Asphalt Emulsions

“A Green Technology Comes of Age”

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Presentation

1. What are asphalt emulsions
2. What are the types of asphalt emulsions
3. Manufacturer of emulsions
4. Setting and breaking of emulsions
Some Figures

- First asphalt emulsion use 1900–1910 in U.S.
- 10 million ton of asphalt emulsion worldwide
- 2–3 million ton of asphalt emulsion in USA
- 10% of asphalt used as emulsion
- 25% in France, 5–10% in U.S.A.
- Spain, France, Brazil are important
Emulsions Surrounds us
Emulsion Basics

- Emulsions are MIXTURES of two immiscible liquids, such as oil and water, STABILIZED by an EMULSIFIER.

- Emulsifier PROTECTS the droplet.

How?
Why Use Emulsions?

- Cold processes save energy
- Easier handling and storage (low viscosity)
- Safe and environmentally friendly
- Low-cost on-site and in-place techniques
- Water dilutable
- Easily mixed with latex
The emulsion is a chemically stabilized system; all components contribute to the stability of the system
Asphalt Emulsion composition

- Water: 30–50%
- Chemicals: 0.2–2.5%
- Solvent: 0–10%
- Asphalt: 40–70%
Emulsion Applications

Surface
- Fog seal
- Chip seal
- Cold mix
- Slurry Seal
- Microsurfacing
- Cape seal
- Scrub seal

Structure
- Cold in place recycling (CIR)
- Full depth reclamation (FDR)
Emulsion Stability

= Balance of attractive and repulsive interactions

Attractive >> Van der Waals Forces
Repulsive >>>> Electrostatic forces
DLVO = Derjaguin-Landau-Verwey-Overbeek THEORY developed in 1930

\[ V_T (d) = V_A (d) + V_R (d) \]

Primary minimum: irreversible flocculation

Emulsion breaking

Secondary min
Weak flocculation

Sieve development

Emulsion breaking

Primary minimum: irreversible flocculation
Effect of constant shear at 50 RPM and 50°C on emulsion viscosity

- Microstructure breakdown
- Steady-state viscosity
- Breaking of emulsion
Surfactants and Emulsifiers

- **Surfactant** = Surface Active Agent
- **Emulsifier** = Type of Surface active agent
- **Wetting Agent** = type of surface active agent
Emulsifiers lowers energy at the interface

- Water–air or water–oil interface is high tension (energy)
- Surface Active Agent adsorbs at interface
- Lowers the tension (energy) at the interface
- Lowers the work needed to make new interface
Functions of the Emulsifier

- Determines type of emulsion formed, i.e. O/W or W/O
- Reduces energy needed to emulsify asphalt
- Determines charge on emulsion droplets
- Stabilizes emulsion droplets as they are formed in the colloid mill
- Stabilizes the droplets during storage of the emulsion
- Provides the right setting behavior
- Influences the physical properties of the emulsion
- Influences properties of cured road material.
Stabilization of Asphalt Droplets

No emulsifier-droplets can come into contact and coalesce

Cationic emulsifier-electrostatic repulsion prevents close approach of drops

Anionic emulsifier-electrostatic repulsion prevents close approach of drops
Surfactants

Oil Loving Tail

Water Loving Head

Lipophilic Part

Hydrophilic Part

Hydrophobic Part = Hydrophobe
If an asphalt droplet were the size of the earth, then the emulsifier head would occupy an area of 4 square miles and the hydrocarbon tail would penetrate 5 miles deep.
Surfactants at Water-Oil Interface

There is an equilibrium between surfactants at the interface and those in the water.

When the concentration of surfactants in the water reach the “CMC” then micelles start to form.

Water hating tails point out in the oil or air

Water loving heads immersed in the water

Surfactant molecule
Emulsifiers stabilize particles - cationic example:

Asphalt particle

Positively charged emulsifier
Popular Emulsion types

Cationic

Anionic

Cationic Bitumen Particle

Anionic Bitumen Particle
**Cationic Emulsifier**

*Head Group (Water Loving)*

*Hydrocarbon Chain (Oil Loving)*

*Counter ion (Water Loving)*

- **H**
- **C**
- **NH₃⁺**
- **Cl⁻**
Anionic Emulsifier

Hydrocarbon Chain (Oil Loving)

Head Group (Water Loving)

Counter ion (Water Loving)

H
C
Na+
SO₃⁻
Na⁺
**Typical Emulsifier Structures**

- **Hydrocarbon tail with 12-20 carbons**
  - Hydrophilic head group
  - Counter ion

R = long chain hydrocarbon

- **R(tallow)**
  - \( N^+ (\text{CH}_3)_3 \)
  - Cl-

- **R(tallow)**
  - \( \text{NH}_2 + \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{NH}_3^+ \)
  - 2Cl-

- **R(nonylphenyl)**
  - None

- **R(tall oil)**
  - COO-
  - Na+

- **R(lignin)**
  - SO_3^-
  - Na+
Cationic Soaps are prepared from amines and acid

\[ \text{RNH}_2 + \text{HCl} = \text{RNH}_3^+ + \text{Cl}^- \]

 insoluble neutral form + acid = soluble cationic 'soap'

\[ \text{RNH}_2 + \text{H}_3\text{PO}_4 = 2\text{RNH}_3^+ + \text{HPO}_3^{2-} \]

 insoluble neutral form + acid = soluble cationic 'soap'

\[ R = \text{Hydrocarbon chain} \]
Some charged emulsifiers do not need pH adjustment

$$\text{RN(CH}_3\text{)}_3 + \text{Cl}^-$$

soluble quaternary amine

$$\text{R SO}_3^- \text{ Na}^+$$

soluble olefin sulphonate
**rapid-setting:**
reactive emulsion sets quickly even with unreactive aggregates

**medium-setting:**
medium reactive emulsion which can be mixed with open graded aggregates with low fines content

**slow-setting:**
low reactive emulsion which can be mixed with reactive aggregates with high fines content
Naming of Emulsions (ASTM)

- **CRS - 2**
  - Cationic
  - Rapid-setting
  - High viscosity (65% asphalt)

- **CSS - 1h**
  - Cationic
  - Slow-setting
  - Hard asphalt

- **HFMS - 2s**
  - High-float
  - Low viscosity (57% asphalt)
  - With solvent

- **RS - 2P**
  - Anionic rapid setting
  - Polymer modified

- **Medium-setting (anionic)**
Emulsions are classified according to Setting Rate and Particle Charge

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<td>RS</td>
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<td>CSS</td>
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Manufacture of Asphalt Emulsions
**Emulsifiers in Emulsion Manufacture**

Emulsifiers stabilize the asphalt droplets.

Emulsion

Water-phase

Colloid Mill

Bitumen

**Emulsifiers stabilize the asphalt droplets**
Disperse asphalt in water & chemical under high energy
An Emulsion Process Diagram

AC Tank

Soap Concentrate Tank

Soap Process Tank

Latex Tank

Gear Pump

Colloid Mill

Fuel Tank

Cooling Tower

Heat Exchanger

Hot water

Cooling water

Emulsion Sales Tank

Centrifugal pump

• Diesel
• Naphtha

• NX-1118

• Emulsifier
• Process Water
• HCl
• Additives (i.e. salt)

• HCl

• Process Water
• HCl
• Additives (i.e. salt)
Cost Contributions per Ton of Emulsion

- Asphalt 66%
- Emulsifier 20%
- Other raw materials and energy 6%
- Fixed costs 4%
- Investment cost 4%

- Accurate flow control minimizes excess asphalt
- Inline water heating saves energy
- Innovative chemical dosage system reduces chemical waste
Setting and Curing of Asphalt Emulsions
Breaking and Curing

Breaking/Setting: Emulsion is destabilized and no longer can be diluted in water

Curing: Water and solvent is lost from the system and the final properties of the residual asphalt are reached
Breakdown of the Emulsion
Evaporation of Water

• Evaporation of water forces droplets together and eventual coalescence
Factors Affecting Breaking and Curing

- **Aggregate reactivity**
  - surface area, surface charge, surface chemistry
  - filler chemistry e.g. cement, lime
- **Temperature, humidity, wind speed**
- **Emulsion reactivity**
  - emulsifier chemistry, concentration
  - other additives
  - asphalt viscosity
- **Mechanical treatment e.g. compaction**
Possible Stages in the Setting of a Cationic Asphalt Emulsion

1. Contact of emulsion with aggregate
2. Adsorption of 'free' Emulsifier, pH rises
3. Rise in pH leads to flocculation
4. Coagulation/spreading over surface
Increasing Mixing Time

Equilibrium between interfacial and bulk emulsifier concentrations upset by introduction of charged aggregate.

Adhesion of emulsifier to aggregate surface causes a decrease in bulk and interfacial concentrations. Droplets begin homo- and hetero-flocculation.
**Breakdown of the Emulsion**

**Flocculation and Coalescence**

**Emulsion Droplets**
Charge on droplets prevents close approach.

**Flocculation**
Close approach of droplets leads to adhesion between droplets. Water is squeezed out.

**Coalescence**
Water drains between droplets and surfactant film breaks down, droplets fuse, trapping some water.

**Coalescence**
Trapped water diffuses out.

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**Setting**

**Curing**
Breakdown of the Emulsion
Flocculation and Coalescence

• Flocculation and coalescence in contact with aggregate
What’s on the horizon for asphalt emulsion technology?

- Application of rheological type tests
- Faster curing spray seals
- Cold-pour crack sealant
- Use of emulsions for warm mix
- High residue emulsion
- Solvent free emulsions-penetrating prime coat
Studies and Resources

- Manual for Emulsion-Based Chip Seals for Pavement Preservation-NCHRP #14-7 (end: 2-13-2009)
- Asphalt Emulsion Technology, TRB Circular, EC102, August, 2006
- Asphalt Emulsion Technology, TRB Circular, EC-122
  Review of Asphalt Emulsion Residue Procedures, October, 2007
- Basic Asphalt Emulsion Manual, AEMA & Asphalt Institute (see www.aema.org)
- Putting Fog and Rejuvenator Seals to the Test: Helen King, in BETTER ROADS, January, 2008