

ROAD SCIENCE

by Tom Kuennen, Contributing Editor

Modifiers a Must in a World of High-Performance Asphalt



Enhanced durability and the defeat of rutting, such as this on a Los Angeles street, are the main goals of asphalt modification

Photo courtesy of Tom Kuennen

The universe of modifiers has expanded far beyond polymer modifiers of yesterday; phosphoric and polyphosphoric acids get look.

More and more, modifiers are a must in producing the high-performing, durable asphalts — such as the performance graded (PG) binders used with Superpave — that can be predicted to behave in a certain way throughout time.

Asphalt modifiers are used principally to optimize durability and rut resistance in hot-mix asphalt (HMA). It is the menace of rutting and age-related ills that most actively motivates the use of asphalt modifiers in hot mix asphalt.

The more familiar polymer modifiers mix with the liquid binder to help it perform bet-

ter. Mineral modifiers perform physically to enhance adhesion of binder to aggregate, or keep liquid asphalt binder from draining from an aggregate structure, as with stone matrix asphalt.

But in the new millennium, a new breed of modifiers is going beyond making asphalt perform better, to making it easier to place by reducing the heat or energy required to produce the mix. These waxy or water-yielding modifiers make low-energy asphalt mixes — such as warm mix asphalt (WMA) and cold mixes — possible. The use of low-energy asphalt mixes offers significant environmental benefits the asphalt industry may need if it going to survive the environmental onslaught now building on the horizon.

At the same time use of conventional polymer modifiers is being

expanded to make more durable and versatile surface treatments, including chip seals, fog seals, an microsurfacing, with new research on the way from the pavement preservation community.

And a new bunch of modifiers, including phosphoric acid and polyphosphoric acid, are getting a close look by researchers in an effort to determine whether they do more good than harm in asphalt mixes.

Polymer modifiers in asphalt

Why modify?

“Improvement in resistance to rutting, thermal cracking, fatigue damage, stripping, and temperature susceptibility have led polymer modified binders to be substituted for asphalt in virtually all paving and maintenance applications, including hot-mix,

warm-mix/cold lay, cold mix, chip seals, hot and cold crackfilling, patching, recycling, and slurry seal,” says Stylink polymer modified asphalt technology provider Sem Materials L.P. “They are used wherever extra performance and durability are desired. In many cases they are selected to reduce life cycle costs.”

Polymer modified binders have allowed the use of techniques previously not practicable such as microsurfacing and use of asphalt emulsion chip seals on high-volume roads, according to Sem. And specifiers are finding that many of the Superpave binder grades require polymer modification to concurrently meet the requirements for high temperature resistance to rutting, and low temperature resistance to thermal cracking.

Asphalt cement properties are highly temperature-sensitive. As temperature of the asphalt cement increases, its stiffness decreases, increasing the propensity for permanent deformation under load. The high temperature susceptibility of asphalt cement may be reduced through the addition of polymer modifiers such as natural latex, synthetic latex, block copolymers, reclaimed rubber (tires), polypropylene, polyethylene, and ethyl-vinyl-acetate (EVA). The addition of modifiers substantially improves rutting resistance by improving the high temperature stiffness characteristics of the asphalt cement, thereby reducing shear deformation.

The term polymer refers to a very large molecule made by chemically reacting many (poly) smaller molecules (monomers) to one another in long chains or clusters. Polymer modifiers for asphalt can be either elastomeric or plastomeric.

Specific binder and mix properties can be engineered by choosing the right polymer for a given application, and making sure it's compatible with the asphalt. In general, elastomers give a more resilient, flexible pavement, while plastomers result in mixes with higher stabilities and stiffness values.

Elastomers include copolymers

of styrene and butadiene (such as, styrene butadiene diblock, styrene butadiene triblock or radial, styrene isoprene, and styrene ethylbutylene. Other elastomers include styrene butadiene rubber (SBR) latex, polychloroprene latex, polyisoprene, and crumb rubber modifier. Plastomers include EVA, polyethylene, and various compounds based on polypropylene.

In addition to polymer modifiers, other additives such as liquid anti-stripping agents or hydrated lime are used to enhance the bond between the asphalt cement and the aggregate particles to prevent moisture damage, also known as “stripping.” Loss of asphalt cement due to stripping allows aggregates to shift under traffic loading, leading to severe rutting. Use of anti-strips can reduce rutting by reducing the loss of asphalt cement through moisture damage.

Better performing pavements

The Superpave binder specification uses various tests performed at multiple temperatures to characterize the binder, said John D'Angelo, P.E., asphalt team leader, FHWA Office of Pavement Technology.

Polymer modification has become an essential part of Superpave mix designs, even though its binder specification doesn't adequately determine the performance characteristics of modified binders. As a result, many state Departments of Transportation (DOTs) are including additional tests to the Superpave binder specification to make sure a desired modifier is included in the binder. These Superpave “plus” tests do not relate directly to performance, but only relate to the presence of a particular modifier in the binder, D'Angelo said. For example, for additional (“plus”) tests for Superpave, a number of states have specified elastic recovery testing to assure that some type of SBS material in the binder purchased.

“Essentially the PG system was designed to describe asphalt binder in a similar manner that the motor oil industry developed

a half-century ago, a 10W40 asphalt,” says engineering consultant Dale Decker, P.E., D.S. Decker LLC, and former vice president, research and technology, National Asphalt Pavement Association, in the July 2008 issue of the National Asphalt Pavement Association's (NAPA) publication, “Focus on HMAT” (hot-mix asphalt technology).

“Unfortunately, the PG (performance-graded) system does not adequately describe asphalt binders that are modified,” Decker said. “In the meantime, users are resorting to descriptive tests to adequately specify the desired modified asphalt. This PG+ approach uses the existing PG requirements, but adds some type of physical test to determine the presence of a modifier in the asphalt binder.”

D'Angelo called said Superpave's omission of modifier specs a “gap” in the system. “The full application of modified systems and performance-related specifications based on the actual material properties is a gap which we are trying to close,” he told *Better Roads*. “We want to make Superpave ‘blind’ to polymer modification.”

Despite all this, D'Angelo says modifiers can be a positive for boosting the qualities of liquid asphalt. “There is no question that polymer modification can improve the performance properties of an asphalt binder,” he says. “At the Federal Highway Administration's (FHWA) Accelerated Load Facility, polymer modified asphalts far exceeded their expected performance.”

For example, polymer modified asphalts are essential to a successful race track pavement, said Brian Prowell, P.E., principal engineer at Auburn, Ala.-based Advanced Materials Services LLC. AMS designs race track mixes and also serves as quality assurance/quality control manager for projects. In June at Lime Rock Park near Lakeville, Conn., AMS was performing QA testing on the mix and density, as well as developing specifications and overseeing the work.

There the mix was highly poly

While polyphosphoric acid promises improvement with some asphalt binders, it doesn't work well with all liquid asphalts.

mer modified, a 12.5 NMA mix with a PG 82-22 modified binder. "We added Sasobit warm-mix modifier as well, to help the sulfoning point of the mixture. The sulfoning point is a phase change between solid and liquid," Prowell tells *Better Roads*. "Below that temperature we don't feel that the race car tires can ravel the aggregate particles out from the surface of the pavement, so we set a 180 degree Fahrenheit sulfoning point, which is pretty stiff."

The idea is to give the stones good adhesion, and make sure the asphalt doesn't get soft enough that the suction of the tires can pull the aggregate out.

Polyphosphoric acid enters the arena

After years on the fringes, a new polymer, polyphosphoric acid, has entered the modifier arena. While it promises improvement with some asphalt binders, especially in conjunction with polymer modifiers, it doesn't work well with all asphalts.

The literature indicates that the addition of PPA to asphalt increases the viscosity of the asphalt. PPA is commonly used to shift the high-temperature PG grade of asphalt to the next higher grade.

But while its benefits are lauded, PPA also has come under fire. "State agencies in the United States have known for years the benefits associated with asphalt binders that are modified with elastomer-type polymers to improve the rutting and fatigue cracking properties of the hot mix asphalt," says Thomas Bennert, Rutgers University, and Jean-Valery Martin, Innophos, Inc., a supplier, in their 2008 Transportation Research Board paper, "Polyphosphoric Acid in Combination with Styrene-Butadiene-Styrene Block Copolymer: Laboratory

Mixture Evaluation."

"However, in recent years, a majority of asphalt binder suppliers are now using PPA in combination with decreased percentages of polymers to meet various performance graded asphalt binder requirements," they said in January. "This has raised concerns among the state agencies that the combination of PPA and reduced polymer percentages will result in an inferior asphalt binder when compared to the same asphalt binder solely modified by polymer.

"Some states have responded to this lack of understanding in PPA asphalt modification technology by banning the use of PPA through specific clauses in their specifications," they said. "Other states have examined the issue and decided that their current PG and PG+ binder specifications are sufficient to ensure a quality performing binder. Any prohibition on the use of an effective modification technology without valid reasoning can lead to a more expensive product in the marketplace."

Combining PPA with other modifiers

The combined use of PPA and other polymer modifiers is widely seen and has become increasingly popular as state agencies move to PG+ specs, they said, including specifications for items such as elastic recovery and ductility. "A broad range of polymers have been claimed to be used beneficially in combination with PPA," they wrote. "Those preferred have been the elastomeric polymers (SBS and SB), which have been used by a wide margin for almost 10 years with PPA."

Shin-Che Huang, Thomas F. Turner, Francis P. Miknis, and Kenneth P. Thomas, Western Research Institute, Laramie, Wyo. reported in their 2008 Transpor-

tation Research Board paper, "Long-Term Aging Characteristic of Polyphosphoric Acid Modified Asphalts," that polyphosphoric acid has the ability to improve asphalt binder. "Recent work has demonstrated that PPA can replace some of the SBS in polymer modified asphalt," Huang, et. al. write. "However, the mechanism of action of PPA in stiffening asphalt is still unknown, and the longevity of action is uncertain. It is hypothesized that addition of polyphosphoric acid to asphalt alters the long term aging mechanism of asphalt binders."

The objective of their study was to determine how the rheological and chemical properties of PPA-modified asphalts vary with aging time at temperatures in the pavement temperature range when compared with untreated asphalt aged.

"Based on the results of the present study," they concluded, "it appears that PPA-modified asphalts should (1) increase early resistance of the pavement to rutting by increasing initial stiffness and (2) extend the useful life of the pavement by improving the low-temperature flow properties. These improved properties should result in both reduced fatigue cracking and reduced low temperature cracking."

In the Asphalt Institute's "Polyphosphoric Acid Modification of Asphalt" brochure (No. IS-220), the organization says that "PPA just one of many additives used to modify and enhance paving grade asphalts. Correct use of PPA, in the appropriate amount, can improve the physical properties of bituminous paving grade binders. Appropriate testing on the modified binder should be performed after the addition of all additives to ensure the final product specification is met. Incorrect application of PPA technology can result

in field performance or construction problems.”

PPA should not be confused with another modifier, phosphoric acid, says Alan James, Akzo Nobel Surfactants, in his presentation “Advantages of Phosphoric Acid In Slurry,” at the 2008 joint meeting of the Asphalt Emulsion Manufacturers Association, International Slurry Surfacing Association, and Asphalt Recycling & Reclaiming Association in February 2008.

In asphalt emulsions, he says, phosphoric acid reliably builds cohesion with low acid value asphalts, including SBS modified binders and petroleum resins. “Naphthenic acid additives are not required,” James says. “Emulsions are higher pH and less corrosive. Soluble calcium salts are not formed so surface staining is avoided. Surfaces are blacker.”

New modified asphalts center

The Asphalt Research Consortium is a group of five organizations bringing an unprecedented depth and range of asphalt pavement experience to bear on the needs of the asphalt pavement community. The participants are Western Research Institute (lead organization), Texas A&M University, University of Wisconsin-Madison, University of Nevada-Reno, and Advanced Asphalt Technologies, under the direction of the FHWA, and with input from the Binder, Mixture and Construction, and Models Expert Task Groups.

This ambitious ARC team effort aims to accelerate progress in addressing key asphalt pavement performance issues. As part of ARC research, use of asphalt modifiers is being explored at the new Modified Asphalt Research Center (MARC) at the University of Wisconsin-Madison.

“The conventional asphalts are not meeting our needs, and the problem that we face is that the refineries cannot easily produce better asphalts,” says UWM civil and environmental engineering professor, and MARC leader, Dr. Hussain Bahia. “There are limitations on their equipment, economics, and their procedures that limit the capability of modifying asphalt at the refinery.”



Research at lab of Modified Asphalt Research Center, University of Wisconsin-Madison, will lead to better performing asphalt pavements.

Photo courtesy of Jeff Miller, UWM

Bahia is determining which asphalt modifiers work best, and when. “There is a need, not only for evaluating new materials for their initial performance, but also for how they resist damage,” he says.

Ultimately, Bahia’s research will enable asphalt manufacturers to develop new and improve existing asphalt additives. The results also will provide state DOTs the information they need to customize asphalt specifications for specific conditions, such as roads with frequent heavy truck traffic or those that experience wide temperature swings. “We give them very specific information about how we think the material is improving the asphalt, and by how much,” he says.

A current undertaking at MARC is a National Cooperative Highway Research Center (NCHRP) project, “Test Methods and Specification Criteria for Mineral Filler Used in HMA.” This \$500,000 project, which began in 2007 and will continue through June 2010, is investigating the role mineral filler plays in the construction and performance of HMA pavements. Very little attention was given to the study of mineral filler (often referred to as the minus 200 fraction) during the Strategic Highway Research Program. This study will identify or develop test methods for mineral filler that characterize its mechanical and chemical effects on the performance of mastics (combinations of asphalt binder and mineral filler) and HMA, and recommend speci-

fication criteria for mineral filler that optimize HMA performance.

Modified asphalt emulsions

Emulsions — a dispersion of microdroplets of one liquid in another — have tremendous application in the preservation of pavements. With asphalt emulsions, asphalt is the dispersed phase in water. With polymer-modified emulsions, the dispersed phase is a polymer-modified asphalt — usually created by use of SBR latex — in water.

The best polymer-modified chip seal designs optimize the chemical, mechanical, and electrostatic variables of an emulsion to best weld aggregate to asphalt cement as the emulsion water carrier evaporates or breaks.

In particular, microsurfacing requires polymer modifiers. Microsurfacing is a mixture of high-quality aggregates and polymer-modified asphalt emulsion. Together they inhibit raveling and surface oxidation, improve surface friction, seal the pavement surface, and unique to microsurfacing, fill ruts and minor surface irregularities.

A new polymer modified emulsions “technology deployment” study, “Modifiers for Asphalt Emulsions: Synthesis of Best Practices,” is now underway at the National Center for Pavement Preservation (NCP), sponsored by the FHWA Central Federal Lands Highway Division and FHWA Office of Asset Management.

NCP is developing a best practice guide and model speci-

Some states responded to a lack of understanding of PPA use by banning the use of PPA via specific clauses in their specs.

fications, and working with a consortium of industry experts to recommend specifications and use of polymer-modified emulsions for chip seals, microsurfacing and polymer modified slurry, and cape seals.

New preservation research released

The new NCPP best practice guide comes on the heels of release of a six-year research project, "Spray Applied Polymer Surface Seals," administered by the Foundation for Pavement Preservation (FP2). The project report includes input from users and producers, a DOT survey, and field projects in Michigan, California, Arizona, and Minnesota.

"Understanding polymerized spray seals and the use of rejuvenators to arrest aging and oxidation of our surface courses will go a long way in establishing

effective surface seals and low cost preservation techniques," says Jim Sorenson, FHWA construction and system preservation team leader. "We cannot afford to apply the wrong treatment. This research is filling a gap in our understanding of what to apply when."

Fog and rejuvenator seals are water-based emulsions that are diluted and lightly sprayed through distributors on road surfaces in good condition. They arrest raveling and pitting, seal and waterproof the existing pavement, mitigate traffic and snow plow damage and rejuvenate the properties of the existing, aging asphalt cement binder. The blackened surfaces improve visibility and appearance. Agencies' greatest concern is loss of skid resistance.

The study shows that fog and rejuvenator seals are effective when the right product is used on the right pavement. The seals pre-

vented surface water intrusion up to four years and inhibited cracking and raveling caused by age hardening. They did decrease friction, but the pavements regained skid resistance with time, and applying sand after placement immediately increased friction.

The New Mexico DOT successfully maintains many miles of open-graded friction course with a scheduled fog seal program, usually using dilute polymer-modified emulsions.

The Minnesota DOT has actively expanded its fog sealing program, and feels that a diluted rapid-setting, polymer modified emulsion give better results on fog sealing shoulders and pavements. CRS-2Pd emulsion (d for "diluted") has been used, diluted by the manufacturer with three parts emulsion to one part water solution, for a specified 51 percent residue content. The emulsion is

For More Information

Visit these sites for more information about the topics discussed in this article:

- The 2001 NCHRP Report 459, 'Characterization of Modified Asphalt Binders in Superpave Mix Design,' may be downloaded at http://onlinepubs.trb.org/onlinepubs/nchrp/nchrp_rpt_459-a.pdf.

- The overall objectives, strategic plan, and work plans of the Asphalt Research Consortium can be accessed through its Web site, www.arc.unr.edu.

- The Web site of the Association of Modified Asphalt Producers (AMAP) may be visited at www.modifiedasphalt.org/.

- The Web site of the Modified Asphalt Research Center (MARC) at the University of Wisconsin-Madison is <http://uwmarc.org/>.

- Find out more about the two polymer modified emulsion research projects at the National Center for Pavement Preservation Web site, www.pavementpreservation.org.

- More information about NCHRP's active 09-45 research project at the MARC, "Test Methods and Specification Criteria for Mineral Filler Used in HMA," is downloadable at www.trb.org/TRBNet/ProjectDisplay.asp?ProjectID=979.

- The Federal Highway Administration published its brief flyer, "Phosphoric Acid as an Asphalt Modifier Guidelines for Use: Acid Type, in May 2008." It is available at www.fhwa.dot.gov/pavement/asphalt/pubs/08061/08061.pdf.

- The Asphalt Institute's 2005 brochure, "Polyphosphoric Acid Modification of Asphalt" (No. IS-220), is available for purchase. Visit www.asphaltinstitute.com.

The six-year research project, "Spray Applied Polymer Surface Seals," administered by the Foundation for Pavement Preservation (FP2), may be viewed in an interactive format at www.pavementpreservation.org/fogseals/index.htm, or in one publication at www.pavementpreservation.org/fogseals/Docs/Final_Report.pdf.

- FHWA also published its "International Scan on Warm Mix Asphalt" report earlier this year, compiling impressions and data on European warm mix asphalts. Download it at <http://international.fhwa.dot.gov/pubs/pl08007/pl08007.pdf>.

supplied by Flint Hills Resources, LP from its St. Paul, Minn., plant.

Carbon Seal-P is a high molecular weight polymer modified asphalt used for sealing, and Steel Guard 70 is a polymer modified, slate and mineral-filled asphalt product also used for sealing. Both are manufactured by Rayner Protective Materials.

Western Emulsions' Pass-QB "quick-break" emulsion is designed specifically for fog seal applications. The emulsion residue contains asphalt, rejuvenator oil, and polychloroprene latex polymer. For a project at Winslow, Ariz., the emulsion was diluted 1:1 with water.

Low-energy mix modifiers

Today's warm-mix, or low-energy, asphalt mixes are getting road agencies, paving contractors, and asphalt producers closer to a fumes-free asphalt mix that will result in lower mix emissions and radiated heat. Warm asphalt mixes attract interest because of their potential for reduced plant emissions in different stages of production, benefits in construction in the field, and reduced energy consumption in the plant.

Other benefits may be a construction season which extends well into the cooler seasons, longer hauls of asphalt mix with less worry about the mix losing heat, less fuel needed to bring mixes to temperature, and perhaps less problematic siting of asphalt plants, important for metro areas.

Warm-mix asphalt (WMA) is not a single product, but a variety of asphalt modifier-based technologies that reduce the temperatures at which asphalt mixes are produced and placed. WMA processes generally reduce the viscosity of the asphalt through a variety of means, and enable the complete coating of aggregates at lower temperatures at temperatures 35 to 100 degrees Fahrenheit lower than conventional HMA.

Warm-mix asphalt reduces mix viscosity

In North America, the vast majority of pavements are made in hot-mix asphalt plants. The liquid asphalt is a relatively small part of the mix (typically 5 to 7



Santa Barbara County, Calif., places polymer modified asphalt emulsion on local road prior to placement of aggregate chips.

Photo courtesy of Kevin Donnelly, Santa Barbara County

percent) and performs as a viscoelastic binder between the fine and coarse mineral aggregate.

Because WMA technologies generally reduce viscosity, they may reduce compaction challenges associated with cooled mixes or cold weather, possibly lower the amount of rollers required at a job site, and reduce the risk of failed compaction with stiff mixtures. These benefits, though, come at a higher price.

Conventional HMA production takes place above 280 degrees Fahrenheit, not to exceed 325 degrees Fahrenheit, and placement and compaction between 260 and 300 degrees Fahrenheit. Before mixing with hot liquid asphalt, fine and coarse aggregates are

heated to high temperatures to drive off moisture, to ease coating of the mineral aggregates with the liquid asphalt, and to keep the complete mix fluid enough to be workable during placement.

In addition to consumption of prodigious amounts of natural gas, fuel oil or powdered coal, heating of liquid asphalt to these temperatures produces volatile organic compound (VOC) fumes which may either be vented to exterior, or collected with fume enclosures and revented back in the process.

Like any other industrial facility, fumes from asphalt plants are an issue for regional air quality areas that are not in compliance with federal air quality standards. However, plentiful research indicates there is no evidence that these fumes are harmful to either workers or nearby residents.

Nonetheless, use of today's warm mixes has the potential to all but eliminate emissions, giving a plant owner a powerful tool to use in the permitting process. Warm asphalt mixes produce emissions at a greatly reduced level from conventional HMA plants, thus enabling permitting of asphalt plants in air pollution non-attainment areas, or where there is local opposition. BR

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