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Asphalt Emulsion Technology

Assembled by
Delmar R. Salomon

for the
Transportation Research Board
Characteristics of Bituminous Materials Committee

August 2006
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Bituminous emulsions are complex fluids. Their stability is governed by intermolecular forces—a result of a balance of repulsive and attractive forces. The formulator skillfully must understand and balance these forces such that the emulsion can be produced consistently, stored, pumped, transported, and applied by the practitioner in the field without experiencing any downtime in the operation.

Bituminous emulsions form the basis for many paving applications in our asphalt industry, including driveway sealants, cold-pour crack sealants, and roofing emulsions. Their rheological (i.e., flow) properties often dictate the uses for which they are suitable. For example, the viscoelastic properties of a slow setting versus a rapid-setting emulsion are different. We expect one day to be able to use rheological properties of bituminous emulsions to predict their success or failure in their respective applications. Even when rheological properties are not critical in the final product, they influence the workability of the emulsion as it is applied in the field. This is true for fog or chip sealing emulsions.

Significant improvement has occurred over the years to make quality bituminous emulsion products and their subsequent application in the field. However there remains considerable work to be done in the sense that further improvement can only occur when the principles of chemistry and physics are fully incorporated into the practical engineering component of road building. The study of bituminous emulsion in our industry can only become less of an intellectual backwater when we begin to incorporate the new advances in experiment and theory of colloid science to create a renaissance in bituminous emulsions in our paving industry.

Bituminous emulsions were discussed in a technical session at the 84th Annual Meeting of the Transportation Research Board (TRB). The papers in this document were written following the session and are based on the presentations; the papers in this circular have not undergone a formal peer review.

The four papers serve as an overview of the chemistry, production, quality assurance testing, and application of bituminous emulsions. They offer the beginner a start in this exciting and challenging field of bituminous emulsions.

Appreciation is expressed to the authors for their contributions; to Robert McGennis, who facilitated the first TRB bituminous emulsion technology session; and to Rebecca McDaniel, who provided valuable editorial input to the text.

—Delmar R. Salomon

_Pavement Preservation Systems_
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**Overview of Asphalt Emulsion Applications in North America**

Peggy L. Simpson, *Western Emulsions, Inc.*
Overview of Asphalt Emulsion

ALAN JAMES
Akzo Nobel Surface Chemistry, LLC

The use of asphalt emulsions began in the early part of the 20th century. Today 5% to 10% of paving-grade asphalt is used in emulsified form, but the extent of emulsion usage varies widely between countries. The United States is the world’s largest producer of asphalt emulsion.

The advantages of asphalt emulsion compared to hot asphalt and cut back binders are related to the low application temperature, compatibility with other water-based binders like rubber latex and cement, and low-solvent content.

The paper gives an introduction to the chemistry of asphalt emulsion. The role of the emulsion components—asphalt, emulsifiers, acids or alkalis, and additives—in determining the physical properties and reactivity of the emulsion is described. Recent advances in the understanding of the setting process are outlined. The classification of emulsions into grades according to their reactivity, particle charge, and physical properties is explained and typical recipes of various emulsion grades are given. The selection of the correct emulsion grade for the various applications based on emulsion reactivity and physical properties of the emulsion is covered in general terms.

The past 20 years have seen considerable progress in the understanding of how emulsion chemistry influences performance. Consequently formulations can be developed to optimize the performance of the construction material or construction process rather than simply to meet standard specifications. The result has been faster-setting surface treatments, quick-drying tack coats, penetrating emulsion primes that are superior to cut backs, and cold-mixed materials with improved properties.

USE OF ASPHALT EMULSION

The first asphalt (bitumen) emulsions used in road construction were prepared in the early part of the 20th century. Today approximately 3 million tons of emulsions are produced in the United States representing about 5% to 10% of asphalt consumption. More than 8 million tons of emulsions are produced worldwide. Emulsion production varies greatly among countries with the United States, France, Mexico, and Brazil being significant producers (1).

ADVANTAGES OF EMULSION

With viscosities in the range 0.5–10 Poise at 60°C, asphalt emulsion is of considerably lower viscosity than asphalt itself (100–4,000 Poise), allowing it to be used at lower temperature. Low-temperature techniques for construction and maintenance reduce emissions, reduce energy consumption, avoid oxidation of the asphalt, and are less hazardous than techniques using hot asphalt. They are also more economical and environmentally friendly than cold techniques using cut back asphalts. The environmental benefit of asphalt emulsion is particularly positive when used for in-place or on-site techniques which avoid the energy usage and emissions associated
with heating, drying, and haulage of aggregate. The construction of a roadway with cold techniques has been calculated to consume approximately half the energy of one of similar bearing capacity made with hot-mix asphalt (HMA) (2). An environmental impact analysis (EIA) technique called “eco-efficiency” has been applied to emulsion maintenance techniques (microsurfacing and chip seal) and it was concluded that the emulsion system had less environmental impact than a thin hot-mix overlay (3).

Emulsions are water-based and in many cases can be diluted further with water for applications such as dust control and priming. They are also compatible with hydraulic binders like cement and lime as well as water-based polymer dispersions like natural and synthetic latex. When mixtures of cement, latex, and asphalt emulsion cure, a composite binder is produced with a structure that cannot be duplicated with hot asphalt and with significantly improved properties compared to pure asphalt (4,5).

EMULSION DEFINITION

An emulsion is a dispersion of small droplets of one liquid in another liquid. Typical examples include such everyday products as milk, butter, mayonnaise, and cosmetic creams. Emulsions can be formed by any two immiscible liquids, but in most emulsions one of the phases is water. Oil-in-water (O/W) emulsions are those in which the continuous phase is water and the disperse (droplet) phase is an “oily” liquid. Water-in-oil (W/O) “inverted” emulsions are those in which the continuous phase is an oil and the disperse phase is water. Emulsions can have more complex structures. In multiple emulsions, the disperse phase contains another phase which may not have the same composition as the continuous phase (Figure 1).

![Figure 1](image-url)  
**FIGURE 1** Types of emulsions:  
(a) O/W emulsion, (b) W/O emulsion, and (c) multiple W/O/W.
Standard bitumen (asphalt) emulsions are normally considered to be of the O/W type and contain from 40% to 75% bitumen, 0.1% to 2.5% emulsifier, 25% to 60% water plus some minor components which are described below. The bitumen droplets range from 0.1–20 micron in diameter. Emulsions with particle sizes in this range are sometimes referred to as macro-emulsions. They are brown liquids with consistencies from that of milk to double cream, which depend mostly on the bitumen content and the particle size. Some bitumen droplets may contain smaller water droplets within them; a better description of asphalt emulsion would be a W/O/W multiple emulsion. The viscosity of the emulsion and especially changes in the viscosity of the emulsion during storage are strongly influenced by this internal water phase (6,7).

There is a distribution of particle sizes in the emulsion, and this distribution is influenced by the emulsion recipe and the mechanics and operating conditions of the emulsion manufacturing plant (Figure 2). The particle size and the particle size distribution of the emulsion droplets strongly influence the physical properties of the emulsion, such as viscosity and storage stability; larger average particle size leads to lower emulsion viscosity, as does a broad or bimodal particle size distribution (8). Particle size also influences the performance of emulsion. In general, smaller particle size leads to improved performance in both mix and spray applications (9). Some recent developments in asphalt emulsion technology have focused on the ability to control the particle size and size distribution of the emulsion during the emulsification process, and consequently to influence the emulsion properties (10–12).

Macroemulsions are inherently unstable. Over a period of time, which may be hours or years, the asphalt phase will eventually separate from the water. Asphalt is insoluble in water, and breakdown of the emulsion involves the fusion of droplets (coalescence) (Figure 3).

The asphalt droplets in the emulsion have a small charge. The source of the charge is the emulsifier, as well as ionisable components in the asphalt itself. These small charges on the droplets normally provide an electrostatic barrier to their close approach to each other (like charges repel). However, when two droplets do achieve enough energy to overcome this barrier and approach closely then they adhere to each other (flocculate). This flocculation may sometimes be reversed by agitation, dilution, or addition of more emulsifier. Over a period of

![FIGURE 2](a) Typical particle size distributions of asphalt emulsions with different asphalt contents (13) and (b) micrograph of asphalt emulsion.
time the water layer between droplets in a flocule will thin and the droplets will coalesce. The coalescence cannot be reversed. Factors which force the droplets together such as settlement under gravity, evaporation of the water, shear or freezing will accelerate the flocculation and coalescence process, as does anything which reduces the charge on the droplets. Lower viscosity asphalts coalesce more rapidly than high viscosity asphalts. Of course, eventually we want the emulsion droplets to coalesce after the asphalt emulsion has come in contact with the aggregate and been placed on the roadway. Setting and curing of emulsion are discussed in more detail below.

CLASSIFICATION AND NAMING OF EMULSIONS

Bitumen emulsions are classified according to the sign of the charge on the droplets and according to their reactivity. Cationic emulsions have droplets which carry a positive charge. Anionic emulsions have negatively charged droplets. Rapid-setting (RS) emulsions set quickly in contact with clean aggregates of low-surface area, such as the chippings used in chip seals (surface dressings). Medium-setting (MS) emulsions set sufficiently less quickly that they can be mixed with aggregates of low surface area, such as those used in open-graded mixes. Slow-setting (SS) emulsions will mix with reactive aggregates of high surface area. RS emulsions are reactive and are used with unreactive aggregates; SS emulsions are unreactive and are used with reactive aggregates. The actual setting and curing time in the field will depend on the technique and materials being used as well as the environmental conditions.

In the naming of emulsions according to ASTM D977 and D2397, cationic RS, cationic MS, and cationic SS emulsions are denoted by the codes CRS, CMS, and CSS, whereas anionic emulsions are called RS, MS, and SS, followed by numbers and text indicating the emulsion viscosity and residue properties. For example SS-1H would be a slow-setting (i.e., low reactivity) anionic emulsion with low viscosity and a hard asphalt residue. CRS-2 would be a reactive cationic emulsion of high viscosity. The QS (quick-setting) and CQS (cationic quick-setting) designations for quick-setting emulsions have been introduced for emulsions intermediate

FIGURE 3 Stages in the breakdown of emulsions.
in reactivity between MS and SS, which do not need to pass the cement mix test, and are used primarily in quick-set slurry surfacing applications.

Local authorities have many other naming schemes associated with emulsions with particular properties. In state department of transportation (DOT) specifications letters such as P or LM may indicate polymer-modified or latex-modified asphalt emulsion, S may indicate high solvent content, and terms such as AEP (asphalt emulsion prime) and PEP (penetrating emulsion prime), and ERA (recycling agent emulsion) may indicate emulsions with specific uses.

TESTING EMULSION

Emulsion testing will be addressed in detail in another paper. Most test methods have been accepted as ASTM standards. The tests fall into three groups: those that test the handling properties of the emulsion, such as residue content, viscosity, and storage stability sieve residue; those that classify the emulsion into rapid-, medium-, or slow-setting grades, such as demulsibility, cement mix test, and coating tests; and tests on the residue recovered by evaporation, such as penetration or ductility. The emulsion may then be subject to additional performance tests related to the particular application of the emulsion in cold mix, chip seal, etc., using job aggregates.

EMULSION APPLICATIONS

Applications will be addressed in detail in other papers. Some typical applications of the various grades of emulsion are summarized in Table 1, but local practice varies considerably. The choice of emulsion for each application is a question of matching the reactivity of the emulsion with the reactivity of the aggregate and the environmental conditions. Aggregate reactivity is mostly associated with the very finest-size fractions which make the highest contribution to surface area. So a reactive RS emulsion is used with the low-surface area unreactive aggregates used in chip seal, whereas a low-reactive SS emulsion would be used for a dense cold mix which has a high content of –75 micron material and consequently high reactivity. Environmental conditions also have to be taken into account. High temperatures accelerate the chemical reactions and physical processes involved in emulsion setting, and therefore demand slower setting emulsions.

MANUFACTURE OF EMULSION

Emulsions are made by mixing hot bitumen with water containing emulsifying agents and applying mechanical energy sufficient to break up the bitumen into droplets. The effect of manufacturing variables on emulsion properties will be described in detail in a later paper.

It is clear that the manufacturing process can not only affect the physical properties of the emulsion but also affects the performance of the emulsion.

Emulsification is opposed by the internal cohesion and viscosity of the bitumen and the surface tension of the droplet which resists the creation of new interface. Smaller droplets are favored by a high energy input, a low bitumen viscosity at the emulsification temperature and by
## TABLE 1  Typical Uses of Emulsion

<table>
<thead>
<tr>
<th></th>
<th>Anionic</th>
<th></th>
<th>Cationic</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RS</td>
<td>MS</td>
<td>SS</td>
<td>RS</td>
</tr>
<tr>
<td><strong>Plant Mixes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Open-graded</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Dense-graded</td>
<td></td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Reclaimed asphalt pavement (RAP)</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Stockpile mix</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Pre-coated chips</td>
<td></td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td><strong>Mix Paving</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Open-graded</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Slurry</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Slurry for capeseal</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Microsurfacing</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>In-Place Mixes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RAP</td>
<td>✓</td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Dense-graded</td>
<td></td>
<td></td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Soil stabilization</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Spray Applications</strong></td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chipseal</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Fog seal–cement curing</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Tack coat</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Prime</td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Dust palliative</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mulch</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Penetration macadam</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waterproofing coatings</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Driveway and footpath sealers</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* May contain solvent.

*b* Need not pass cement mix test.

*c* May contain clay.

The choice and concentration of emulsifier (which reduces the interfacial tension). In the most common process, the emulsifier is dissolved in the water phase of the emulsion, and this water solution or “soap” is mixed with the hot liquid asphalt in a colloid mill (Figure 4).

## CHEMICAL NATURE OF EMULSIFIERS

Water molecules at the interface between oil and water have higher energy than those in bulk water. The result is an interfacial energy or tension which acts to minimize the interfacial area. The production of emulsion involves the creation of a large interfacial area between the asphalt and water, approximately 500 m² per liter (10). Emulsifiers are surface active agents (surfactants).
Surfactants have nonpolar lipophilic (oil-loving) and polar hydrophilic (water-loving) portions in the same molecule (Figure 5). The molecules concentrate at the interface between water and bitumen, orientated with the polar group in the water and the nonpolar parts of the molecule in the oil (Figure 6). This both reduces the energy required to emulsify the asphalt and prevents coalescence of the droplets once formed. The choice and concentration of emulsifier also largely determines the charge on the asphalt droplet and the reactivity of the emulsion produced.

A typical emulsifier has a hydrophilic “head” group and lipophilic (hydrophobic) hydrocarbon “tail” comprising 12 to 18 carbon atoms. This hydrocarbon tail is represented by “R” in chemical formulas. It is most often derived from natural fats and oils, tall oil, wood resins, or lignin.

Emulsifiers can be classified into anionic, cationic, and nonionic types depending on the charge their head groups adopt in water, although this charge may depend on pH (Table 2). Cationic emulsifiers are ammonium compounds contain positively charged nitrogen (N) atoms in their head group; anionic emulsifiers typically contain negatively charged oxygen (O) atoms. The charge on the head group is balanced by a counterion. The charge on the emulsifier head group largely determines the charge on the asphalt droplets, since the counterion diffuses away from the asphalt surface (Figure 6). Several studies have shown that even nonionic emulsifiers produce emulsions whose droplets have a small negative charge in water (14), and nonionic emulsifiers are often used in slow-setting asphalt emulsions. In the case of asphalt emulsions, the asphalt itself contains surface active species which can also concentrate at the interface (15). The size and sign of the charge on the asphalt droplets can be measured and is expressed as the “zeta potential” of the droplet. The zeta potential is strongly pH-dependent both because of the pH dependence of the charge on the emulsifier and also because polar components of the asphalt itself may ionize. Zeta potential measurements show that the charge on the asphalt droplets becomes more negative as the pH rises.

As the concentration of the emulsifier increases, the particle size of the emulsion is reduced. SS emulsions, which contain higher concentrations of emulsifier, generally have smaller particle size than RS grades.
Figure 5: Cationic emulsifier molecule.

Figure 6: Origin of charge on asphalt droplets. Emulsifier concentrates at the interface. Counterions diffuse into the water phase leaving net positive charge on the asphalt droplet.

Table 2: Chemistry of Asphalt Emulsifiers

<table>
<thead>
<tr>
<th>Lipophilic Portion</th>
<th>Head Group</th>
<th>Counterion</th>
<th>Head Group Charge, pH2</th>
<th>Head Group Charge, pH11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tallowalkyl-</td>
<td>-NH₂CH₂CH₂CH₂NH₃⁺⁺</td>
<td>2 Cl⁻</td>
<td>Positive</td>
<td>Neutral</td>
</tr>
<tr>
<td>Tallowalkyl-</td>
<td>-N(CH₃)₃⁺</td>
<td>Cl⁻</td>
<td>Positive</td>
<td>Positive</td>
</tr>
<tr>
<td>Nonylphenyl-</td>
<td>-O(CH₂CH₂O)₁₀₀H⁻</td>
<td>None</td>
<td>Neutral</td>
<td>Nonionic</td>
</tr>
<tr>
<td>Tall oil-</td>
<td>-COO⁻</td>
<td>Na⁺</td>
<td>Neutral</td>
<td>Negative</td>
</tr>
<tr>
<td>Alkylbenzene</td>
<td>-SO₃⁻</td>
<td>Na⁺</td>
<td>Negative</td>
<td>Negative</td>
</tr>
</tbody>
</table>
Generally more emulsifier is required to provide good stability and the right performance properties to the emulsion than is necessary to fill the interface, so asphalt emulsions will contain some “free” emulsifier in the water phase, present partly in micellar form, which acts as a reservoir helping to prevent coalescence after emulsification and storage and transport. This free emulsifier plays an important role in the setting process (see below) (10, 11). During storage of asphalt emulsion after production there may be slow changes due to migration of polar asphalt components and adsorption of emulsifier from the water phase into the interface (16). This reduces the free emulsifier concentration in the water phase and can influence the emulsion properties.

**FORMULATION OF THE EMULSION**

Emulsifiers are often supplied in a water-insoluble form to the emulsion producer and need to be neutralized with acid or alkali by the emulsion manufacturer to generate the anionic or cationic water-soluble form used to prepare the soap solution. The choice of the acid or alkali and the final pH of the emulsion influence the emulsion properties. Hydrochloric acid and occasionally phosphoric acid are the acids used, and sodium and potassium hydroxide are the most common alkalis. Cationic emulsions are usually acid, and anionic emulsions are typically alkaline (Table 3).

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

\text{insoluble form} \quad \text{water-soluble cationic form}

\[
\text{RCOOH} + \text{NaOH} = \text{RCOO}^- + \text{Na}^+ + \text{H}_2\text{O}
\]

\text{insoluble form} \quad \text{water-soluble anionic form}

Some emulsifier types, like quaternary ammonium compounds and alkylbenzenesulphonates, have permanent head group charges and do not need to be reacted with acids or alkalis (Table 2). These products, as well as nonionic emulsifiers, allow the formulation of emulsions which are neutral in pH.

Increasing emulsifier concentration decreases the reactivity of the emulsion. MS emulsions are generally formulated with the same emulsifiers as RS grades but at higher concentration (0.4%–0.8%). The emulsion producer can adapt the emulsion recipe to cope

<table>
<thead>
<tr>
<th>CRS</th>
<th>CSS</th>
<th>Anionic RS</th>
<th>Anionic SS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asphalt</td>
<td>65</td>
<td>Asphalt 65</td>
<td>Asphalt 60</td>
</tr>
<tr>
<td>Tallowdiamine</td>
<td>0.2</td>
<td>Tallow Oil 0.6</td>
<td>Tall Oil 0.3</td>
</tr>
<tr>
<td>Hydrochloric acid, 35%</td>
<td>0.15</td>
<td>diquatinary ammonium chloride 0.6</td>
<td>Sodium hydroxide 0.2</td>
</tr>
<tr>
<td>Soap pH</td>
<td>1.5–2.5</td>
<td>Soap pH 3–7</td>
<td>Soap pH 11–12</td>
</tr>
<tr>
<td>Water</td>
<td>to 100</td>
<td>Water to 100</td>
<td>Water to 100</td>
</tr>
</tbody>
</table>
with reactive aggregates or high temperatures, generally by increasing the emulsifier concentration or blending emulsifiers of lower reactivity.

A wide range of chemistries have been used for asphalt emulsifiers. In addition to cationic, nonionic, and anionic emulsifiers, there are products with amphoteric head group character which may adopt positive or negative charges depending on pH.

OTHER COMPONENTS AND THEIR FUNCTION

Calcium and Sodium Chlorides

Asphalt contains a small amount of salt, which can lead to an osmotic swelling of the droplets in an emulsion as water is drawn into the droplet. This results in an increase in emulsion viscosity, often followed by a decrease as the salt slowly escapes. Calcium chloride or sodium chloride is included in the emulsion at 0.1%–0.2% to reduce the osmosis of water into the bitumen and minimize the changes in viscosity. Sodium chloride is used in anionic emulsions (6).

Adhesion Promoters

Water resistance is an important property of asphalt mixes and seals. The cured film from some anionic emulsions and occasionally also cationic emulsions may not have sufficient adhesion to aggregates, in which case adhesion promoters can be added to the asphalt or to the finished emulsion. Generally these adhesion promoters are surface active amine compounds.

Solvent

Solvents may be included in the emulsion to improve emulsification, to reduce settlement, improve curing rate at low temperatures, or to provide the right binder viscosity after curing. The maximum amount of distillate in the emulsion is usually specified. MS emulsions often contain up to 15% solvent to provide the right workability characteristics and stockpile life to asphalt mixtures. Emulsions used in recycling may also contain solvents and fluxes in order to rejuvenate old asphalt.

Latex

Polymer modification can improve the properties of bitumen in terms of cohesion, resistance to cracking at low temperatures, and resistance to flow at high temperatures. Latex is a water-based dispersion of polymer which is particularly suited to the modification of emulsions. Latex comes in anionic, nonionic, and cationic forms, and it is important that the latex type should be compatible with the emulsion. Styrene butadiene rubber, polychloroprene, and natural rubber latex are most commonly used in paving grade emulsions.
THE SETTING PROCESS

Emulsified asphalt must revert to a continuous asphalt film in order to act as cement in road materials. This involves flocculation and coalescence of the droplets and removal of the water (Figure 3). Evaporation and absorption of water by the aggregate may be the main breaking mechanism for very slow-setting emulsions, but in most cases chemical reactions between the aggregate and the emulsion contribute to the emulsion setting and it is not necessary for all the water to evaporate before curing takes place. The strength of the reaction of emulsion with aggregate is in many cases sufficient to squeeze the water from the system. Clean water can be seen separating from the mixture. The speed of these setting and curing processes depends on the reactivity of the emulsion, the reactivity of the aggregate and environmental factors, such as temperature, humidity, wind speed, and mechanical action. Less viscous asphalts tend to give faster coalescence. It may take a few hours in the case of a chip seal to several weeks in the case of a dense cold mix for the full strength of the road material to be reached.

A considerable amount of research effort, partly sponsored by the European community, has been expended to elucidate the mechanism of setting and curing of asphalt emulsion (17–19). Important factors are changes in pH caused by reaction of the aggregate with acids in the emulsion, adsorption of free emulsifier onto the aggregate surface, and flocculation of the emulsion droplets with the fines. The relative timescale of flocculation (setting) and coalescence (curing) depends on the system, but in general flocculation is the more rapid process in which some water can be expelled from the system and some cohesive strength develops, followed by a slower coalescence process which results in a continuous asphalt phase. This asphalt phase must also adhere to the aggregate. Coalescence is an inversion process; the O/W emulsion is transformed into a W/O type which then slowly loses its internal water phase. This inversion process is favored as the ratio of asphalt to water in the system increases. The tendency for an emulsion to invert can be determined in laboratory tests and has been related to curing behavior in the field (21).

Aggregates take up a characteristic surface charge in water which depends on the nature of the minerals, the pH, and the presence of soluble salts. So-called “acid” aggregates high in silica tend to take up a negative charge.

Some aggregates, like carbonates, and fillers, like cement, may neutralize acid in cationic emulsions causing the pH to rise and the emulsion to be destabilized. Anionic emulsions may be destabilized by soluble multivalent ions. We can consider two extreme cases of emulsion breaking (17). In the case where the charge on the emulsion droplets is quickly destroyed by pH changes, for example, then the emulsion very quickly flocculates and coalescence begins to occur at a slower rate. This rate is dependent on the viscosity of the binder, as well as environmental conditions; coalescence is slower with high viscosity asphalts and lower temperatures. At the other extreme where the emulsion droplets remain charged, loss of water, either by evaporation or by absorption of water into porous aggregate, eventually forces the droplets close enough for attractive forces to predominate, forcing out water and starting the coalescence process. The attractive forces between the droplets can generate significant cohesion even before coalescence occurs.

In a simplified process (Figure 7) of the setting of a RS cationic emulsion where the aggregate does not contain significant fines, important stages in the setting process can be considered as follows:
1. Free emulsifier adsors onto the (oppositely charged) mineral surface, which neutralizes some charge on the surface while at the same time making the surface somewhat lipophilic. Too high a free emulsifier concentration in relation to the surface area of the aggregate can actually reverse the charge on the minerals and so inhibit the setting of the emulsion.

2. Minerals neutralize acids in the emulsion, causing loss of charge on the emulsion droplets, leading first to flocculation of the asphalt droplets and then to a slower coalescence of the droplets.

3. Water is adsorbed by the mineral, as well as evaporates from the system.

4. Droplets in contact with the mineral spread on the surface, especially that surface made lipophilic by adsorbed emulsifier, eventually displacing the water film on the aggregate surface.

In the breaking of SS grades, where the aggregate contain high content of fines, heteroflocculation of the droplets of asphalt and the oppositely charged fines may occur, which is sufficiently strong to squeeze out water and form an asphalt mastic. A similar situation is achieved in microsurfacing where filler is intentionally added to initiate setting. Mechanical action, such as compaction or traffic, may squeeze the droplets together, promoting coalescence and squeezing water out of the coalesced film.

In practical situations too early coalescence of the asphalt droplets can hinder final curing by skin formation (20, 21) reducing the evaporation of water. Coalescence throughout the asphalt emulsion film, before water is trapped in the system, is promoted by smaller asphalt droplets with narrow size distribution. Too early coalescence of asphalt droplets in some systems can interfere with the formation of a composite binder formed from latex and asphalt, which depends on latex curing before asphalt (4).
RECENT DEVELOPMENTS

Emulsion Manufacture

The factors influencing the properties of the emulsion are better understood today. The particle size of the emulsion and the free emulsifier concentration can be determined by the manufacturing conditions and viscosity can also be controlled. High residue (>75%) emulsions can be prepared by the production of bimodal particle size distributions (22). Production of emulsion by static mixer technology (SMEP = static mixer emulsion process) is fully commercialized and holds the possibility of adjusting the particle size distribution of the emulsion and so controlling physical and performance properties of the emulsion (23).

Emulsion Chemistry

In the area of emulsifier chemistry there continues to be innovation, especially in emulsifiers for SS emulsions. The use of phosphoric acid instead of hydrochloric acid in emulsions for microsurfacing and cold mix has been established in Europe, Asia, and recently also in the Americas. The phosphoric acid system allows a wider range of asphalts to be used (24).

Setting Process

As mentioned above there has been a tremendous improvement in our understanding of the setting process of asphalt emulsion. Some innovative techniques related to the setting process have included the use of breaking agents in cold mix and spray applications (25, 26) to provide accelerated curing; the use of wetting agents as compaction aids in cold mix (27) to allow quicker removal of water and hence earlier bonding of the coalesced asphalt with the mineral surface; cement-free slurry seal systems in which reactive filler is generated chemically in the slurry (28); and emulsions of mixed hard and soft binders for cold mix applications which allow some control over the coalescence process (29). In some novel processes SS and RS emulsions are used in combination in order to provide the right coating and curing behavior.

Applications

The last 20 years have seen several emulsion-based new technologies for road construction and repair, as well as significant improvements over previous emulsion systems. These include ultrathin hot-mix friction courses with modified emulsion bond coat (30); DRM (spray-applied crack seal with emulsion seal surfacing); P.A.S.S. (scrub seal with modified emulsified binder) (31); glass fiber-reinforced chip seal (32); trackless tack coats (26, 33); WAM (warm mix using emulsion or foamed asphalt) (34); and improved chip seal systems (35). Several new systems for cold mix have also been commercialized.
FUTURE DEVELOPMENTS

With the high cost of petroleum-derived materials and environmental pressures on HMAs, the future of asphalt emulsion will be in thin performance-based overlays and seals that use less asphalt, replacing cutbacks in priming applications, reducing the mixing and paving temperatures of asphalt mixes, and general stepwise improvements in current applications to provide more reliable, longer-lasting treatments. There is also the potential to develop more cost-effective materials, particularly when the use of emulsion can create structures and microstructures not easily duplicated by hot techniques.

REFERENCES


29. French Patent 2695664, CECA S.A.


The most scientific, precise, and complete definition of emulsion is given by P. Becher in *Emulsion Theory and Practice* (1961):

An emulsion is a thermodynamically unstable heterogeneous system including at least two immiscible liquid phases of which one is dispersed in the other in the form of droplets whose diameter is generally greater than 0.1 micrometers. The minimum stability inherent to this type of system may be increased by adding appropriate agents, such as surfactants or finely divided solids (I).

A more specific definition, with respect to asphalt emulsions, might be

A heterogeneous system with two or more liquid phases, made up of a continuous liquid phase (water) and at least a second liquid phase* (asphalt) dispersed in the former in fine droplets. (I)

(* Although typical asphalts used to manufacture most emulsions may appear to be a solid at room temperature, they are actually viscous liquids, also referred to as viscoelastic.)

Asphalt emulsion production is a science in which much research, time, and money are invested. Asphalt emulsion production is as much art as it is science; the art of asphalt emulsions production is in understanding the science and putting it to practical use.

COMPONENTS

The components of an asphalt emulsion include the following.

Asphalt

Asphalt is defined as the residual product of nondestructive distillation of crude oil in petroleum refining. Asphalt is an engineering material and is produced to meet a variety of end-use specifications based upon physical properties. This basic product is sometimes referred to as “straight run” asphalt. The vast majority of asphalt produced in North America and Europe conform to the characteristics of straight run, however, another common product often referred to as “oxidized” asphalt is produced by blowing air through the asphalt at elevated temperatures to alter its physical properties for commercial applications. Asphalt used in the production of asphalt emulsions is generally of the straight run variety.
Diluents and Fluxes

Other refinery products that may be blended with basic asphalts without altering their properties include, but are not limited to raffinates, vacuum residuum, asphaltenes, and petroleum resins. The addition of any refinery streams or products other than these, and all nonrefinery products introduced into asphalt in significant quantities, may affect asphalt properties and should be considered prior to emulsion manufacture.

Water

Water used to manufacture emulsions may be from various sources: municipal systems, wells, etc. Whatever the source of water, it must contain a minimum amount of mineral and organic impurities. It is often necessary to add salts to the water to create an ion exchange in the water. Ion exchange generally consists of replacing the magnesium and calcium ions in the water by adding sodium ions. Magnesium and calcium ions tend to react with some types of emulsifiers to form compounds which no longer have emulsifying properties.

Surfactants

Surface active agents (surfactants), also known as emulsifiers or emulsifying agents, are needed to provide the stability required over time. The stability of the emulsion determines its appropriate use. Surfactants are chemical compounds with a surface activity which, when dissolved in a liquid, especially water, lowers its interfacial or surface tension by preferential adsorption at the vapor/liquid surface or other interfaces.

Surfactant molecules have two opposite affinities, one part is made up of a polar group yielding hydrophilic (water-loving) properties and one part is made up of a non polar radical giving it lipophilic (oil-loving) properties.

There are numerous natural compounds that act as surfactants, but more commonly chemical compounds are synthesized to produce the desired characteristics. Surfactants can be grouped according to the type emulsions they yield. The typical types of emulsions are anionic, cationic, amphoteric, and nonionic. Commonly used surfactants are amine class chemicals that are of a liquid or paste consistency not soluble in water.

Zeta Potential of Cationic Emulsifiers

As defined, asphalt emulsions are colloidal systems in which asphalt is dispersed in a continuous aqueous phase. The asphaltic-dispersed phase has certain properties with respect to electrical charge. Knowledge of these electrical properties makes understanding the behavior of the emulsion colloidal system easier. In the case of cationic asphalt emulsions, each asphalt droplet has multiple positive charges due to the emulsifier cation. Around each positively charged asphalt droplet, there is a negative ion layer whose electric charge exactly compensates for the positive particle charge ($I$). The zeta potential can be determined by placing the colloid particles in an electric field and measuring their movement energy. This is usually done with a microelectrophoresis device where the electrophoretic mobility is measured in millivolts (mV). The behavior of the emulsions with respect to measurement of zeta potential is similar to that which is observed when aggregates and emulsions are mixed.
Zeta potential is both a function of emulsifier concentration and emulsion pH. Cationic asphalt emulsions range in pH from 1 to 7, more specifically in the 2- to 4-pH range, and typically have zeta potentials in the range of 15 to 150 mV. As a general rule, the higher the cationic zeta potential is, the more cationic the emulsion is and the more rapid is the breaking speed. Lower zeta potential yields a more stable emulsion with a much slower breaking speed. Therefore, emulsion breaking speed onto aggregates is directly proportional to the zeta potential of the emulsion.

**Acid**

As emulsifiers are insoluble in water, it is necessary to convert them into salts so as to dissolve them in the dispersing phase. This is generally done by reacting with acid, most often hydrochloric acid in a 20°C to 22°C solution. Acid dosing is the regulatory factor which determines final emulsion pH.

**MANUFACTURING PARAMETERS**

The parameters to consider in the manufacture of asphalt emulsions are outlined below.

**Dispersion Energy**

Emulsion dispersion is caused by mechanical energy and physicochemical energy. The mechanical energy (provided by the mill) divides the asphalt into fine particles and the emulsion fineness increases with fractioning capacity (mill capabilities). The physicochemical energy is provided by the emulsifier and must

- Reduce the interfacial tension between the hydrocarbon phase (asphalt) and the aqueous phase (water) so as to facilitate emulsification and
- Create a protective film around the particles.

In simple terms, there must be sufficient mechanical energy (mill energy) to provide asphalt particles of the correct size and concentration. And there must be sufficient surfactant to maintain stability.

**Particle Size Distribution**

Particle size and particle size distribution are important variables and are controllable with formulation, raw materials, and the equipment used to manufacture the emulsion. Many of the processes of breaking and curing are directly dependant on particle size and particle size distribution (4). The importance of particle size in emulsions has been discussed in many papers (2–4). It is a determinant of emulsion stability, coating, break rate, and cure rate. Methods to improve particle sizing of emulsions by formulation and adjustment of asphalt chemistry are described in the literature (2, 3). These methods usually involve improvement of the dispersing phase, doping of asphalt with surfactants, and tailoring asphalt composition and optimization of manufacturing conditions. The intention is to improve formation and dispersion of asphalt
particles by the mill and stabilize the resulting emulsion. The mill and milling process are the main determinants of initial particles size for a given asphalt–emulsifier system as particle size is determined by the shear in the mill and mill residence time (2, 4, 5, 7).

The relationship of the milling process to particle size can be expressed by

\[ \text{Shear rate} = \frac{2\pi RV}{60 E} \]  

(1)

where

- \( R \) = colloid mill radius (rotor and stator combination);
- \( V \) = velocity of rotation or rotation speed (rpm); and
- \( E \) = gap dimension.

From Equation 1, it can be concluded that particle size is a function of mill diameter, gap, and peripheral speed. A correlation between shearing and the \( d_{50} \) value, a correlation between particle size distribution and initial particle size in the mill, has been reported by Holleran in U.S. Patent 5,518,538.

Internal mill configurations are quite different, with varying tooling and effective gap dimension, therefore, the relationship presented in Equation 1 should be changed to:

\[ \text{Shear rate} = \frac{2\pi RV}{60 E} M_f \]  

(2)

where \( M_f \) = mill factor, and the mill factor is the increase or decrease in shear created by the mill configuration and tooling.

There are several methods available to determine the average diameter of emulsion asphalt particles which are all aimed at measuring the particle size and distribution in water. These methods range from sophisticated laser measurement of particle sizes and distribution to simple opacity measurements.

**Component Viscosity and Temperature**

Often the mechanical energy required to provide asphalt particles of correct size and concentration is aided by increases in the temperature of the hydrocarbon phase (asphalt). In other words, in order to enable the asphalt binder to properly disperse in the aqueous phase, it is necessary that its viscosity be relatively low. From practical experience, the optimal viscosity is 200 centipoises, which is obtained by maintaining the asphalt at a temperature that yields this viscosity; it is called the equiviscous temperature (EVT). The EVT of some common asphalts are given in Table 1.

<table>
<thead>
<tr>
<th>Asphalt Grade</th>
<th>Approximate EVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC-5</td>
<td>140°C (284°F)</td>
</tr>
<tr>
<td>AC-10</td>
<td>150°C (302°F)</td>
</tr>
<tr>
<td>AC-30</td>
<td>160°C (320°F)</td>
</tr>
<tr>
<td>7–9 dmm</td>
<td>185°C (365°F)</td>
</tr>
</tbody>
</table>
The EVT limit of 200 centipoises is obtained from practical experience. In actual practice we know this works because emulsions from the asphalts listed above are typically produced at these temperatures. If these temperatures are significantly exceeded, unwanted and undesirable effects may occur. In fact, if the emulsion at the mill outlet is at a temperature greater than 100ºC (212ºF) the emulsion aqueous phase will boil, as water typically has a boiling point of 100ºC (212ºF). At higher altitudes the boiling point of water will be lower. A good rule of thumb for emulsion manufacturing purposes is to not exceed 95ºC (203ºF) at the mill outlet.

Often manufacture of the aqueous phase requires that the water (soap solution) be at a temperature of around 40ºC (104ºF) or higher to provide proper activation of the emulsifying agent, therefore, it is necessary that the asphalt binder temperature does not exceed a certain temperature to prevent boiling of the emulsion. Keeping in mind that the asphalt has a characteristic EVT, which is important for proper particle size and concentration, it may not be possible to successfully manufacture quality emulsion at a temperature below the boiling point of the emulsion.

**Emulsion Temperature**

The relationship of asphalt binder temperature to temperature of the aqueous phase and resulting emulsion temperature is represented by:

\[
\frac{(AC \text{ wt\%} \times AC \text{ temp} \times 0.5) + (Soap \text{ wt\%} \times Soap \text{ temp} \times 1.0)}{(AC \text{ wt\%} \times 0.5) + (Soap \text{ wt\%})} = \text{Emulsion}
\]

As the boiling point of water varies directly with respect to decreases and increases in pressure of its environment, we can increase the boiling point of water by increasing the pressure of its environment. Put more simply, if we maintain a certain amount of pressure on the emulsion, until the temperature is below its boiling point, boiling of the emulsion can be prevented. Therefore, if temperature requirements dictate, e.g., minimum soap temperature and asphalt EVT, the emulsion can be manufactured under pressure without fear of boiling the emulsion.

**Pressurized Manufacturing**

Relatively high EVTs of some asphalt binders or minimum soap temperatures require that the emulsions be manufactured under a pressure of a few bars (30–60 psi) to satisfy the mandatory parameters corresponding to these components and simultaneously prevent boiling of the emulsion. The EVT of an asphalt and its importance in the manufacture of asphalt emulsions has been presented. It is obvious that another important emulsion manufacturing parameter is the emulsion exit temperature or what is defined as the minimum emulsion exit temperature (MEET). MEET is considered to be equivalent to the temperature of the asphalt where the viscosity is approximately equal to 20,000 centipoises. As with EVT this limit is obtained from practical experience. It is a common belief that if the emulsion exit temperature is maintained at or above the MEET, emulsion stability is improved during manufacturing, cooling, and storage.

The EVT and MEET can be obtained from a viscosity profile of the asphalt. An example of rotational viscosity profiles of a neat AC-30 (PG 67-22) and a 4.0% styrene-butadiene-styrene (SBS) -modified asphalt are given in Figure 1.
From Figure 1, the MEET can be obtained as the point where the viscosity of the asphalt is equal to 20,000 centipoises; for the PG 67-22, the MEET equals 82°C (180°F), and for the 4.0% SBS-modified asphalt, the MEET equals 118°C (245°F). The EVT can be obtained as the point where the viscosity of the asphalt is equal to 200 centipoises; for the PG 67-22, the EVT equals 177°C (350°F), and for the 4.0% SBS modified asphalt, the EVT = 218°C (425°F). (Note: Often it may be necessary to actually heat asphalt to about 6°C (25°F) higher than the EVT to ensure that the asphalt is at EVT at the milling surfaces.)

An emulsion manufactured from the PG 67-22 represented in Figure 1 could be manufactured under normal atmospheric conditions, while an emulsion manufactured from the 4% SBS asphalt must be manufactured under pressure. As a general rule, if the MEET is greater than 95°C (203°F) the emulsion will have to be produced under pressure. The amount of pressure required can be obtained by consulting steam data temperature tables \(^8\) using the absolute pressure value plus 20%. It should be noted that this pressure is absolute pressure and not gauge pressure; gauge pressure would be equivalent to absolute pressure less 1 bar (14.5 psi). For demonstration purposes, consider the SBS-modified asphalt presented in Figure 1. The manufacturing pressure of the SBS-modified asphalt emulsion based on the MEET of 118°C (245°F) can be obtained from Figure 2.
From Figure 2 we see that the emulsion manufacturing pressure for the MEET of 118°C (245°F) is approximately 1.3 bars (19 psi) gauge pressure. At this point, it is important to note that the actual emulsion exit temperature for this asphalt may be higher than 118°C (245°F) depending on the soap temperature requirements and the recommended asphalt temperature of 218°C (425°F) based on EVT. The mill outlet temperature may also be slightly higher than calculated from Figure 1 as the milling process, mill resonance time and pressure effects will contribute to the final emulsion outlet temperature.

The following equation yields the soap temperature for a given emulsion.

$$\text{MEET} \left[ (\text{AC wt\%} \times 0.5) + (\text{Soap wt\%}) - (\text{AC wt \%} \times 0.5 \times \text{EVT}) \right] = \text{Soap temp}$$

Using Equation 4, a 65% residue emulsion with an asphalt binder having a 218°C (425°F) EVT and a 118°C (245°F) MEET, the soap temperature would be 25°C (77°F). It is not likely that the soap solution would be properly activated at this temperature.
Component Dosing

As component dosing in emulsions must be extremely precise, especially the emulsifier and the activator (e.g., HCl or NaOH), proper activation and temperature of the soap solution is important. Variation, even very slight, may have far reaching consequences. Soap solutions for typical cationic emulsions are usually in the 40°C (104°F) to 70°C (160°F) range.

Understanding this, consider a 65% residue emulsion with the 218°C (425°F) EVT asphalt from Figure 1 and a soap temperature of 60°C (140°F). This emulsion would have an emulsion exit temperature of 136°C (277°F), from Equation 3, which would require an emulsion manufacturing gauge pressure of 2.8 bars (40 psi) (Figure 2). Note that the actual outlet temperature could possibly be 10–15 degrees higher due to milling energy and pressure effects.

The following is a step by step summary of the emulsion manufacturing parameters using the information presented thus far.

1. Determine the rotational viscosity profile of asphalt.
2. Determine asphalt EVT (asphalt temperature).
3. Determine MEET (minimum mill exit temperature).
4. Determine pressure requirements (from steam tables).
5. Establish soap temperature based on emulsifier chemistry and/or manufacturer’s recommendations.

EMULSION MANUFACTURING

There are also parameters to consider in the manufacture of asphalt emulsions, including the following.

Heat

Asphalt is practically solid at ambient temperature; therefore, it must be heated and maintained in a liquid state to facilitate transfer and emulsification. In addition, water used in the emulsion manufacturing process is generally added above ambient temperature; thus a heat source is required for both asphalt and water.

For many years, steam was used for heat in emulsion manufacturing. Today the range of heating methods is widely extended. Heating methods currently used are steam, heat-exchange oil, and electric heat.

Dispersing Phase Preparation

The asphalt emulsion dispersing phase, also known as the “soap” phase, consists of water and various emulsifying agents which make up most often a sodium fatty acid salt for anionic emulsions or an amine hydrochloride for the cationic emulsions.

Depending on the manufacturing mode, the dispersing phase is either in one operation, meaning the emulsifiers and acid are added to the water in their exact doses, or in two operations where a concentrated product of emulsifiers and acid are added at a high dose rate to water
which is diluted with hot water during emulsion manufacture at a dosing corresponding to the final dosing required.

To prepare the dispersing phase, the manufacturing facility must provide a method of dosing the components (by weight or by volume), mixing and diluting, if necessary, and heating of water. Dosing of components in the preparation of the soap solution may be controlled by simple graduated vessels or highly accurate load cells and mass flow meters. Some plants are equipped with a pH meter to be able to continuously check compliance of the pH indicated to that provided by formulation during the dispersing phase production and subsequent emulsion production.

**Dispersed Phase Preparation**

The dispersed phase “asphalt” may be either pure asphalt or a blend of asphalt in predetermined proportions with a flux or diluents and possibly other agents, such as elastomer in the case of polymer-modified emulsions. In some cases the emulsifier is fully or partially added to the asphalt prior to it being emulsified.

The various dispersed phase compositions may require equipment whose sophistication may vary from a simple “in-line” mixer to a more elaborate high-performance mixer. Continuous viscosity measurements can be obtained through incorporation of in-line viscometers such as rotational or vibrating (sphere or rod) technology, the latter of which is less susceptible to turbulent flow errors.

**Emulsifying Equipment**

Industrial manufacture of asphalt emulsion uses custom made equipment to provide thorough mixing capability to provide the fineness and stability of dispersion required to meet the desired asphalt emulsion properties. While high-pressure static mixers and high shear mechanical mixer may be used, colloid mills are more common in the manufacture of asphalt emulsion.

While there are various types of colloid mills, the most common characteristics are an adjustable or fixed air gap between the rotor and stator and fixed or variable rotor rotation speed. The air gap spacing has a direct effect on emulsion fineness, while rotor speed affects the size and distribution of the asphalt particles. At certain critical speeds, a decantation phenomena may occur causing a reduction in emulsion quality.

The emulsion manufacturing process is a continuous process whereby the dispersing medium is continuously fed with the dispersing and dispersed phases by adjustable flow rate pumps. Mass flow meters may be incorporated to regulate material feed. As stated previously, certain emulsions have special characteristics and must be manufactured under pressure in specially designed colloid mills with necessary cooling provide to prevent boiling of the finished emulsion.

**Storage**

The production rate of emulsion plants is generally greater than demand; therefore, storage facilities make it possible to have longer production runs, thus improving plant productivity. Present day emulsions may be stored for up to several months without major changes in physical properties. It is advisable to use small diameter vertical storage tanks with a minimum horizontal
cross section with a dip tube filling pipe which reaches to or near the bottom of the storage tank. Emulsions of different ionic types should never be mixed and tanks should be thoroughly cleaned before refilling with a different ionic type. Provisions should also be made to ensure proper agitation of stored emulsion to prevent settling, decantation or creaming. Emulsions are sensitive to frost which can cause irreversible breaking; therefore, provisions should also be made to prevent stored emulsion from freezing.

SUMMARY

From the information given in the preceding discussion one can see why the art of emulsion manufacturing is in the practical use of available science. Understand that this is strictly a guideline based on discussions with industry professionals and their experience and information from the SFERB text, *Bitumen Emulsions: General Information and Applications* (1). Remember, “Nothing under the sun is absolute, except death, and we are not sure about that.” In science nothing is absolute, therefore, these guidelines should be used as a starting point in the venture to manufacture asphalt emulsion with adjustments made, within limits, to obtain desired outcome.

REFERENCES

Asphalt emulsions have been in existence for almost 100 years in the United States and the rest of the world. They were first developed in the early 1900s, used in road applications in the 1920s, with continued growth due to World War II and the energy crisis of the 1970s (1). Asphalt emulsions have found their way into every road building application from sealing surfaces, to bonding layers of pavement, to mixes for road bases and surfaces. The test methods for their identification, handling, application, and quality control have advanced as the industry has embraced their many uses. This paper gives an introduction to these test methods based on four categories: plant quality control, shipping and storage, application, and identification. A brief look at the future evolution of the testing of emulsified asphalt products will be given to summarize this paper.

**PLANT QUALITY CONTROL**

For a plant to manufacture a good quality emulsion for a specific application in industry, a good testing protocol must be established for the components going into the product as well as the manufacturing process. Whether an emulsion is cationic, anionic or nonionic, a solution must be made prior to milling the emulsion. This solution is made by adding water in a tank at the appropriate temperature for blending or reacting an emulsifier. The order of addition of emulsifiers, additives, acids, or bases is critical to the consistency of manufacture.

The proper massing, or volume measurements, of the components is the first critical step to a quality production process. Once the components are in solution, the pH of the solution should be checked to ensure it is within the requirements for production. If the solution meets the pH requirements, the asphalt emulsion can be prepared by running the solution and asphalt through a milling process. The milling process includes blending the proper amount of asphalt into the solution, which must be monitored by emulsion residue or water content. The emulsion residue is quickly checked during the milling process by the heated evaporation of water from the emulsion, usually using a hot plate. Depending on the application for the emulsion, the water component in the emulsion can be 30%–45% of the product. After the run of emulsion is complete, a distillation residue is usually completed on the tank to verify the production values.

**SHIPPING AND STORAGE**

Once the asphalt emulsion has been manufactured for an application, tests must be conducted on the material to ensure it has the appropriate stability for storage and shipping. The weight of asphalt is very close to that of water, which helps in the ability of the asphalt to not settle to the bottom or cream to the top of the final product. Tests such as settlement and storage stability are done at 24 h and 5 days after manufacture to ensure the product maintains a good consistency.
The tests involve taking samples for residue testing from the top and bottom of a cylinder after the specified time has elapsed. The differences in residue properties from the top to the bottom are compared to make sure they are within specifications for the application.

The temperatures at which the emulsions are shipped for various applications can also be important. Some emulsions may need to be cooled prior to shipping, while others need to have their temperature maintained at those close to the temperature at manufacture.

Although there are no pump stability tests currently specified by agencies, many asphalt emulsion manufacturers incorporate internal procedures to verify that the final product will maintain stability during the pumping that is required between tanks and on the machines that are used for application. These tests usually require cycling the emulsion through positive displacement (usually gear type) pumps and checking for material that may break out during pumping.

APPLICATION

Asphalt emulsions are used for various applications in the road building industry. The main properties that are required from the emulsion are the ability to coat aggregates during the mixing process, form a uniform film for sealing or bonding layers, and enough stability for the application.

Emulsion viscosity is a main test for the application of products. In a mixing application of dense graded aggregates, a thinner viscosity of emulsion is usually required. For an open-graded application, a thicker emulsion is usually desired to get the appropriate film thickness. An asphalt emulsion used for bonding layers of asphalt needs to be thin enough to make a uniform layer and may need to be diluted with water to achieve the desired properties. For seal coating with aggregate chips, the emulsion needs to be thick enough to form the appropriate layer of emulsion for the size of chip while not forming drill marks or running off the road.

Over a period of time, the asphalt emulsion that is manufactured at the plant may have its particles grow in size due to many different effects. The sieve test for asphalt emulsion can verify that the emulsion has not deteriorated to a degree that would interfere with passing through spray nozzles or possibly even cause a pump stability issue. A particle size analyzer can also be used to test the degree of homogeneity.

IDENTIFICATION

Since asphalt emulsions are used for many different applications, there are test methods to classify emulsions by charge as well as speed of setting (slow, medium, or rapid) to determine the appropriateness for specific uses.

A particle charge test is done to verify whether an emulsion is cationic. This can be important if mixing with certain aggregate mineralologies. Some aggregates will mix better with anionic or nonionic types of emulsions, while others perform better with cationic materials.

Demulsibility and breaking index tests can be done to verify a proper break for many seal coating applications. The demulsibility test takes a known salt solution and mixes it with an emulsion to cause the emulsion to chemically break. The amount of this break can be used to determine the rapid setting nature of the emulsion. A breaking index test can also be performed
that uses a silica flour to blend into an emulsion. The break that occurs in this test is usually more of a surface area effect than a chemical break. Together these tests can be useful tools to verify a rapid setting emulsion.

The cement mix test is an important test for cold mix applications. A Type III high early strength portland cement is blended with an emulsion at a specified ratio to ensure that the emulsion is stable for the mixing process. Although this is a useful test, the stability of the actual components to be used in the field should be verified through coating tests with the aggregates and emulsions to be used.

Some emulsions require the addition of solvents such as naphtha, kerosene or diesel fuels to perform appropriately. An oil-in-distillate value from the distillation process can be used to verify the amounts of these materials in the emulsion. Distillation temperatures can vary from 135ºC to 260ºC. The oil distillate is measured as a layer of oil on the water recovered from this process in a graduated cylinder.

Table 1 and Table 2 show emulsion tests used to specify a comparable rapid setting type of emulsion that is used in the United States and Europe.

### TABLE 1 Specification for CRS-2 Cationic Emulsified Asphalt (2)

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity, Saybolt Furol at 50°C (122°F) SFS</td>
<td>100–400</td>
</tr>
<tr>
<td>Storage stability test, 24 h, %</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Demulsibility, 35 mL, 0.8% dioctyl sodium sulfocuccinate, %</td>
<td>&gt;40</td>
</tr>
<tr>
<td>Particle charge test</td>
<td>positive</td>
</tr>
<tr>
<td>Sieve test, %</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Distillation</td>
<td></td>
</tr>
<tr>
<td>Oil distillate, by volume of emulsion, %</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Residue, %</td>
<td>&gt;65</td>
</tr>
</tbody>
</table>

### TABLE 2 Specification for ECR 65 Cationic Emulsion (3)

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engler pseudoviscosity at 25°C</td>
<td>&gt;6</td>
</tr>
<tr>
<td>Storage stability by decantation</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Breaking point</td>
<td>&lt;100</td>
</tr>
<tr>
<td>Charge sign for particles</td>
<td>positive</td>
</tr>
<tr>
<td>Homogeneity</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Particles greater than 0.63 mm</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Particles between 0.63 and 0.16 mm</td>
<td>&lt;0.25</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>34–36</td>
</tr>
</tbody>
</table>
WHAT IS NEEDED FOR THE FUTURE?

Many of the tests described above have been in the asphalt emulsion industry for years and have been effective for producing and applying the products. There are areas for improvement that the industry has determined, however, which will advance the use and consistency of the asphalt emulsion products.

Probably the greatest need that exists is the method of recovering a residue that is appropriate for field applications of the materials. The distillation methods used are completed at temperatures that are well above those that the product is exposed to in the field. Even with vacuum procedures to bring the temperature down, the question remains as to the true values one can achieve on the residue as compared to that which is seen in the field. With the use of polymer modified asphalts or latex additions to the emulsions, there is even a greater concern to recover the appropriate material representative of what is applied in the field. Recent efforts that have used evaporative techniques on thin films at 25-60°C have produced encouraging results.

Improved ways of measuring asphalt emulsion viscosity are also being evaluated. The great concern is the consistency of values achieved comparing those of a Saybolt type of viscometer to a paddle wheel or rotational spindle viscometers. Viscosity measurements at field application temperatures are also important to better define the performance.

There are also improvements that can be made in the identification tests. Testing that includes the actual materials being used to mix or seal coat in the field should be considered. Testing that would tie together the asphalt emulsion products with their final application for performance should be the ultimate goal.

REFERENCES

Overview of Asphalt Emulsion Applications in North America

PEGGY L. SIMPSON
Western Emulsions, Inc.

According to the 10% of paving-grade asphalt in North America is used in the emulsified form. The advantages of low temperature application, solventless, or low solvent content formulations and easy modification with water-based latex emulsions make asphalt emulsions the material of choice for sealers and binders in many pavement maintenance and construction applications. Although asphalt emulsions have been in use for almost a century, use in specific applications varies significantly throughout North America, with some applications in common use throughout Mexico, the United States, and Canada, and other applications used extensively in some areas and not in others. Since lack of awareness of and exposure to the broad range of construction and maintenance applications for emulsions can determine usage, this paper gives an overview of practical applications carried out with asphalt emulsions for construction, maintenance, and preventive maintenance applications. The purpose of each treatment, the type of emulsion used, and the equipment involved is indicated.

CONSTRUCTION APPLICATIONS

The most common construction applications of asphalt emulsions include the following.

**Tack Coat**

*Purpose*

Tack coats are used in construction applications to provide a good bond between the existing surface and a surface treatment (Figure 1).

*Types of Emulsions Used*

Emulsions used for tack coats can be anionic or cationic, slow-setting emulsions. Tack coats are intended to break quickly (usually within 15 min of application). They have very low application rates (around 0.1 gsy), usually at a dilution rate of one part emulsion to one part water. In order to be able to dilute tack coat emulsions to guard against over application and potential bleed through, these emulsions must be sufficiently stable and therefore are slow setting by category. The very thin film application rate results in a fast break. The intent is to ensure a good bond between pavement layers by allaying any dust on the existing surface and wetting existing oxidized surfaces with a bond coat, without adding excess binder to the surface treatment.

*Equipment*

Tack coats are applied through an asphalt distributor spray bar. Distributors are generally computer controlled to achieve a very accurate application rate.
Emulsion Mixes

Purpose

Emulsion chemistry is such that it enables excellent coating and adhesion of the residual asphalt cement to aggregate surfaces in both dense and open-graded mixes, base stabilization, and stockpiled patching mixes (Figures 2, 3, 4, and 5). Emulsion mixes are economical where small quantities of mix need to be produced at locations remote from hot plants and when ambient temperatures make the use of hot mix problematic.

Types of Emulsion

Slow- and medium-setting, mixing-grade anionic, and cationic emulsions, with and without solvent or adhesion agents, are used for both mixes and base stabilization. Polymer modifiers may be used to control the performance properties of the residual binder.

Equipment

Emulsion mixes can be produced with a wide variety of equipment, either on-site, with in-place pulverizers, mixer/pavers, or at central plants. Both blade- and paver-laid mixes are commonly used. Mixing and laydown equipment is essentially the same as that for hot mix production. Processes vary to accommodate the difference in binders including the following: pavers with a
heated screed are not used; delayed rolling may be implemented to accommodate evaporation of excess moisture; lime stabilization and subsequent sanding of solvent containing mixes may be necessary prior to rolling; and rolling patterns may differ significantly from those used for hot mix.

![FIGURE 2 Emulsion mix mixing table.](image)

![FIGURE 3 Central plant-mixed (pugmill) emulsion mix.](image)
FIGURE 4  Dense-graded emulsion mix, paver laid.

FIGURE 5  Windrow laydown, paver-laid emulsion mix.
Penetrating Prime

Traditionally penetrating primes were cutback asphalts. With increased knowledge of the chemistry of emulsions and control over the breaking and setting characteristics, solventless emulsions are successfully being used as penetrating primes on compacted base courses to seal and prime the surface prior to surface treatments to ensure adequate bond or as an application for dust abatement.

Types of Emulsions

Specially formulated penetrating grade, slow-setting cationic and anionic emulsions are used and are designated AEP (asphalt emulsion prime) or PEP (penetrating emulsion prime, generally dilute). Some emulsions for prime coats may still contain low levels of solvents.

Equipment

Standard, computer-controlled asphalt distributor trucks are used to apply penetrating primes.

PAVEMENT MAINTENANCE APPLICATIONS

Scrub Seals

Purpose

Scrub seals are an effective surface treatment for oxidized or distressed pavements (Figure 6). Scrub seals function by sealing fine cracks prior to application of surface chips or by creating a mastic seal on distressed pavements.

Type of Emulsion

Emulsions for scrub seals may be anionic or cationic, with or without rejuvenating agents and polymer modifiers. Emulsions for scrub seals should be formulated to give adequate time and stability to enable scrubbing of the emulsion into the existing surface prior to chip placement and, when necessary, scrubbing of the chip and emulsion into a distressed pavement.

Equipment

Scrub brooms are added to conventional chip seal equipment for scrub seal application (Figure 7). Primary scrub brooms are designed to force emulsion (generally polymer modified) into microcracks in the pavement surface. Secondary scrub brooms designed to force the emulsion–chip blend into fatigue cracks in a distressed pavement may be used also. Technology in design of scrub brooms ensures filling of cracks and uniform application of binder and chip across pavement cross-section without excess binder at the edges of pavement (Figure 8).
FIGURE 6  Scrub seal application.

FIGURE 7  Fatigue cracks sealed with scrub broom before chipping.
Chip Seals

Purpose

Chip seals are an effective maintenance tool for restoring a wearing course to a pavement. As a preventive maintenance tool, chip sealing prevents ingress of moisture into a pavement or base course and can prevent deterioration due to oxidative aging of a pavement.

Type of Emulsion

Emulsions for chip sealing include anionic, cationic, rejuvenating, polymer-modified, and high float formulations. Chip seal binders do not generally contain solvents but some, such as high floats, have a provision for solvent content, as required, to wet chips and ensure adhesion.

Because many different geologic types and gradations of cover aggregate are used for chip sealing (single size, graded, hard, porous) the emulsion should be selected to accommodate the aggregate in a performance system.

Equipment

Chip sealing utilizes computer controlled asphalt distributor trucks, chip spreaders designed and calibrated to deliver accurate quantities of chip, pneumatic rollers, and brooms for removal of excess chip (Figures 9, 10, 11). Steel wheeled rollers may be used on multiple application chip seals to “rack-in” aggregate.
FIGURE 9 Chip spreader.

FIGURE 10 Pneumatic roller.
Slurry Seals

Purpose

Slurry seals are fine aggregate emulsion mixes that can provide a smooth to moderately textured surface for low-speed, low-traffic volume streets and roads. Slurry seals cure quickly and have the advantage over chip seals of being water-based systems that produce no dust or loose chip during resurfacing. Slurry seals can produce smooth, aesthetically pleasing surface textures similar to hot mix in a very thin (<3/8 in.) application (Figure 12).

Type of Emulsion

Slurry seal technology has advanced over the past 40 years from slow-setting systems using anionic emulsions. These systems were dependent on atmospheric conditions for adequate curing by evaporation before the surface could be opened to traffic. Current slurry seal technology provides for very rapid cure systems based on the use of cationic emulsions with and without polymer modification. Slurry technology derives its success from joint development of appropriate emulsions, equipment and additive systems, which combine with well-defined aggregate characteristics to ensure production of a controlled cure mix which resists raveling.
Equipment

Sophisticated slurry machines are on-grade traveling production plants that provide storage and mixing capability for aggregate, emulsion binder, water for consistency control and additives, which may be used for control of breaking and setting characteristics. Slurry machines include a pull-along laydown box for application of the slurry to the roadway (Figure 13). Laydown boxes are equipped with augers to ensure uniform mixing and application and to prevent premature breaking of the mix prior to placement.

Microsurfacing

Purpose

Microsurfacing is state of the art resurfacing of pavements with a thin layer emulsion mix designed to withstand heavy traffic. Like slurry sealing, microsurfacing produces no dust or loose chip. Microsurfacing design enables rapid cure of the surface regardless of the depth of placement and is therefore an excellent treatment for rutted or irregular surfaces.

Types of Emulsion

Microsurfacing emulsions are specially formulated cationic emulsions designed to work with a specific aggregate in a performance mix composition. The emulsion formulation is tailored to the aggregate characteristics to produce a mix which must comply with stringent specifications.
designed to ensure against rutting, raveling, bleeding, or premature aging. Microsurfacing emulsions are highly polymer modified.

**Equipment**

Microsurfacing machines are sophisticated travel plants designed to store and mix the aggregate, emulsion, mix water and additives for breaking control. Microsurfacing machines generally have twin shaft mixing chambers specially designed to eliminate dead spots associated with a pugmill. Laydown boxes also have augers for uniform mixing and application. Special boxes have been designed for rut-filling prior to full-width resurfacing (Figures 13, 14, 15, and 16).

![Augered laydown box on microsurfacing machine.](image)

**FIGURE 13** Augered laydown box on microsurfacing machine.

![Rut-filling application, (a) before and (b) after.](image)

**FIGURE 14** Rut-filling application, (a) before and (b) after.
FIGURE 15 Rut-filling box on microsurfacing machine.

FIGURE 16 Rut-filling application of microsurfacing.
MULTIPLE APPLICATION SURFACE TREATMENTS

Double and triple chip seals are commonly used for new construction sealing in rural areas. In addition to these multiple seals, the following multiple application seals are also frequently used.

**Cape Seals**

*Purpose*

Cape seals consist of an application of slurry seal or microsurfacing placed over a chip sealed surface. The chip seal is placed to ensure sealing and waterproofing of the existing surface. The slurry or microseal is placed over the chip seal to eliminate the risks associated with loose chips as well as to establish the desired surface texture.

*Types of Emulsion*

Emulsions for the chip seal portion of cape seals are the same as for regular chip seals. Slurry or microemulsion are most always cationic and generally polymer modified.

*Equipment*

Equipment for both chip and slurry or micro portions of a Cape Seal are the same as for the individual treatments.

**Cape Scrub Seals**

*Purpose*

Cape scrub seals are cape seals where the polymer-modified emulsion has been scrubbed into the existing distressed surface prior to chip and slurry or microsealing (Figure 17).

*Types of Emulsion*

Emulsions for each of the applications are the same varieties as those used for the individual applications.

*Equipment*

The equipment used for cape scrub seals is the same as that for cape seals with the addition of the emulsion scrub broom used before applying chip.
Ultrathin Bonded Wearing Course

Purpose

An ultrathin bonded wearing course is an application of an asphalt emulsion immediately covered by a thin layer of hot mix (Figure 18). The emulsion is effectively drawn up into the hot mix to form a strong cohesive bond with both the pavement and the hot mix.

Types of Emulsion

Emulsions for ultrathin bonded wearing courses are mostly cationic polymer-modified emulsion formulations.

Equipment

Equipment for this surface treatment is a specially modified paver equipped with an emulsion spray system which places the emulsion on the pavement surface just before the hot mix screed.
PREVENTIVE MAINTENANCE APPLICATIONS

Fog Seals

Purpose

Light applications of anionic or cationic, dilute emulsions, with and without rejuvenating agents and polymer modifiers are applied routinely to pavement surfaces as a preventive or corrective maintenance tool. Fog seals may be applied to virtually any asphalt surface treatment, hot mix or emulsion mix (Figure 19). Fog seals are the most cost-effective preventive maintenance tool and should be considered for routine maintenance programs (Figure 20).
Types of Emulsions

There are numerous anionic and cationic emulsion formulations with and without rejuvenating agents and/or polymer modifiers for use in fog sealing. To minimize the temporary reduction in skid resistance which results immediately after fog seals are applied, light sanding may be carried out (Figure 21).

Equipment

Equipment for application of fog seals are computer-controlled asphalt emulsion distributors. Because of reduction in skid resistance which is aggravated by over application of emulsion, equipment should be accurately calibrated. Sand spreaders may be required if a sand bond breaker is desired to minimize loss of skid resistance.
Recycled Asphalt Pavement Mixes

Purpose

Both new construction and reconstruction are possible utilizing recycled asphalt pavement (RAP) mix technology. Mixes composed of graded RAP millings and state of the art emulsion binders can produce mix properties equal to those of hot mix in dense, gap, and open-graded mixes. These mixes can be produced more economically than hot mix.

Types of Emulsions

Mixing grade emulsions, both anionic and cationic, with and without solvent, are used in RAP mixes. Emulsions may contain rejuvenating agents or polymer modifiers and adhesion agents. Emulsion chemistry is responsible for immediate coating and subsequent cohesive strength development. Residual binder properties determine long term performance.

Equipment

Equipment for processing and placement of RAP mixes is essentially the same as that for producing emulsion mixes from virgin materials. A wide variety of crushing, sizing, mixing, laydown, and compaction equipment is used.

New construction mixes (placed on compacted base) are generally on-site mixed and hauled to grade for paver laying (Figures 22 and 23).

Reconstruction of existing pavements is generally more economical using cold-in-place recycling trains consisting of sizing, crushing, mixing, placement, and compaction equipment on grade (Figure 24).
FIGURE 22 On-site mixing of RAP emulsion mix.

FIGURE 23 Central plant mix, paver-laid RAP mix.
RAP Millings in Slurry Surfacing

Purpose

RAP millings, when properly screened and graded, provide a cost effective aggregate for slurry surfacing (Figure 25).

Types of Emulsion

Primarily cationic mixing grade emulsions are used in RAP slurry mixes. These emulsion slurry mixes are designed for compliance with all standard slurry mix performance requirements.

Equipment

RAP slurry mixes are placed with standard slurry mixing and application equipment.

SUMMARY

Asphalts in their emulsified form are used in a wide range of applications for construction, maintenance and preventive maintenance treatments. Development of technologies utilizing asphalt emulsions are a product of cooperation among emulsion manufacturers, equipment manufacturers and contracting companies.
The advantages of low-temperature, low-volatile emission application without the safety issues of hot asphalt make emulsions the preferred material in many applications. Asphalt emulsion usage will certainly increase for the above reasons as well as due to efficiencies in use, which will increase with rising fuel and energy costs.

REFERENCE

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The National Academy of Sciences is a private, nonprofit, self-perpetuating society of distinguished scholars engaged in scientific and engineering research, dedicated to the furtherance of science and technology and to their use for the general welfare. On the authority of the charter granted to it by the Congress in 1863, the Academy has a mandate that requires it to advise the federal government on scientific and technical matters. Dr. Ralph J. Cicerone is president of the National Academy of Sciences.

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