



SECTION 2 CHEMISTRY

Many types of emulsion products are used in our daily lives. Mayonnaise, latex paint, and ice cream are some of the more common emulsions. In each case, certain mechanical and chemical processes are involved to combine two or more materials that will not mix under normal conditions. An entire scientific field is devoted to the study of emulsification. Just as an understanding of how an engine works isn't necessary to operate an automobile, neither do you have to understand complex emulsion chemistry to build a good pavement with an asphalt emulsion. The key is to select the right emulsion for the aggregate and construction system involved. Throughout this text when the term "emulsion." is used it is intended to mean "asphalt emulsion."

2.1 Composition of Asphalt Emulsions

An asphalt emulsion consists of three basic ingredients: asphalt, water, and an emulsifying agent. On some occasions, the emulsion may contain other additives, such as stabilizers, coating improvers, anti-strips, or break control agents.

It is well known that water and asphalt will not mix, except under carefully controlled conditions using highly specialized equipment and chemical additives. The blending of asphalt and water is the same as an auto mechanic trying to wash grease from his hands with only water. Only with a detergent or soapy agent can grease be successfully removed. The soap particles surround the globules of grease, break the surface tension that holds them, and allow them to be washed away.

Some of the same physical and chemical principles apply in the formulation, production, and use of asphalt emulsions. The object is to make a stable dispersion of the asphalt cement in water — stable enough for pumping, prolonged storage, and mixing. Furthermore, the emulsion should "break" quickly after contact with aggregate in a mixer or after spraying on the roadbed — "breaking" is the separation of the water from the asphalt. Upon curing, the residual asphalt retains all of the adhesion, durability, and water-resistance of the asphalt cement from which it was produced.

2.2 Asphalt Emulsion Classification

Asphalt emulsions are classified into three categories: anionic, cationic, and nonionic. In practice, the first two types are more widely used in roadway construction and maintenance. Nonionics may become more important as emulsion technology advances. The anionic and cationic classes refer to the electrical charges surrounding the asphalt particles. This identification system stems from a basic law of electricity — like charges repel one another and unlike charges attract.

When two poles (an anode and a cathode) are immersed in a liquid and an electric current is passed through, the anode becomes positively charged and the cathode be-



comes negatively charged. If a current is passed through an emulsion containing negatively charged particles of asphalt, they will migrate to the anode. Hence, the emulsion is referred to as anionic. Conversely, positively charged asphalt particles will move to the cathode and the emulsion is known as cationic. With nonionic emulsions, the asphalt particles are neutral and do not migrate to either pole.

Emulsions are further classified on the basis of how quickly the asphalt droplets will coalesce; (i.e., revert to asphalt cement). The terms RS, MS, SS and QS have been adopted to simplify and standardize this classification. They are relative terms only and mean rapid-setting, medium-setting, slow-setting and quick-setting. The tendency to coalesce is closely related to the speed with which an emulsion will become unstable and break after contacting the surface of an aggregate. An RS emulsion has little or no ability to mix with an aggregate, an NIS emulsion is expected to mix with coarse but not fine aggregate, and SS and QS emulsions are designed to mix with fine aggregate, with the QS expected to break more quickly than the SS.

Emulsions are further identified by a series of numbers and letters related to viscosity of the emulsions and hardness of the base asphalt cements. The letter “C” in front of the emulsion type denotes cationic. The absence of the “C” denotes anionic in **American Society for Testing and Materials** (ASTM) and **American Association of State Highway and Transportation Officials** (AASHTO) specifications. For example, RS-1 is anionic and CRS-1 is cationic.

The numbers in the classification indicate the relative viscosity of the emulsion. For example, an MS-2 is more viscous than an MS-1. The “h” that follows certain grades simply means that harder base asphalt is used. An “s” means that softer base asphalt is used.

The “HF” preceding some of the anionic grades indicates high-float, as measured by the float test. Highfloat emulsions have a gel quality, imparted by the addition of certain chemicals, that permits a thicker asphalt film on the aggregate particles and prevents drain off of asphalt from the aggregate. These grades are used primarily for cold and hot plant mixes, seal coats and road mixes.

ASTM and AASHTO have developed standard specifications for these grades of emulsion:



Table 2-1 Grades of Emulsion

Asphalt Emulsion	Cationic Asphalt Emulsion
(ASTM D977, AASHTO M140)	(ASTM D2397, AASHTO M208)
RS-1	CRS-1
RS-2	CRS-2
HFRS-2	—
MS-1	—
MS-2	CMS-2
MS-2h	CMS-2h
HFMS-1	—
HFMS-2	—
HFMS-2h	—
HFMS-2s	—
SS-1	CSS-1
SS-1h	CSS-1h

Most producers may not stock all grades of emulsion. As well, many states have their own specifications that do not follow ASTM or AASHTO guidelines for naming emulsions. Communication and planning between user and producer helps facilitate service and supply of a given grade.

Quick-setting emulsions have been developed for slurry seals. Cationic quick set (CQS) emulsions are widely used for their versatility with a wide range of aggregates and rapid setting characteristics. Several states use CQS and QS emulsion specifications for slurry seal applications. These specifications are similar to ASTM and AASHTO CSS-1h and SS-1h requirements except that the cement mixing requirement is waived.

Micro-surfacing uses an emulsion often referred to as CSS-1h-p. As with quick set emulsions, microsurfacing emulsions are required to meet ASTM and AASHTO CSS-1h requirements with the exception of the cement mixing test. In addition, a minimum polymer content normally is specified as 3% of solids based on the weight of the asphalt in the emulsion. This addition enhances the high temperature performance of the asphalt and permits application of micro-surfacing in wheel ruts and other areas where multiple stone depths are required.

The expanding use of polymer modified asphalts has contributed a whole new family of emulsion grades. Adding one letter (usually P, S or L) to the end of the grade (e.g., HFRS-2P) normally designates modified emulsions.

Cationic emulsion specifications (ASTM D 2397, AASHTO M 208) permit solvent in some grades but restrict the amount. Some user agencies specify an additional cationic sand-mixing grade designated CMS-2s that contains more solvent than other cationic grades.

The general uses of asphalt emulsion are given in [Table 5-1 General Uses of Asphalt Emulsion](#) and are discussed in detail later in this publication.

2.3 Variables Affecting Quality and Performance



There are many factors that affect the production, storage, use, and performance of an asphalt emulsion. It would be hard to single out any one as being the most significant. Variables having a significant effect include:

- Chemical properties of the base asphalt cement
- Hardness and quantity of the base asphalt cement
- Asphalt particle size in the emulsion
- Type and concentration of the emulsifying agent
- Manufacturing conditions such as temperature, pressure, and shear
- Ionic charge on the emulsion particles
- Order of addition of the ingredients
- Type of equipment used in manufacturing the emulsion
- Properties of the emulsifying agent
- Addition of chemical modifiers or polymers
- Water quality (hardness)

These factors can be varied to suit the available aggregates or construction conditions. It is always advisable to consult the emulsion supplier with respect to a particular asphalt-aggregate combination, as there are few rules that apply under all conditions.

2.4 Emulsion Ingredients

An examination of the three main constituents — asphalt, water, and emulsifier — is essential to an understanding of why asphalt emulsions work as they do.

2.4.1 Asphalt

Asphalt cement is the basic ingredient of asphalt emulsion and, in most cases it makes up from 50 to 75 percent of the emulsion. Asphalt chemistry is a complex subject, and there is no need to examine all the properties of asphalt cement. Some properties of the asphalt cement do significantly affect the finished emulsion. There is not an exact correlation, however, between the properties and the ease with which the asphalt can be emulsified. Although hardness of base asphalt cements may vary, most emulsions are made with asphalts in the 60-250 penetration range. On occasion, climatic conditions may require a harder or softer base asphalt. In any case, chemical compatibility of the emulsifying agent with the asphalt cement is essential for production of a stable emulsion.

The principal source of asphalt is the refining of crude petroleum. Asphalt is primarily composed of large hydrocarbon molecules, and its chemical composition is diverse. The colloidal makeup of the asphalt depends on the chemical nature and percentage of the hydrocarbon molecules and their relationship to each other. The varying chemical and physical characteristics of asphalt, therefore, are primarily due to inherent variations in crude oil sources and refining practices. Of course, the properties of the asphalt cement will have an effect on the performance of the residual asphalt on the road.



The complex interaction of the different molecules makes it almost impossible to predict accurately the behavior of an asphalt to be emulsified. For this reason, constant quality control is maintained on emulsion production. Each emulsion manufacturer has its own formulations and production techniques. They have been developed to achieve optimum results with the asphalt cement and emulsifying chemicals that are used.

2.4.2 Water

The second ingredient in an asphalt emulsion is water. Its contribution to the desired properties of the finished product cannot be minimized. Water may contain minerals or other matter that affect the production of stable asphalt emulsions. Accordingly, water considered suitable for drinking might not be suitable for asphalt emulsions.

Water found in nature may be unsuitable because of impurities, either in solution or colloidal suspension. Of particular concern is the presence of calcium and magnesium ions. These ions benefit the formation of a stable cationic emulsion. In fact calcium chloride is often added to cationic emulsions to enhance storage stability. These same ions, however, can be harmful in anionic emulsions. That is because water-insoluble calcium and magnesium salts (often referred to as “soap scum” are formed in the reaction with water soluble sodium and potassium salts normally used as emulsifiers. In a like manner, carbonate and bicarbonate anions can help stabilize an anionic emulsion because of their buffering effect, but they can destabilize cationic emulsions by reacting with water soluble amine hydrochloride emulsifiers.

Water containing particulate matter should not be used in emulsion production. It can be especially harmful in cationic emulsions. The usually negatively charged particles quickly absorb the cationic emulsifying agents, destabilizing the emulsion. The use of impure water may result in an imbalance of the emulsion components that can adversely affect performance or cause premature breaking.

2.4.3 Emulsifying Agents

Asphalt emulsion properties greatly depend on the chemical used as the emulsifier. The emulsifier is a surface-active agent, or a surfactant. The emulsifier keeps the asphalt droplets in stable suspension and controls the breaking time. It is also the determining factor in the classification of the emulsion as anionic, cationic, or nonionic.

In the early days of asphalt emulsion production, materials such as ox-blood, clays, and soaps were used as emulsifying agents. As emulsion demand increased, more efficient emulsifying agents were found. Many chemical emulsifiers are now commercially available.

The most common anionic emulsifiers are acids, which are wood-product derivatives such as tall oils, rosins, and lignins. Anionic emulsifiers are saponified (turned into soap) by reacting with sodium hydroxide or potassium hydroxide.

Most cationic emulsifiers are fatty amines (e.g., diamines, imidazolines, and amidoamines). The amines are converted into soap by reacting with acid, usually hydrochloric. Another type of emulsifying agent, fatty quaternary ammonium salts, is used to pro-

duce cationic emulsions. They are water soluble salts and do not require the addition of acid. They are stable, effective cationic emulsifiers.

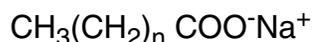


By broad definition, surface active chemicals are water soluble substances whose presence in solution markedly changes the properties of the solvent and the surfaces they contact. They are categorized by the way they dissociate or ionize in water. Structurally they possess a molecular balance of a long lipophilic (oil-loving), hydrocarbon tail and a polar, hydrophilic (water-loving) head. Surfactants are adsorbed at the interface between liquids and gases or liquid and solid phases. They tend to concentrate at the interface such that the hydrophilic groups orient themselves towards the more polar phase, and the lipophilic groups towards the less polar phase. The surfactant molecule or ion acts as a bridge between two phases.

Basically, there are three types of surfactants that are classified according to their dissociation characteristics in water:

1. **Anionic Surfactants** — Where the electrovalent and polar hydrocarbon group is part of the negatively charged ion, when the compound ionizes:

ANIONIC



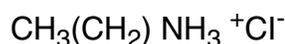
2. **Nonionic Surfactants** — Where the hydrophilic group is covalent and polar, and which dissolves without ionization:

NONIONIC



3. **Cationic Surfactants** — Where the electrovalent and polar hydrocarbon group is part of the positively charged ion when the compound ionizes:

CATIONIC



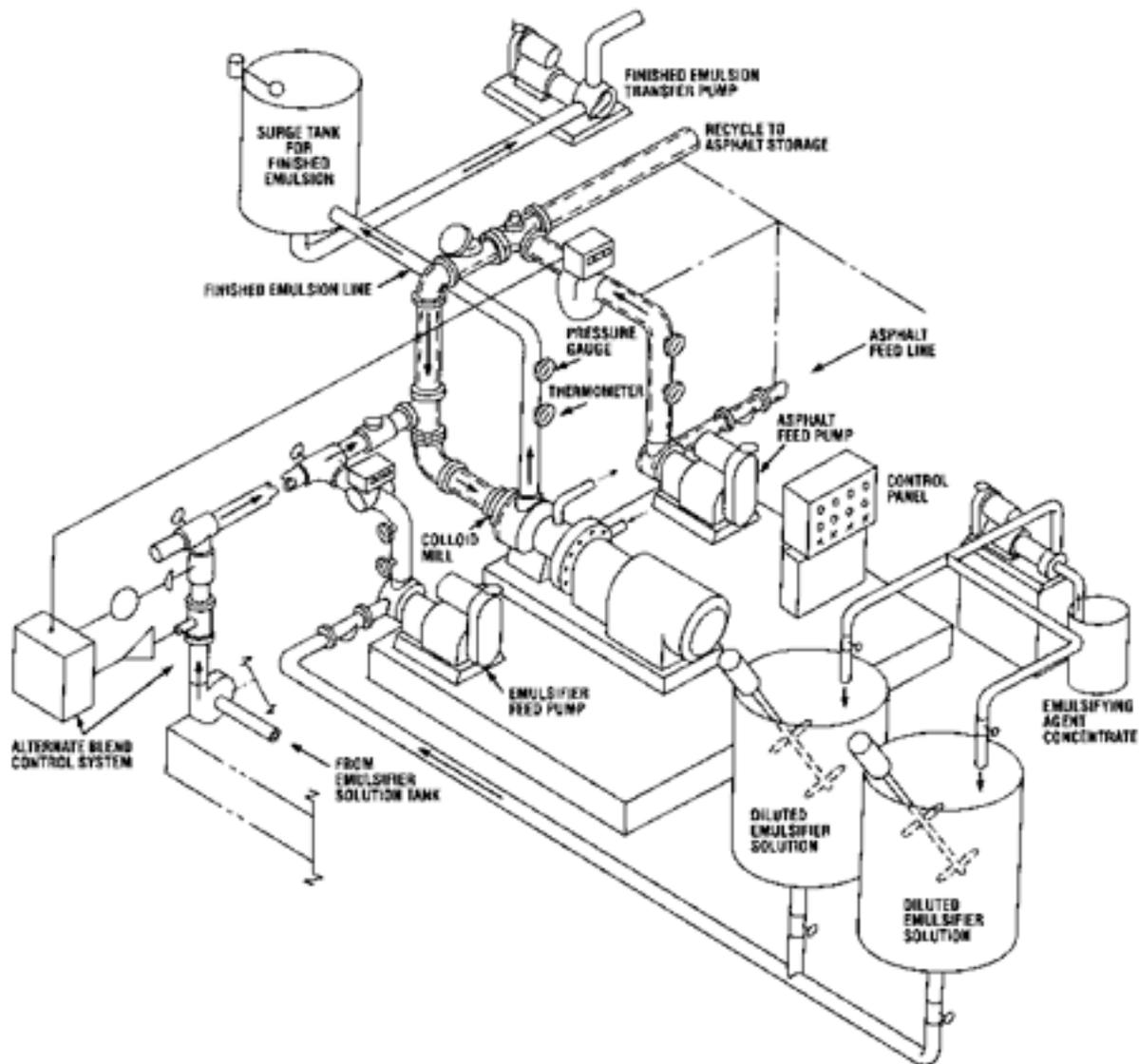


Figure 2-1 Diagram of an Asphalt Emulsion Manufacturing Plant

The emulsifier is the single most important component in any asphalt emulsion formulation. To be an effective emulsifier for asphalt, a surfactant must be water soluble and possess a proper balance between the hydrophilic and lipophilic properties. The emulsifier, used in combination with an acceptable asphalt, good quality water and adequate mechanical input, is the major factor in emulsification, emulsion stability and ultimate field application performance.

Each manufacturer has its own procedure for using surfactants in asphalt emulsion production. In most cases, the surfactant is combined with the water before introduction into the colloid mill. However, it may be combined with the asphalt cement just before it goes into the colloid mill.

2.5 Producing the Emulsion



2.5.1 Emulsifying Equipment

The basic equipment to prepare an emulsion includes a high-speed, high-shear mechanical device (usually a colloid mill) to divide the asphalt into tiny droplets. A schematic diagram of a typical asphalt emulsion manufacturing plant is shown in Figure 2.4-1. Also needed are an emulsifier solution tank, heated asphalt tank, pumps, and flow-metering gauges.

The colloid mill has a high-speed rotor that revolves at 17 - 100 Hz (1,000 - 6,000 rpm) with mill clearance settings in the range of about 0.25 - 0.50 mm (0.01 - 0.02 in.). Typically asphalt emulsions have droplet sizes smaller than the diameter of a human hair, or about 0.001 - 0.010 mm (0.00004 - 0.0004 in.). Particle size analyzers are commonly used to characterize emulsion quality. Asphalt droplet sizes depend upon the mechanical energy density imparted by the mill.

Separate pumps are used to meter asphalt and the emulsifier solution into the colloid mill. Because the emulsifier solution can be highly corrosive, it may be necessary to use equipment made of corrosion resistant materials.

2.5.2 The Emulsifying Process

In the emulsification process, heated asphalt is fed into the colloid mill where it is divided into tiny droplets. At the same time, water containing the emulsifying agent is fed into the colloid mill. The asphalt entering the colloid mill is heated to a low viscosity, and the water temperature is also adjusted to optimize emulsification. These temperatures vary and depend upon the emulsification traits of the asphalt cement and the compatibility between the asphalt and the emulsifying agent. Extremely high asphalt temperatures are not used because the temperature of the emulsion leaving the mill must be below the boiling point of water, unless a heat exchanger is used to cool the emulsion. The emulsion is then usually pumped into bulk storage tanks. These tanks may be equipped with mechanical agitation to keep the emulsion uniformly blended.

The method of adding the emulsifier to the water varies according to the manufacturer's procedure. Some emulsifiers, such as amines, must be mixed and reacted with an acid to be water soluble. Others, such as acids, must be mixed and reacted with an alkali to be water soluble. Emulsifier mixing is typically done in a batch mixing tank. The emulsifier is introduced into warm water containing acid or alkali and agitated until completely dissolved.

Asphalt and emulsifier solution must be proportioned accurately. This is normally done with flow meters, but monitoring the temperature of each phase and the mill discharge can also control the proportioning. If temperature regulation is used, the desired outlet temperature of the finished emulsion is calculated from the various emulsion ingredients and then used to control the asphalt content percentage.

Asphalt particle size is a vital factor in making a stable emulsion. A microscopic photograph of a typical emulsion (**Figure 2-2 Relative Sizes and Distribution of Asphalt Particles in an Emulsion**) reveals these average particle sizes:



Smaller than 0.001 mm (1 μ m)	28 percent
0.001-0.005 mm (1-5 μ m)	57 percent
0.005-0-010 mm (5-10 μ m)	.5 percent

These microscopic-sized asphalt droplets are dispersed in water in the presence of the chemical surface active emulsifier (surfactant). The surfactant causes a change in the surface tension at the contact area between the asphalt droplets and the surrounding water, and this allows the asphalt to remain in a suspended state. The asphalt particles, all having a similar electrical charge, repel each other, which aids in keeping them suspended.

2.6 Breaking and Curing

2.6.1 Breaking

If the asphalt emulsion is to perform its ultimate function as a binder, the water must separate from the asphalt phase and evaporate. This separation is called “breaking.” For surface treatments and seals, emulsions are formulated to break chemically upon contact with a foreign substance such as aggregate or a pavement surface. When using anionic and cationic rapid-setting and medium-setting emulsions, the initial placement of the asphalt emulsion droplets on the aggregate develops through electrochemical phenomena.

For slow-setting emulsions, the mechanism is water evaporation. For dense mixtures, more time is needed to allow for mixing and placement. Therefore, emulsions used for mixtures are formulated for delayed breaking. A rapid-set emulsion will have a short breaking time (within one to five minutes after being applied), whereas a medium- or slow-set material may take considerably longer.

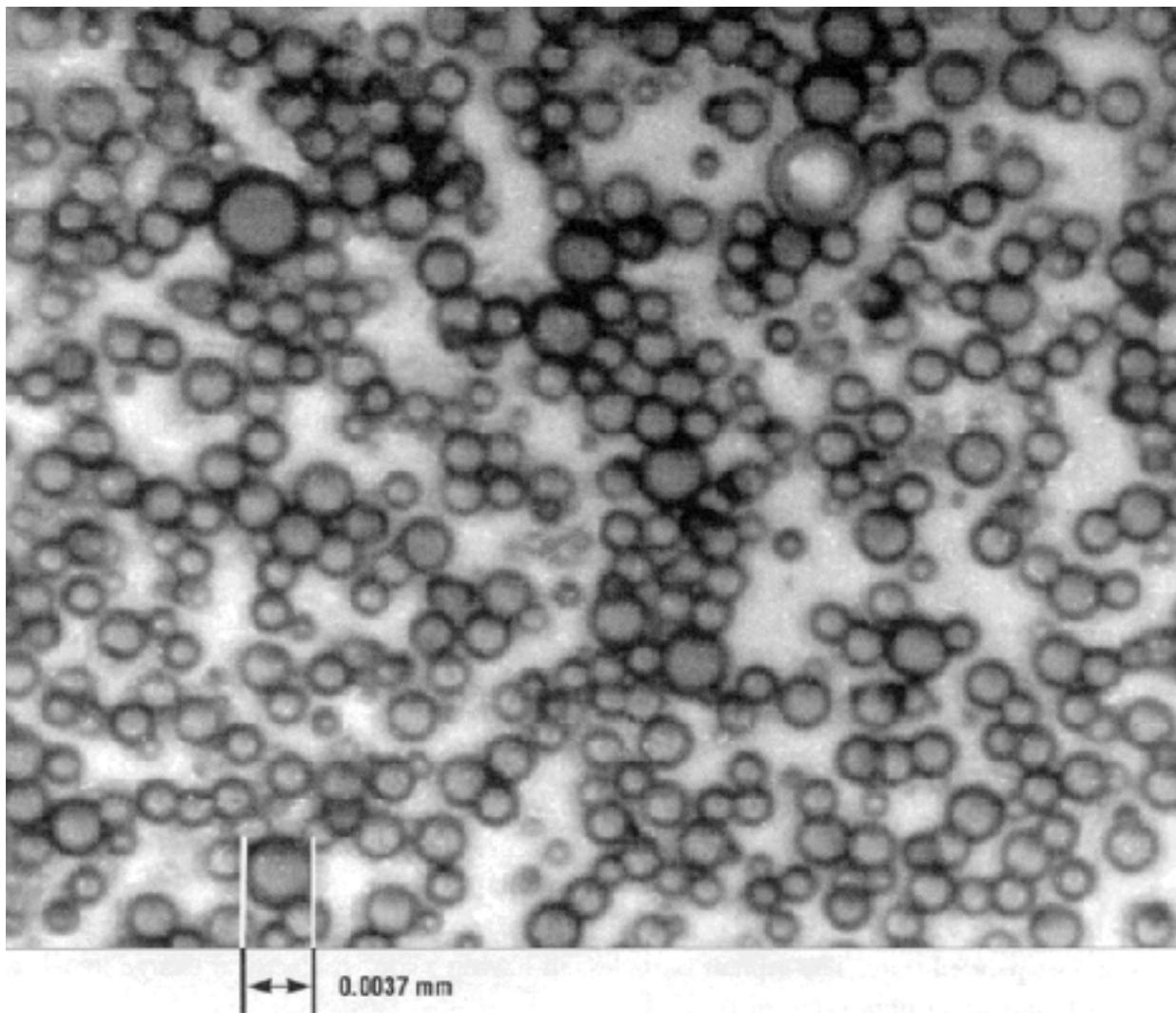


Figure 2-2 Relative Sizes and Distribution of Asphalt Particles in an Emulsion

The specific type and concentration of emulsifying agent primarily control the rate of breaking. However other factors, listed below, also play an important role in breaking the emulsion. In order to achieve optimum results, it is necessary to control all of these factors to meet the specific requirements of the field use of the asphalt emulsion. The supplier should have more information regarding the optimum use of its emulsions.

2.6.2 Curing

Curing involves the development of the mechanical properties of the asphalt cement. The end result is a continuous cohesive film that holds the aggregate in place with a strong adhesive bond. For this to happen, the water must completely evaporate, and the asphalt emulsion particles have to coalesce and bond to the aggregate. The water is removed by evaporation, by pressure (rolling), and by absorption into the aggregate. Water evaporation can be fairly rapid under favorable weather conditions, but high hu-

midity, low temperatures, or rainfall soon after application can deter proper curing. When medium setting and slow setting grades are used for paving mixes, the use of slightly damp aggregates facilitates the mixing and coating process. The development of strength in the SS types depends mainly on evaporation and absorption.



Mixing grade emulsions usually contain some petroleum solvent to aid in the mixing and coating process. During curing, some of this solvent evaporates. There has been recent emphasis on the development of solventless mixing grade emulsions. For example, the cure of micro-surfacing is rapid enough to allow traffic within one hour.

2.6.3 Factors Affecting Breaking and Curing

Some of the factors affecting breaking and curing rates of asphalt emulsions include:

- **Water Absorption** — A rough-textured, porous aggregate speeds the setting time by absorbing water from the emulsion.
- **Aggregate Moisture Content** — While wet aggregate may facilitate coating, it tends to slow the curing process by increasing the amount of time needed for evaporation.
- **Weather Conditions** — Temperature, humidity, and wind velocity all have a bearing on water evaporation rate, emulsifier migration and water release characteristics. While breaking usually occurs more quickly at warmer temperatures, that is not always the case. Hot weather can cause skin formation on chip seals, trapping water and delaying curing. Some chemical formulations have also recently been developed to break rapidly at cool temperatures.
- **Mechanical Forces** — Roller pressure and, to a limited extent slow moving traffic, forces the water from the mix and helps attain mix cohesion, cure and stability.
- **Surface Area** — Greater aggregate surface area, particularly excessive fines or dirty aggregate, accelerates the breaking of the emulsion.
- **Surface Chemistry** — Intensity of the aggregate surface charge, in combination with the intensity of emulsifier charge, can impact setting rate, particularly for cationic emulsions. Calcium and magnesium ions on the aggregate surface can react with and destabilize certain anionic emulsifiers, accelerating setting.
- **Emulsion and Aggregate Temperature** — Breaking is retarded when emulsion and aggregate temperatures are low. This is particularly evident in micro-surfacing.
- **Type and Amount of Emulsifier** — The surfactant used in the manufacture of the emulsion determines the breaking characteristics of seal coat and mixing grade emulsions.

These factors must be considered in determining working time after the emulsion has been sprayed or mixed with the aggregate in the field. The emulsion supplier is the best source of information.

