Polyphosphoric Acid Modification of Asphalt

By Mark Buncher, Ph.D., P.E.

The Asphalt Institute supports the responsible modification of asphalt materials for improved performance and better life cycle costs, without endorsing any specific or proprietary form of modification.

Polyphosphoric acid, or PPA, is a liquid mineral polymer and just one of many additives used to modify and enhance paving grade asphalts. It is the Asphalt Institute's position that the correct use of PPA, in the appropriate amount, can improve the physical properties of bituminous paving grade binders. On the other hand, incorrect application of PPA technology can result in construction or performance problems.

When used in combination with a polymer, PPA provides flexibility in reaching the requested test specifications (Dynamic Shear Rheometer, Elastic Recovery, etc.) while limiting the increase in asphalt viscosity at 135°C (275°F).

To assist agencies in making informed decisions, the Asphalt Institute recently published Informational Series (IS) 220, *Polyphosphoric Acid Modification of Asphalt.* The purpose of this educational document is to clarify the issues regarding acid modification, particularly, PPA modification. This article provides some highlights of IS-220.

Orthophosphoric Acid versus Polyphosphoric Acid

It is important to understand that there are major differences between the two generic acid types, and how they behave in asphalt. Orthophosphoric acid, which includes purified phosphoric acid, is not recommended for use in asphalt modification. Orthophosphoric acid has approximately 15 percent free water content which creates poor miscibility in asphalt and leads to separation issues. The free water also leads to corrosion problems when the orthophosphoric acid is blended in asphalt and stored in steel tanks.

PPA, on the other hand, has no free water allowing a total miscibility with asphalt. The PPA blended with a neat or polymer modified asphalt does not create any binder storage issues such as separation or corrosion.

Literature and Presentations

The first patent describing asphalt modification using PPA was published in 1973. Since the early 1990s, PPA has also been used in combination with various polymer modifiers to enhance the quality of paving grade asphalts.

Concerns by some users within the bituminous supply and paving sectors regarding the performance quality of acid modified binders have resulted in numerous studies by researchers. The process of orthophosphoric and PPA modification has been examined as well as their impact on asphalt and hot mix asphalt mixtures. The IS-220 publication summarizes nine technical papers that have been published since 2001 on the topic of acid modification. The Federal Highway Administration is currently conducting a study at their Turner Fairbanks Research Center on the use of PPA and other acids in asphalt.

In addition to the nine published papers, IS-220 also provides a partial listing and summaries of many recent formal presentations at events such as a one-day symposium on acid modification hosted by the Rocky Mountain User Producer Group (March 2003), a symposium on predicting pavement performance sponsored by the Western Research Institute (2004), and the annual Petersen Conferences.

Effects on High and Low Temperature Performance

PPA can be an effective and economical tool for chemical modification, used alone or in conjunction with a polymer. PPA can improve the high temperature PG grade, and with some asphalts may improve the low temperature PG grade. This modification does not oxidize the asphalt, thereby avoiding the low m-value issues that have been associated with binder brittleness at low temperatures. PPA chemically modifies the asphalt as a result of irreversible and sometimes partially reversible reactions. Two main reactions may be considered—phosphate ester formation (irreversible reaction) and acid-basic neutralization (reversible reaction).

Although the oxidation of some petroleum compounds is known to be catalyzed by strong acids, such mechanisms have not been found for PPA modified bitumens. Comparison of Dynamic Shear Rheometer measurements after short-term and long-term lab aging, chromatography results and infrared data all indicate there is no accelerated aging of PPA modified asphalt as compared to the neat asphalt.

Moisture Sensitivity and Antistrip Compatibility

For acidic aggregates such as granite, PPA typically enhances the moisture resistance of the asphalt mix, possibly to a level where an antistrip additive may not be required. When an amine-based antistrip additive is used, a partial neutralization between the PPA and the antistrip can occur, possibly leading to a partial loss of the increased binder stiffness ($G^*/\sin\delta$) achieved from the PPA modification. According to recently published research, this partial neutralization does not affect the improved binder-aggregate adhesion properties from the addition of antistrip.

The partial neutralization that may occur is dependent on the nature of the asphalt, aggregate and antistrip, and may be avoided by correctly formulating the mix with a compatible antistrip. One class of antistrip chemicals known as phosphate esters does not react with PPA functionality, so they are effective in both conventional and PPA modified binders.

Summary

PPA modified binder has no additional safety issues beyond those of neat asphalt. However, PPA by itself is a corrosive agent, so the Material Safety Data Sheet information should be reviewed carefully.

The improvements realized with the addition of PPA are not the same with all asphalts. As with most modifiers, the interaction is dependent on the asphalt's chemistry (aromaticity, asphaltene content, etc.). PPA modified mixtures are generally resistant to moisture degradation or can be made moisture resistant through the use of appropriate antistrip additives.

Good communication between the asphalt supplier, contractor and agency regarding potential use of amine-based antistripping agents is necessary. This is because under certain conditions, PPA may react with some liquid amine antistrips leading to a partial decrease of the PG high temperature improvement realized with PPA modification. Correct formulation is required to address the effects of amines on binder stiffness. Binder testing, especially for stiffness, is recommended both before and after the addition of antistrip.

Mixture testing may also be used to evaluate moisture susceptibility. Tests, such as AASHTO T-283 or any suitable under water wheel tracking test, can be used as an additional assurance of compatibility and performance.

Mark Buncher is Director of Field Engineering for the Asphalt Institute.