Basic Emulsion Chemistry

AEMA Asphalt Emulsion Technologies Workshop
November 14, 2011

Andrew Bickford
Asphalt Innovations
MeadWestvaco
Topics

- What is an asphalt emulsion?
- Emulsion chemistry
- Emulsion composition and performance
What is an Emulsion?

- **Solution**
  - A homogeneous mixture of two substances
  - Individual molecules of one substance (solute) are surrounded by molecules of the other substance (solvent)
- **Examples:**
What is an Emulsion?

- Colloid or emulsion
  - A homogeneous mixture of two *insoluble* substances
  - *Particles* of one substance (dispersed phase) are surrounded by molecules of the other substance (continuous phase)
What is an Emulsion?

- Colloid or emulsion
  - A homogeneous mixture of two insoluble substances
  - Particles of one substance (dispersed phase) are surrounded by molecules of the other substance (continuous phase)
  - Examples:
What is an Emulsion?

- **Asphalt**
  - Composed of crystalline particles generally classified as “asphaltenes”
  - Asphaltenes are suspended in an oily liquid continuous phase generally classified as “maltenes”
  - The balance of composition determines asphalt physical properties such as rheology
What is an Emulsion?

- Why emulsify asphalt?
  - Viscosity reduction and safer use at lower temperatures
  - Change from “oil based” to “water based” system
  - Reduced energy use, worker exposure, burn hazard and job site odor
  - Properly formulated emulsion systems provide long term performance benefits
What is an Emulsion?

Rotor

Gap

Stator
What is an Emulsion?

Molten asphalt and emulsifier solution go in...

Rotor

shear

Time

Stator
What is an Emulsion?

Molten asphalt and emulsifier solution go in...

Rotor

shear

Stator

...and a water-based asphalt emulsion comes out
What is an Emulsion?

Asphalt particle (5 microns)

Human hair (50 microns)

- TRB circular E-C102
What is an Emulsion?

- The asphalt particles will stick together (the emulsion will break) if only water and asphalt are used.
- The emulsifier is added to coat the asphalt particle surfaces and keep them from sticking together.
What is an Emulsion?
What is an Emulsion?

- Average 3-7 microns diameter
- Asphalt is usually 57-70% of the emulsion
- 1 gram of asphalt will form more than 10 billion particles
- The total surface area of 1 gram of asphalt is 1-2 m²
- One drop of emulsifier would stabilize as much as 100 billion particles or 10-20 m² of asphalt particle surface area.
Emulsion Chemistry

- General emulsifier chemical structures
- “Salt” formation
- Surface activity of emulsifiers
Asphalt Emulsifiers Have in Common...

- An oil soluble part
- A water soluble part
- Some characteristic that allows the molecule to protect the surface of the asphalt droplet
  - Electrical charge...
  - ...or no charge, but large size
Emulsifiers

Tail group (oil soluble)

CH₃CH₂CH₂CH₂CH₂
CH₂CH₂CH₂CH₂CH₂
CH₂CH₂CH₂CH₂CH₂

Head group (water soluble)

O
NH₂CH₂CH₂
NH₂CH₂CH₂

"Short hand" picture

+/−
The Oil Soluble Part

- In most cases based in animal or vegetable fats
- Contains chemically reactive sites to allow attachment/modification of the water soluble part
The Water Soluble Part

- Polar substituents (those that share bond electrons unevenly) are water loving.
- Types include oxygen, nitrogen and salts of O and N (full +/- electrical charges).
- Compounds containing these atoms can be chemically attached to the acid end of the fatty acid molecule.
Anionic Emulsifier Molecule

Tail group

CH₃CH₂CH₂CH₂CH₂
|     CH₂CH₂CH₂CH₂CH₂
|                      CH₂CH₂CH₂CH₂CH₂
|                                CH₂CH₂CH₂

Head group

O
| C
| OH
Cationic Emulsifier Molecule

Tail group

Head group
Salt Formation

Anionic

\[ \text{R–C–OH} + \text{NaOH} \rightarrow \text{R–C–O–Na}^+ + \text{H}_2\text{O} \]

Fatty acid

sodium salt

“R” = Hydrocarbon tail

Cationic

\[ \text{R–C–NH}_2 + \text{HCl} \rightarrow \text{R–C–N}^+\text{H}_3\text{Cl} \]

Fatty amide

hydrochloride salt
Emulsifier Orientation at the Asphalt/Water Interface

Asphalt particle surface

Emulsifier solution

Micelle

+/-
The Emulsifier - Stability

The emulsifier coats the surface of asphalt droplets in the emulsion and makes them storage stable.
The Emulsifier - Performance

The emulsifier coats the surface of asphalt droplets in the emulsion and makes them storage stable.

Upon application, the emulsifier provides a predetermined breaking speed.
Application

- "Application" usually refers to spraying the emulsion onto surfaces or mixing them with aggregates.
- To understand emulsion performance, we need to know more about aggregate or other surfaces.
A Short Interlude - Aggregate

Definition – A mass of distinct things gathered into a total or whole

**Homblende** – $\text{Ca}_2(\text{Mg,Fe,Al})_5(\text{Al, Si})_8\text{O}_{22}(\text{OH})_2$
Surface Properties of Rocks

- Surface charge measurements (Zeta potential) show that general mineral categories fall in two zones.
- This affects the rock’s interaction with asphalt emulsions.

<table>
<thead>
<tr>
<th></th>
<th>Positive</th>
<th>0</th>
<th>Negative</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aged asphalt</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surfaces</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silicates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slag</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Aged asphalt surfaces can contain carbonates, silicates, and slag.
The Emulsifier - Performance

1. Light weight, fast moving surfactants interact with aggregate
2. Asphalt particle attracted to surface
3. Opposite charges neutralize each other and emulsion breaks
4. Asphalt particles stick to each other and to the aggregate
Adhesion – Silicate Mineralogy (Granite, Trap Rock, Basalt, Slag…)

**Cationic Emulsion**
Opposite charge interaction produces a **tight bond**

**Anionic Emulsion**
Similar charge interaction produces a **weak bond**

Asphalt film

Stone
Adhesion – Carbonate Mineralogy
(Limestone, Dolomite...)

**Cationic Emulsion**
Similar charge interaction
produces a weak bond

**Anionic Emulsion**
Opposite charge interaction
produces a tight bond
Adhesion - Benefits

- Reduced susceptibility to water damage
- Greater resistance to pavement deformation
- Reduced raveling or chip loss
- Increased pavement life
Adhesion

- Adhesion can be achieved through...
  - ...proper selection of emulsion and emulsifier type (cationic vs anionic) based on aggregate mineralogy, or...
  - ...through use of emulsion chemical additives
Emulsion Additives

- Polymers (rubber)
  - Water based latex polymers may be incorporated in the emulsion water phase or solid polymers incorporated into the binder
  - Polymers provide low temperature flexibility, high temperature stiffness, moisture resistance and improved pavement durability
  - Lower life cycle cost by extension of pavement life
Polymers

Dried emulsion residues (coalesced asphalt particles)

Unmodified asphalt

Asphalt rheology only

Latex modified emulsion

Improved binder properties
- Improved low temperature fatigue properties
- Reduced rutting at high temperature
- Improved early strength development

Emulsion of polymer modified asphalt

Content courtesy of BASF
Questions??