at many State agencies. The unknowns have led some agencies to ban phosphoric acid while others continue its use. Issues include the effect of acid grade, asphalt type, asphalt oxidation, (since it is used as a blowing catalyst in preparing asphalt for roofing applications (1)), increased moisture sensitivity and reaction with commonly used anti-strip additives such as lime and amines.

Background on Phosphoric Acid
Several grades of phosphoric acid containing different amounts of orthophosphoric acid are commercially available. They contain 50% (“Green Acid”), 75%, 85%, and 100% orthophosphoric acid. Two other grades Superphosphoric and Polyphosphoric acids contain 105% and 115% orthophosphoric acid and are mixtures of pyrophosphoric acid, triphosphoric and higher acids. “Green acid”, the precursor of the purified grades, produced by treatment of ground phosphate rock with sulfuric acid, contains strongly acidic impurities, mainly sulfuric and hydrofluoric acids, which may be present at levels up to 2%.
1. Effect of Phosphoric acid Grade on Asphalt Stiffness

To ensure consistency in comparing the different acid grades, the addition levels are normalized to 100% orthophosphoric acid. For example, 2% by weight of green acid (containing 50% orthophosphoric acid) yielded a phosphoric acid concentration of 1% in the asphalt.

The stiffening effect of different phosphoric acid grades was determined by modifying four SHRP reference asphalts and measuring the Superpave high temperature stiffness (G*/Sinδ at 64°C) using a dynamic shear rheometer.

The asphalt was heated to 165°C, stirred with a mechanical stirrer running at 450rpm while adding the acid. Stirring was continued for a further 20 minutes while maintaining the temperature at 165°C. Samples were taken immediately and the stiffness measured.

As shown in the figures 1-4, all grades of purified phosphoric acid yielded similar increases in stiffness. Crude “Green Acid” gave the biggest increase in stiffness. This is attributed to the presence of strong acids (hydrofluoric and sulfuric acid). The corrosive nature of this acid and the likely variability of the crude product is likely to preclude its use in the asphalt industry. Since all the purified grades behaved similarly, all subsequent tests were carried out using 115% Polyphosphoric Acid. The water boiling off when 85% and weaker acids were added to hot asphalt caused some foaming problems on a laboratory scale. This could become a major issue in full-scale production.

FIGURE 1. Stiffness of asphalt AAD-1 modified with different phosphoric acids
FIGURE 2. Stiffness of asphalt AAM-1 modified with different phosphoric acids

FIGURE 3. Stiffness of asphalt AAK-1 modified with different phosphoric acids
FIGURE 4. Stiffness of asphalt ABM-1 modified with different phosphoric acids

To observe some indication of the rate of reaction of phosphoric acid with asphalt the samples were oven aged overnight at 165°C and the stiffness measured again. The results are shown in figure 5. There is a slight change following oven aging for 24 hours, the bulk of the stiffening takes place almost immediately upon the addition of acid to the hot asphalt.

Figure 5. Relationship between modification levels and stiffness following 24 hour aging 165°C on the PPA modified asphalt.
2. Effect of Asphalt from Different Sources

The stiffening effect of phosphoric acid was found to be dependent on the particular asphalt being modified. Asphalt binders from eight different sources were tested; AAD-1, AAK-1, AAM-1, ABM-1, two asphalts from Venezuela provided by Citgo (a 60% Bachequero and a 94% Bachequero), an asphalt from BP Whiting refinery and one from Holly Corporation. The measured high temperature Superpave Performance continuous grade in degrees centigrade plotted against the polyphosphoric acid addition level are shown in figure 6. Of these binders, AAK-1 (Boscan) exhibited the greatest reactivity to phosphoric acid, whereas, ABM-1 (CA Valley) was the least reactive and showed only a very slight increase in stiffness even at high dosage levels. Some of the acid addition levels evaluated are unrealistically high for practical use in paving applications. They are shown merely to demonstrate the stiffening trend.

![Figure 6. Superpave Performance Grading of asphalts modified with polyphosphoric acid](image)

For these eight binders, the amount of PPA required to increase the Superpave Grading by one and two steps is shown in table 1. All yielded a one-grade increase with 0.7% or less acid addition with the exception of ABM-1(California Valley). This sol-type asphalt (2) is insensitive to modification with PPA.

| Table 1. The Amount of Phosphoric acid needed to increase High Temperature Grade one and two steps |
|------------------------------------------|-----------------|-----------------|-----------------|
|                                       | PG-70           | PG-76           | PG-82           |
| AAK-1                                  | 0.0%            | 0.25%           | 0.9%            |
| 60% Bachequero                          | 0.1%            | 0.75%           |                |
| 94% Bachequero                          | 0.1%            | 1.0%            |                |
| AAM-1                                  | 0.1%            | 1.0%            |                |
| Whiting                                 | 0.5%            | 1.5%            |                |
| AAD-1                                  | 0.7%            | 1.2%            |                |
| Holly                                   | 0.7%            | 1.8%            |                |
| ABM-1                                  | 2.4%            | 3.4%            |                |
**Effect of Phosphoric acid on the Heptane insoluble fraction**

In order to understand the relationship between chemical composition of the binder and the stiffening effect, several phosphoric acid modified asphalts were separated into four fractions (asphaltenes, resins, cyclics, and saturates). This employed a solvent separation technique in conjunction with the use of the Iatroscan (Iatron Laboratories Inc.). Separation of the binders into asphaltene and maltene fractions was accomplished using ASTM method D3279 “Standard Test for n-Heptane Insolubles.” The maltene fractions were further separated using a method provided by Gaylon Baumgardner of Paragon Technical Services Inc. (3) This latter technique involves deconvolution of the less polar fractions on thin silica coated quartz rods. After injecting microgram quantities of the maltene solution on the rods, development is carried out with n-pentane followed by a second development using a mixture of 90% toluene and 10% chloroform. Detection of organic fractions on the rods was by flame ionization.

In each case, the level of the n-heptane insoluble asphaltenes increased with increasing acid concentration. This was accompanied by a corresponding decrease in the resins. ABM-1 (CA Valley) showed the same increase in asphaltenes although this was not accompanied by a corresponding increase in stiffness. The results for asphalts AAD-1 and ABM-1 are shown in figures 7 and 8.

![FIGURE 7. Effect of 115% Polyphosphoric Acid Modification on the AAD-1 Solvent Fractions](image-url)
4. Effect of Phosphoric Acid Modification on Moisture Sensitivity

Phosphoric acid is a strongly hydrophilic material. Its use as an asphalt modifier raises the issue of there being an increased sensitivity to moisture as well as potential environmental consequences resulting from the leaching of phosphoric acid from the highway into the groundwater. These hypotheses were tested in two ways. One was to determine the absorption of moisture by binder and mastic samples, and the second method was to measure the leaching of phosphoric acid from asphalt concrete specimens immersed in water.

Effect of Moisture on Binders and Mastics

Samples of neat binders and mastics containing 50% by weight of aggregate fines were cast into both direct tension dog bones and BBR silicone rubber molds. The samples were weighed and then immersed in a water bath held at 45°F. The samples were reweighed at intervals over the next 245 days and the amount of water absorbed determined. All tests were done in duplicate. As shown in figures 9, all the binders tested, except those modified with more than 1.5% PPA, exhibited an initial slight loss of weight. The most likely cause is the extraction of salts originating from the crude oil. This appears to be borne out by analyses of the soak water from the gyratory specimens, which showed the presence of sodium and calcium ions. At PPA modification levels of 0.5%, the water absorption is similar to that of the control, which had no PPA. With 1.0% PPA there is evidence of water absorption (increase in weight) and this continues with increasing levels of phosphoric acid.
Some of the soaked samples were dried and their stiffness measured using the DSR. At PPA levels of 1% or less, there was no change in stiffness. At higher levels of modification, loss in stiffness becomes apparent as shown in Figure 11.

FIGURE 11. Loss of Stiffness of PPA modified Citgo asphalt after 245 days water immersion
The soaking tests were also carried out on 50% mastics using dog bone shaped specimens. Mastics were made using sand, diabase, gravel and montmorillonite. The former three mastics showed very similar results. The diabase behavior shown in figure 12 exemplifies this. At levels of approximately 0.5%-1.0% the absorption was similar to the unmodified control. At higher modification levels, the water absorption increased in all cases except for mastics made with montmorillonite. The combination of this water absorbing expansive clay and phosphoric acid was expected to result in a very water sensitive mastic. In fact, the opposite was observed. The sample of the unmodified montmorillonite mastic swelled significantly whereas the acid modified samples did not swell at all. The unmodified control absorbed 105% moisture whereas the PPA modified samples only 3-4%. These results for the mastics made using montmorillonite and BP Whiting asphalt are shown in Figure 13.

FIGURE 12. Water Absorption of 50% Diabase Modified Boscan Asphalt Mastics
To determine if phosphoric acid is likely to be leached from highways into the groundwater, loose mixes and gyratory specimens were made up and immersed in water. The amount of phosphate leached into the water from each sample was measured regularly over the test period.

To determine the effect of air voids, such as might be found in an open graded friction course, uncompacted loose mixes were tested in addition to gyratory specimens which were compacted to 7% air voids. To test the effect of different binders and aggregates, asphalt from three different sources (BP Whiting, Lion Oil and Citgo), two aggregates (diabase and Georgia granite) were used. The samples were placed in clean 7.5-liter plastic buckets, covered with 2.5 liters of distilled water and the buckets closed with lids and stored at room temperature. Two milliliter samples of the water were taken after 30 minutes and then at intervals over the next 245 days. The water level was periodically topped off to the original 2.5 liter level to compensate for evaporation losses. The samples were analyzed for phosphate content using a Dionex ICS2000 ion exchange chromatograph.

The first sample of water taken after 30 minutes soaking did not show any presence of phosphate extraction indicating that there is no immediate extraction of phosphate from the surface of the specimen. The results after 245 days in water are summarized in figure 14. The level of leaching was found to be sensitive to air voids, aggregate type and asphalt type. As shown in figure 15, more phosphate was extracted from the gyratory samples made with Georgia granite than with diabase aggregate. The effect of different asphalts in cores made with the same diabase aggregate is shown in figure 16. The Citgo asphalt showed higher levels of phosphate leaching than either the Lion Oil or the BP Whiting asphalt. For compacted
specimens leaching only occurred at phosphoric acid levels above 0.5-1.0% except for the Georgia granite samples, which showed leaching at much lower levels of acid modification.

Although some phosphate is leached into the water, only a tiny fraction of the phosphoric acid is lost. Even in the extreme case of 3% PPA modification (Superpave Performance Grade would have been 96°C) the Gyratory specimen made with diabase aggregate and Citgo asphalt lost 60mg of phosphate after 245 days. The 60 mg lost represents only 0.78% of the total acid contained in the binder.

Any phosphoric acid extracted will eventually end up in the groundwater surrounding the highway. Every milligram of phosphate extracted from the gyratory specimen represents leaching of approximately 3 pounds of phosphoric acid per mile of 4-lane highway with lanes 12 feet wide and asphalt 4 inches thick. For acid modification levels of 0.75% or less this is unlikely to pose a problem. If however an unreactive asphalt like CA valley is used (it took 2.4% PPA to increase the Superpave Performance grade from 64°C to 70°C – see table 1), then groundwater pollution could become an issue particularly if the aggregate was granite and the mix was open as would be the case with an open graded friction course.

![Phosphate Extracted From Gyratory Specimens and Loose Mixes After 245 Days Water Immersion](image)

**FIGURE 14. Phosphate Extracted From Gyratory Specimens and Loose Mixes After 245 Days Water Immersion**
FIGURE 15. Phosphate Extracted from Gyratory Specimens containing Georgia Granite and Diabase Aggregate 245 Days Water Immersion

FIGURE 16. Phosphate Extracted from Gyratory Specimens containing Diabase Aggregate and Different Asphalts 245 Days Water Immersion

4. Use of Phosphoric Acid Modified Binders with Antistrip Additives

A common misconception exists that phosphoric acid modified asphalt cannot be used with lime treated aggregates or amine antistrip additives since they are alkaline and would react with the phosphoric acid, whereas a neutral antistrip like Innovalt-W (2-ethylhexylphosphate) could be used. This theory was tested on gyratory specimens using the
Hamburg Rut Tester. Duplicate tests were run on specimens soaked at 50°C and the rut depth measured; the criterion for pass/fail was 20mm rut depth in less than 20,000 cycles. Three aggregates were used, limestone, granite from Georgia and a sandstone aggregate from Maryland known to be a stripping aggregate. All tests were conducted with a PG64-28 binder supplied by Citgo.

Lime is normally added to mixes at a rate of 1% of the aggregate whereas the PPA is added at 0.5-1% of the binder. Stoichiometric calculation shows that if the binder contains 1% of PPA, then it is overwhelmed chemically 25:1 by the lime.

To prepare the lime treated samples, lime as a 50% water slurry, was added to the aggregate. The liquid antistrip additives were added to the binder at 0.5% by weight of the binder. The results are given in table 2. All the lime treated aggregates exceeded 20,000 cycles and were unaffected by PPA modification.

The tests with liquid antistrip additives showed very mixed results. These are also presented in table 2. Here the Hamburg results indicate aggregate and antistrip additive dependence. This clearly demonstrates the need for thorough testing before using a particular asphalt/aggregate/antistrip combination. Generally the acid modification made the stripping worse, but not in every case. The non-amine antistrip worked with some aggregates and not others.

**TABLE 2. Hamburg Testing of Lime and Liquid Antistrip Additives for Citgo PPA modified Asphalt**

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<thead>
<tr>
<th>PPA %</th>
<th>Aggregate</th>
<th>Antistrip</th>
<th>Cycles to Failure</th>
<th>Is PPA Better or Worse?</th>
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<tr>
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<td>Granite</td>
<td>Innovalet-W</td>
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<tr>
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<tr>
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<td>Innovalet-W</td>
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<td>Better</td>
</tr>
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Conclusions

All of the commercially available grades of phosphoric acid can be used to increase the High Temperature Superpave Performance Grade of asphalt binders. The stiffening effect of phosphoric acid is very dependent upon the binder being modified. Most binders reacted well to the addition of phosphoric acid. One binder, CA valley showed little stiffness increase with acid modification, was not very responsive. Generally, a one-step increase in the Superpave Performance Grade was obtained with less than 0.7% acid.

Acid modification of the asphalts resulted in an increase in the asphaltene (n-heptane insoluble material) and a corresponding decrease in the resin fraction. The asphaltene increase was not necessarily accompanied by an increase in stiffness.

The sensitivity of binders to moisture uptake was affected by acid modification. This is probably not an issue at acid addition levels of 0.7% or less. At higher levels, the sensitivity both to moisture absorbed into binders and mastics and acid leaching from gyratory cores and loose mixes increased with increasing levels of acid modification. The high moisture sensitivity of a montmorillonite mastic was almost completely mitigated by phosphoric acid modification. The samples of neat binders with acid modification levels above 1% lost stiffness after soaking in water for an extended period. There was a loss of stiffness after extended soaking for acid levels above 1%. The leaching of phosphate from gyratory specimens was influenced by asphalt type, aggregate type and the level of compaction (air voids). At high modification levels, the leaching could result in phosphate contamination of groundwater.

Based on the Hamburg results, cores of PPA modified asphalt containing lime treated aggregates did not exhibit any potential for moisture damage. Liquid antistrip performance, both amine and non-amine, was aggregate and asphalt dependent and clearly demonstrates the need for thorough testing.

References