This paper was prepared by the Polyphosphoric Acid (PPA) 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 PPA 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.
Summary

Polyphosphoric acid (PPA) has been proven as a successful modifier for asphalt cement either by itself or in combination with polymers. On its own, PPA increases the high temperature performance of asphalt cement, as measured by the PG grading system, with no loss, and sometimes with an improvement, in low temperature performance. In combination with polymers, PPA has shown its ability to use styrene-butadiene-styrene (SBS) polymers more efficiently, either by providing a product with superior properties at equal polymer loadings, or an equivalent product at lower polymer levels. In many instances, the use of PPA in combination with SBS gives rise to enhanced performance that could not be achieved with either product alone. In combination with ethylene terpolymers such as DuPont’s Elvaloy®, the use of PPA accelerates the reaction of the Elvaloy®, broadens the useful temperature range of the finished product, and improves the elastic response of the binder. In addition, PPA also allows the reaction of Elvaloy® and asphalt to proceed at lower temperatures.

This document provides general guidelines for the selection and use of PPA in asphalt modification. Testing is required to demonstrate the performance of each formulation of asphalt, polymer (if any), PPA, anti-strip (if any), and aggregate.

Make sure to use polyphosphoric acid, frequently referred to within the asphalt community as PPA. The typical grades of PPA are 105% and 115%. These grades contain 0% water. DO NOT use phosphoric acids (also called orthophosphoric acid, or purified phosphoric acid, or green acid) which are available in grades of 35% through 93%. These grades contain from 7 wt% to 65 wt% water. The addition of water to an asphalt tank at high temperature, 350°F (177°C) (well above the boiling point of water), will cause the asphalt to foam. NOTE: Certain non-asphalt industry segments use the term "PPA" when referring to purified phosphoric acid. Be sure that the PPA used in asphalt is polyphosphoric acid.
General Considerations for Use of PPA with Asphalt

There are a number of general considerations for asphalt modified with PPA, asphalt co-modified with Elvaloy® + PPA, as well as asphalt co-modified with SBS + PPA.

Proper Base Asphalt Selection

The low temperature properties (below approximately 40°F [4°C]) of a PPA modified asphalt are determined mainly by the base asphalt. The PPA generally provides improvements to the high temperature properties. For example, to meet a PG 64-28 specification, the base asphalt should meet a PG XX-28 specification.

PPA Level Selection

As is true with other asphalt additives, the amount of PPA required will be different for each different base asphalt. The typical range of PPA usage with polymers or alone is from 0.25% up to 1.5% and even higher for some specific applications. The optimum amount is typically determined according to multiple factors:

- Existing specifications (requirement or not of polymer for PG+ specs)
- Reactivity of the base asphalt to PPA
- Performance of the base asphalt and PPA modified asphalt with most representative local aggregates (in terms of moisture resistance)
- Local rules regarding liquid antistripping (mandatory requirement or not)

Anti-Strip Selection

Additives may be required to meet moisture sensitivity specifications (Tensile Strength Ratio, Hamburg Wheel Track Tester, etc). When required, the anti-strip additive should be determined to be compatible with PPA. A simple dynamic shear rheometer (DSR) test at the stated PG grade temperature of the binder will quickly determine whether or not addition of the amine anti-strip material has caused a reduction in binder stiffness. Anti-strip agents that have been found to be compatible with PPA include: hydrated lime, phosphate esters such as Gripper X2™ or INNOVALT® W, and selected amines such as Redicote E-6™.

Whatever anti-strip additive is used, the performance should be tested and verified. It is recommended that the anti-strip of interest be tested with the selected formulation of asphalt, polymer (if any), and PPA. Further, it is strongly recommended that mix tests be conducted on the fully formulated blend of asphalt, polymer (if any), PPA, anti-strip, and aggregate.
Experimental Blends Preparation

PPA chemically reacts with asphalt. The reaction time is usually very short. The typical lab sample is prepared by adding the desired amount of PPA to an asphalt sample at 300°F (149°C), or whatever temperature the base asphalt grade is normally stored, and stirring for at least 30 minutes. Normal lab safety procedures and acid personal protective equipment are recommended for handling PPA. Once a target formulation has been developed, lab blends should be evaluated for all specifications and performance criteria.

Use of PPA in an Asphalt Plant

For modification with PPA, the typical operation includes delivering the PPA in bulk trucks or totes, storing the PPA in a dedicated tank, metering the PPA to control addition, and mixing a small amount of PPA uniformly with a large amount of asphalt. The storage tank, pump, and acid process lines are heated to maintain PPA in a fluent state. The required normal handling temperature for 105% PPA is approximately 100°F (38°C) and for 115% PPA is 200°F (94°C). The product is too viscous to flow efficiently below these respective temperatures. When storing PPA in a bulk tank, it is recommended that a nitrogen blanket be placed over the material. This is a simple and inexpensive process to install and assures that the PPA will not pick up moisture from the atmosphere. The PPA supplier can assist in basic designs for a nitrogen blanketing system. Further, in the handling and storage of PPA, the preferred material of construction is 316ss to minimize corrosion. The mixing of PPA and asphalt is accomplished by (a) using a mixing tee or in-line static mixer in the process line carrying asphalt to a storage tank, or (b) adding the PPA into the top of a well agitated asphalt tank. In this case, in order to avoid potential corrosion issues, care should be taken so that the PPA does not splash or directly contact the walls of the carbon steel tank. However, in a tank with asphalt coated sidewalls, there is little danger of any reaction between the carbon steel and the PPA. Once the PPA has been reacted with the asphalt, lab tests have shown that the bulk PPA modified binder and the head space above the PPA modified binder are NOT corrosive.

Additional Testing

After the formulation has been developed, additional testing is recommended to validate all performance criteria. These tests may include:

a) plant trials to determine how large scale batches correlate with lab results;

b) stability tests to determine how the properties change with storage time;

c) sensitivity studies to determine how variation in base asphalt properties, storage temperature, etc., affect the properties of the final product;

d) correction studies to determine how to correct deficiencies if off-spec product is made.
Modification with PPA only

PPA Level Selection

Typical PPA levels are between 0.5 and 1.2 wt%. With some base asphalts a slightly higher level may produce a value-added result where a marginal increase in %PPA will attain the desired specification. We recommend initial evaluation at 0.4, 0.7 and 1.0 wt% PPA. Results from these tests should provide information for fine-tuning the formulation, as noted previously.

Co-Modification with Elvaloy® and PPA


The guidelines include:
- Proper Base Asphalt Selection
- Polymer Level Selection
- PPA Level Selection
- Experimental Blends Preparation
- Additional Testing
- Plant Operation (equipment & procedures)
- Patent on co-modification of asphalt with Elvaloy® and PPA

Co-Modification with SBS and PPA

Polymer Level Selection

Typical SBS levels are between 2.5 and 5.0 wt%. The appropriate level depends on the base asphalt and the requirements of the desired specification. The SBS supplier will usually recommend SBS levels for initial testing. Results from these tests should provide information for fine-tuning the formulation.

PPA Level Selection

Typical PPA levels for use with SBS are between 0.2 and 1.0 wt%. The appropriate level depends on the base asphalt and the requirements of the desired specification. The addition of PPA may provide a product with superior properties at equal SBS loadings, or an equivalent product at lower SBS levels. Typical reduction of SBS will range from 0.75 to 2.0 wt%, with PPA addition. Typical exchange of SBS to PPA is a ratio of about 3:1.

Experimental Blends Preparation

The SBS and PPA suppliers will usually recommend procedures for lab testing and order of addition (SBS or PPA first). Typical lab samples are prepared by adding the desired amount of SBS to an asphalt sample at 350°F (177°C) to 390°F (199°C) and blending with a high shear mixer for at
least 30 minutes. It is recommended to confirm complete dispersion of both the SBS and PPA in the asphalt. One technique is UV microscope analysis.

**Use of SBS and PPA in an Asphalt Plant**

The SBS and PPA suppliers will usually recommend procedures for plant operation and order of addition. This includes equipment for handling and blending PPA, handling SBS, milling/mixing SBS into the asphalt, and storing the modified asphalt. It is recommended to confirm complete dispersion of both the SBS and PPA in the asphalt. One technique is UV microscope analysis.

The blending of SBS with asphalt may involve preparation of a "concentrate" containing SBS and subsequent dilution of the concentrate with base asphalt. There are a number of manufacturers having patents covering specific materials and procedures for modification technology covering the combination of SBS and PPA, as well as the combination with cross-linkers.

The SBS supplier will usually recommend guidelines for storing asphalt modified with SBS (which can usually be extended to co-modification with SBS and PPA). The typical storage tank is agitated at all times. The storage temperature for shipping and immediate use is usually between 310-350°F (155-177°C). For short-term storage (up to two weeks) the typical tank temperature is usually about 275°F (135°C). For long-term storage (longer than two weeks) the usual procedure is to remove the heat. Reheating of modified asphalt is usually done gently and reheating above 350°F (177°C) is avoided.

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