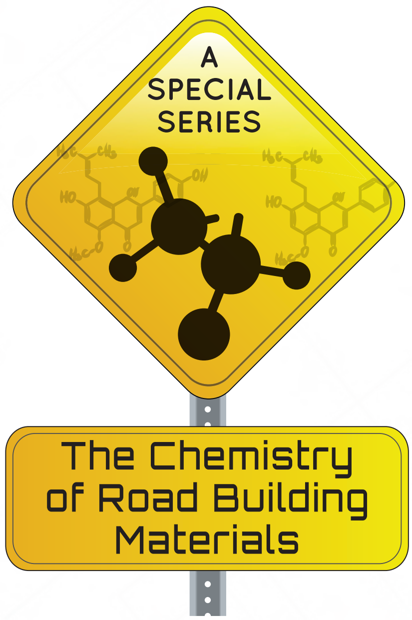
by Tom Kuennen, Contributing Editor



Now That's Cool

Low-energy asphalt mixes reduce viscosity – without the heat

In the last two decades, improvements in the physio-chemistry of asphalt mixes have sparked a revolution in their production and placement.

Today's warm and cold asphalt mixes – which to minimize confusion might be better termed "low energy" mixes – are stealing the spotlight from classic hot mix asphalt.

Warm mix asphalt (WMA) is created by mixing one of a variety of solid or liquid chemical compound additives with asphalt mix in the plant, or by foaming the mix with water in the plant. WMA processes generally reduce the viscosity of the liquid asphalt through a variety of means, and enable the complete coating of aggregates at temperatures 35 to 100 degrees F lower than conventional hot mix asphalt.

As with many trends, low energy mixes began in Europe, where warm mixes were popularized in the 1990s. In 2002, the National Asphalt Pavement Association led a study tour to Europe to examine WMA technologies, and the association began exploring their attributes, most recently, at the 2nd *International Warm-Mix Conference* in October 2011 in St. Louis.

In 2007 a Federal Highway Administration (FHWA) international scanning tour investigated warm mix practices in Europe to gather information on technologies used to produce WMA, with particular emphasis on long-term field performance. Its report – *Warm-Mix Asphalt: European Practice* – was published in February 2008 (download the report by Googling its title).

In the meantime, another type of low energy asphalt mix – a warm mix created by foaming hot mix asphalt with water in a drum plant - began growing in popularity in the 1990s. And yet another foamed asphalt – a cold mix created in a portable plant, or *in situ* in the field, using as much as 100-percent reclaimed asphalt pavement – also is called foamed asphalt or foamed bitumen mix.

The one thing all of these components have in common is that they are "green" technologies that reduce plant emissions, lower fuel consumption at the plant, and create a better environment for workers in the field. Their future is so established that in the past year NAPA changed its web site URL from *hotmix.org* to *asphaltpavement.org*, and changed the name of its magazine from *HMAT* (for *Hot Mix Asphalt Technology*) to *Asphalt Pavement*.

Data indicate plant emissions are significantly reduced with low energy mixes. "Typical expected reductions are 30 to 40 percent for CO_2 and sulfur dioxide (SO_2), 50 percent for volatile organic compounds (VOCs), 10 to 30 percent for carbon monoxide (CO_2), 60 to 70 percent for nitrous oxides (NO_X), and 20 to 25 percent for dust," according to *Warm-Mix Asphalt: European Practice* in 2008. "Actual reductions vary based on a number of factors. Technologies that result in greater temperature reductions are expected to have greater emission reductions."

Burner fuel savings with WMA typically range from 11 to 35 percent, FHWA's report states, with fuel savings possibly higher (possibly 50 percent or more) with other processes.

And workers will benefit as well, according to the scanning tour report. "Tests for asphalt aerosols/fumes and polycyclic aromatic hydrocarbons (PAHs) indicated significant reductions compared to HMA, with results showing a 30- to 50- percent reduction," the report says,

April	May	June	July	August	September	October
THE CHEMISTRY OF ASPHALT MODIFIERS	THE CHEMISTRY OF CONCRETE ADMIXTURES	THE CHEMISTRY OF ASPHALT EMULSIONS	THE CHEMISTRY OF AGGREGATES	**THE CHEMISTRY OF LOW-ENERGY MIXES**	THE CHEMISTRY OF RECYCLED/ RECLAIMED MATERIALS	THE CHEMISTRY OF PAVEMENT FORENSICS

Near-solid asphalt or bitumen from the refinery must be heated to make it workable, with production of hot mix asphalt at 275 to over 330 deg F, and compaction between 260 and 300 deg F. But today's low energy mixes reduce the viscosity of their liquid asphalt through other means, and enable the complete coating of aggregates at temperatures 35 to 100 deg F lower than conventional hot mix asphalt, with significant environmental and workplace benefits

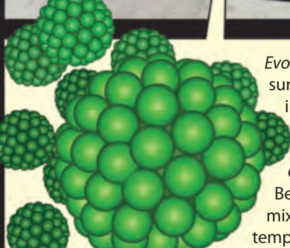
Viscosity-modifying organic additives change the rheological properties of the binder in such a way that mixing and laying temperatures can be reduced. For example, organic additives typically are waxes with molecular sizes greater than 45 atoms of carbon (C45) and melting points greater than 158 deg F. Examples include Fischer-Tropsch wax (*Sasobit*), Montan wax, fatty acid amides (*Licomont BS 100*), and blends of Montan wax and fatty-acid amides (*Asphaltan-B*)

Fischer-Tropsch wax is a synthetic aliphatic hydrocarbon wax, such as Sasobit (shown), the molecular lengths of which range from C40 to C120. As the asphalt-wax combination cools, the wax solidifies into regularly distributed, microscopic, stick-shaped particles, reports the FHWA. It's believed that the distribution of stick-like particles provides the framework that increases the viscosity of the Sasobit-modified binder at in-service pavement temperatures

IMAGE CREDIT: Granite Rock

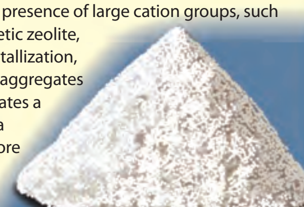
Montan waxes and their derivatives, according to DAV, the German Asphalt Paving Association, are obtained from processing of lignite and consist of high-molecular hydrocarbons with a melting range from 230 to 284 deg F, and are different from naturally occurring bituminous waxes. Once dissolved in liquid asphalt they reduce the asphalt's viscosity; when cooled, they crystallize, increasing stability and resistance to deformation

IMAGE CREDIT: Carmel Wax



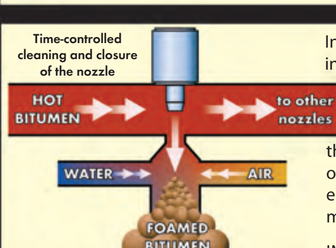
Evotherm is a chemical compound with surfactant activity, which adds lubricity to individual microscopic asphalt particles. The particles or micelles develop "slip planes" which let the asphalt particles move more easily, requiring lower levels of energy. Because the energy is lowered, Evotherm warm mix has the same viscosity properties at lower temperatures as conventional hot mix asphalt

IMAGE CREDIT: Evotherm



Zeolites are crystalline hydrated aluminum silicates that have large empty spaces in their structures that allow the presence of large cation groups, such as water molecules. *Aspha-min*, a synthetic zeolite, contains about 20 percent water of crystallization, which is released when mixed with hot aggregates or asphalt, reports FHWA. The water creates a controlled foaming effect that leads to a slight increase in binder volume, therefore reducing viscosity of the binder

IMAGE CREDIT: Aspha-min



In-place foamed low-energy mixes incorporate liquid "foamed" asphalt as a stabilizing agent, in which hot performance-grade asphalt is foamed with water and air, and is then injected into reclaimed materials or aggregate in a mixing chamber, either in a self-propelled recycling machine, or portable plant

IMAGE CREDIT: Wirtgen America, Inc.

An in-plant foamed system for WMA – such as the *Double-Barrel Green System* – is a manifold mounted on a drum plant, with nozzles that precisely meter water into the drum. Injection of water – along with the liquid asphalt cement – causes the liquid asphalt to foam and expand in volume. The foaming action helps the liquid asphalt coat the aggregate at a temperature that normally is in the range of 230 to 270 degrees F

IMAGE CREDIT: Astec Industries, Inc.

but with a caveat: "It should be noted that all of the exposure data for conventional HMA were below the current acceptable exposure limits."

From Near-Solid to Liquid

At ambient temperatures, "liquid" asphalt or bitumen from the refinery is a near-solid material. To lower its viscosity and make it workable, it is kept hot, and classic hot mix asphalt production – in which liquid asphalt coats aggregate – takes place at 275 to more than 330 degrees F, and compaction between 260 and 300 degrees F.

More heat comes from the aggregates. 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.

Low energy mixes introduce chemicals such as organic waxes or surfactants to lower asphalt mix viscosity *in lieu* of higher temperatures, or water to lubricate the mix.

"WMA technologies can also be classified by type," the scanning tour report says. "Two major types of WMA technologies are those that use water and those that use some form of organic additive or wax to affect the temperature reduction.


Asphalt-treated permeable base (ATPB) warm mix for a new taxiway being paved at O'Hare International Airport

"Processes that introduce small amounts of water to hot asphalt, either via a foaming nozzle or a hydrophilic [water-loving] material such as zeolite, or damp aggregate, rely on the fact that when a given volume of water turns to steam at atmospheric pressure, it expands by a factor of 1,673," the report says. "When the water is dispersed in hot asphalt and turns to steam (from contact with the hot asphalt), it results in an expansion of the binder phase and corresponding reduction in the mix viscosity."

Three different types of products comprise the chemical WMA technologies.

Generically they are **solid, synthetic zeolites**, which release water molecules when mixed with liquid asphalt at the plant, achieving a foamed asphalt binder, an example being *Aspha-min*; **solid organic additives**, which are synthetic paraffin waxes that reduce the viscosity of the binder at mixing and compaction temperatures, an example being *Sasobit*; and **surfactant liquid additives**, which add lubricity to individual microscopic asphalt particles, enhancing workability at various temperatures, an example being *Evotherm*.

Zeolites are crystalline hydrated aluminum silicates that have large empty spaces in their structures that allow the presence of large cation groups, such as water molecules. Aspha-min, a synthetic zeolite, contains about 20 percent water of crystallization, which is released when mixed with hot aggregates or asphalt, reports FHWA. The water creates a controlled foaming effect that leads to a slight increase in binder volume, therefore reducing viscosity of the binder.

While the zeolites release water into a mix to decrease viscosity, the waxes melt and lubricate the mix, then stiffen as temperature declines. "The processes that use organic additives (e.g., Fischer-Tropsch wax, Montan wax, or fatty amides) show a decrease in viscosity above the melting point of the wax," according to *Warm-Mix Asphalt: European Practice*. "The type of wax must be selected carefully so that the melting point of the wax is higher than expected in-service temperatures (otherwise permanent deformation may occur) and to minimize embrittlement of the asphalt at low temperatures."

Fischer-Tropsch waxes are long-chain aliphatic hydrocarbon waxes with a melting point of more than 208 degrees F, high viscosity at lower temperatures, and low viscosity at higher temperatures, the report states, adding "They solidify in asphalt between 149 and 239 degrees F into regularly distributed, microscopic, stick-shaped particles. They may be used to modify binder or added directly to the mixture."

Another wax – Montan wax - is a complex combination of nonglyceride long-chain carboxylic acid esters, free long-chain organic acids, long-chain alcohols, ketones, hydrocarbons, and resins, the scanning tour report states. It's a fossilized plant wax, also known as lignite wax or OP wax, obtained by solvent extraction from certain types of lignite or brown coal. Its melting point is 180 to 200 deg F, and *Asphaltan-B* is a trade name for this type of additive.

Injection of water, along with the liquid asphalt cement, causes the liquid asphalt to foam and expand in volume.

Different from the waxes are the surfactants, such as *Evotherm* and *Rediset*. We have shown how important surfactants are for manufacturing asphalt emulsions (see *Spreading the Wealth: Asphalt Emulsions Mix Oil with Water*, June 2012, pp 18-29).

Evotherm is a chemical compound with surfactant activity, which adds lubricity to individual microscopic asphalt particles. The particles or micelles develop "slip planes" that let the asphalt particles move more easily, requiring lower levels of energy. Because the energy is lowered, Evotherm warm mix has the same viscosity properties at lower temperatures as conventional hot mix asphalt. *Rediset-LQ* is another product.

Water-based, in-plant foamed systems for low energy mixes – such as the Astec Industries, Inc.'s *Double-Barrel Green System* – use nozzles that precisely meter water into the drum of a drum mix plant. Injection of water , along with the liquid asphalt cement, causes the liquid asphalt to foam and expand in volume. The foaming action helps the liquid asphalt coat the aggregate at a temperature that normally is in the range of 230 to 270 degrees F.

A much different kind of foamed asphalt incorporate liquid "foamed" asphalt as a stabilizing agent, in which hot-liquid asphalt is foamed with water and air, and is then injected into RAP or aggregate in a mixing chamber, either in a self-propelled recycling machine, or portable plant.

In this cold-mix foamed asphalt process, the recycled aggregate is not completely coated, as is the process with in-plant foamed injection using mostly virgin aggregate. Instead, as 100 percent reclaimed materials are introduced to the pug mill, foamed asphalt is injected into the material stream, and acts as a binding agent to "glue" the reclaimed aggregates together.

This will permit use of less liquid asphalt and much lower mixing temperatures. With 100 percent of existing aggregates used in cold recycling, 2.2 to 2.5 percent liquid asphalt is used to partially coat the RAP and any added virgin aggregate, opposed to in-plant foamed technologies that completely coat the aggregate – as is needed for critical applications like friction courses – that use 5 percent liquid asphalt.

Moisture Sensitivity Enhanced?

At the 2nd International Warm-Mix Conference in October, presentations heralded the spread of WMA from coast to coast.

For example, NAPA director of engineering Kent R. Hansen, P.E., reported that WMA use was growing very rapidly, with a 148-percent increase in use from 2009 to 2010, the most recent year for which firm data were available, rising from 19.2 million tons to 46.7 million tons in one year. That's drawn from estimated total volume of both HMA and WMA of 358 million tons in 2009 to 360 million tons in 2010. Download the report by Googling *NAPA Information Series* 138.

As usage grows, WMA has moved from a boutique product to the mainstream, and is coming under increased scrutiny, with the question being raised of whether the physiochemistry of warm mixes makes them more sensitive to moisture damage.

Moisture damage is a well-recognized phenomenon, reports The Asphalt Institute in its 2007 pamphlet, *Moisture Sensitivity: Best Practices to Minimize Moisture Sensitivity in Asphalt Mixtures*, with 10 of 50 states reporting fresh hot mixes being treated for moisture damage.

Because in the absence of an emulsifier oil and water don't mix, moisture damage impairs the bond between aggregate and liquid asphalt. "While adhesion failure between the asphalt and aggregate (referred to as stripping) is the most commonly recognized [mechanism], there are others," AI says. "These include moisture-induced cohesion failures within the asphalt mixture, within the aggregate, emulsification of the asphalt and freezing of entrapped water."

"Although moisture damage potential is also possible in some HMA mixtures, due to its method of production, it may be more likely in WMA," say Thomas Bennert, Ph.D., Center for Advanced Infrastructure and Transportation at Rutgers University, and Greg Brouse, Eastern Industries Inc., in their 2011 WMA conference paper, *Influence of Initial Aggregate Moisture Content and Production Temperature on Mixture Performance of Plant Produced Warm Mix Asphalt*.

"Inadequately dried aggregates at lower production temperatures, and even the possible introduction of additional moisture to the WMA from the various WMA foaming technologies, may affect the binder-to-aggregate adhesion, moisture susceptibility and general mixture performance," they write. "Preliminary laboratory testing has shown that when producing warm mix asphalt, both the initial aggregate moisture content and mixing temperature can have a dramatic impact on the performance of the mixtures, especially with respect to the resistance to moisture damage. Unfortunately, it is often difficult to control these parameters outside the laboratory setting."

That's because, as they say, while some lab tests show WMA specimens often fail the Texas DOT *Hamburg Wheel Tracking* test criteria, moisture damage has not been witnessed in the field, and similar results with other tests have been reported outside Texas. "This may indicate modifications to material preparation and/or test procedures are required when evaluating the moisture damage susceptibility of WMA mixtures in the laboratory, so field conditions can be properly simulated," they observe.

For this work, two different initial aggregate moisture contents (less than 1.5 percent and greater than 3.0 percent) were achieved by the use of covered stockpiles. Five different mixtures were produced at both moisture contents, an HMA as control; WMA via foaming system; WMA foaming plus an anti-strip; WMA foaming plus a different anti-strip; and WMA via surfactant additive.

Laboratory performance samples were sampled and compacted at the asphalt plant's QC laboratory after similar conditioning periods. Moisture damage tests (*Tensile Strength Ratio, Hamburg Wheel Tracking*), permanent deformation (*AMTP Flow Number, Asphalt Pavement Analyzer*), dynamic modulus, and fatigue cracking via overlay tester tests were undertaken on the samples.

The study found that at the moisture contents measured, production temperature is more significant than initial aggregate moisture content on performance. Moisture damage tests did not rank performance the same: the tensile strength ratio results were okay, but the Hamburg were bad based on general criteria.

"Not all anti-strips work the same," Bennert and Brouse say. One anti-strip outperformed the other in the TSR test, but with mixed results in the Hamburg. It's important to evaluate each of the materials to ensure they provide the performance required, the authors say. A 10 to 15 degrees F increase in temp clearly increased rutting resistance, but decreased fatigue resistance, they report. Field cores of an actual installation will be undertaken after one year.

"Although moisture damage potential is also possible in some HMA mixtures, due to its method of production, it may be more likely in WMA,"
– Thomas Bennert, Ph.D., and Greg Brouse,

Another October WMA conference paper, *Moisture Damage Potential for Warm Mix Asphalt Containing Reclaimed Asphalt Pavement*, by Mariely Mejías-Santiago and Ray Brown, Ph.D., P.E., U.S. Army Engineer Research and Development Center, Vicksburg; and Jesse Doyle, Ph.D. and Isaac L. Howard, Ph.D., Mississippi State University, stated that increased percentages of RAP in a mix may improve WMA's sensitivity to moisture.

Their moisture damage study of a variety of samples indicated:

- Gravel WMA mixes showed moisture susceptibility for lower mixing temperatures. Limestone mixes did not show this problem.
- WMA additive type did not significantly affect moisture susceptibility at HMA mixing temperature
- The low mixing temperature results in increased moisture susceptibility of WMA for some WMA additives/processes, and
- Increasing RAP tended to increase resistance to moisture susceptibility.

"The use of high percentages of RAP with WMA looks promising and should be considered for selected field projects if additional research supports this effort," they conclude.

Surfactants Exhibit Anti-Strip

In the meantime, surfactant-based warm mix additives can feature an anti-strip function. *Rediset LQ* from AkzoNobel Surface Chemistry allows a reduction in mixing and paving temperatures while providing built in anti-stripping effect, the manufacturer says, while also being used as a compaction aid for hot and warm mixes. Rediset LQ allows the asphalt mixing temperature to be reduced (by 25 to 55 degrees F) while ensuring good coating and workability. "Mixes prepared with Rediset LQ meet moisture resistance requirements without the need for additional liquid adhesion promoter," Akzo says.

And last year, use of Evotherm 3G from MeadWestvaco enabled the U.S. Army Corps of Engineers to preclude use of lime as anti-strip modifier in an open-graded porous asphalt pavement. At the Marine Boot Camp at Parris Island, the U.S. Army Corps of Engineers did not have a specification for an open-graded porous asphalt mix, so it studied specs of the South Carolina DOT, says Dean Frailey, business development manager, MeadWestVaco Asphalt Innovations.

"They opted to go with South Carolina's OGFC standard," he said. "It's a large-stone mix, with 6 percent polymer modified PG 76-22 asphalt binder. Typically, with a mix like this they would put in lime as a stabilizer, adhesion promoter, and for protection against moisture susceptibility, and then add fibers."

Use of the WMA additive greatly simplified things. "They opted to remove the fibers and remove the lime while using the Evotherm warm mix technology. Since both fibers and lime were removed, they added back 8 percent washed screenings to act as fines in the mix," Frailey says. "The additive fights moisture susceptibility, promotes adhesion and blocks drain down. It's very unique for this application."

Premature Aging Diminished

In the hot mix plant, the heat contributes to premature or artificial aging of the binder, which breaks down the liquid asphalt even as HMA is produced. This gives pavement oxidation a head-start which gets worse as the mix ages in-place over time.

Low energy WMA may enhance pavement durability, because with lower production temperatures, the valuable, lightest hydrocarbon fractions from liquid asphalt in the mix aren't driven off by the heat of the burner. Thus the lower heat precludes "premature aging" of binder, with a goal of reducing pavement thermal cracking.

"By lowering the temperature of production, we are avoiding some of the potential degradation to binder that can occur at higher production temperatures," says Everett Crews, Ph.D., technical manager for MeadWestvaco. Evotherm is different from other warm mix technologies in its ability to produce mixes around 200 degrees F, Crews says. "Other warm mix technologies produce material at temperatures up to 260 degrees Fahrenheit," he says. "Evotherm is unique in that we can push the limit lower. We have made mixes at below 200 degrees F that have performed very well." ❖