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# 11 Bitumen Emulsions

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11.1 INTRODUCTION

Even if most of us are not familiar with bitumen, we all know the “black” roads on which we drive every day. The majority of road surfaces are black because the binding agent used to manufacture the surfacing course is bitumen mixed with crushed rock aggregate. Road surfaces can also come in gray to white color, in which case another alternative binder has been used: Portland cement concrete.

Bitumen is the residue from crude oil distillation. It is a black visco-elastic solid at ambient temperature that turns into a viscous liquid as temperature increases. Bitumen presents unique adhesive and waterproofing properties that make this material particularly ideal to bind together aggregate.

To prepare an asphalt mix bitumen can simply be brought to a high enough temperature (usually above 150 °C) to reach a sufficiently low viscosity to be directly applied to dried and preheated aggregate material. Among its numerous properties, bitumen can also be emulsified using specific surfactants. Mixing can then be carried out at ambient temperature and these techniques do not require that the materials be first dried.

Road surfacing was invented centuries ago, possibly by the Romans who used large stone slabs to build permanent roads. The Roman road-construction method was abandoned at the end of the Roman Empire and very little improvement took place during the following centuries in terms of road technology. Roads were either not surfaced, surfaced with wood or rock cobbles in urban areas, or “surfaced” with hand crushed rock usually bound with soil in rural areas until the end of the 19th century. It is only at the end of the 19th century and in the early 20th century that the first applications of a binder, initially coal tar rather than bitumen, was used to stabilize crushed rock and slag aggregate. Road history literature refers to an early use of tar in the city of Auch, France, to surface the “Place Sallinis” in 1854 (1) and a patent was placed on the application of tar to stabilize slag by Purnell Hooley around 1901 in the UK (2). At the time, coal tar was sprayed hot onto a crushed rock mat to bind the stones together. The use of bitumen in road surfacing is more recent and related to the parallel development of the petroleum and car industries at the beginning of the 20th century.

References to the use of anionic bitumen emulsions for dust control go back to 1904 in the Ardennes race track in France. As cars became popular, road dust generated by vehicles became a real nuisance and the need for even and lasting wearing surfaces became more and

more urgent. Despite an early start, emulsion remained secondary to hot sprayed tar and bitumen. One hypothesis to explain the development of hot processes over emulsions is that tar was initially more abundant, particularly in Europe. As tar cannot be emulsified, it was used in hot process and the transition from tar to bitumen may have given preference to the hot process over emulsions.

Tar, then combinations of tar and bitumen, was sprayed on roads throughout the Western world until the Second World War. A new breakthrough in the U.S.A. took place at that time: the invention of pre-mixed bituminous concrete (asphalt) where special equipment had been developed to blend in a controlled way crushed aggregate with hot bitumen. This approach was a real success and led to the generalized use of bituminous concrete in the U.S.A. and everywhere in the world where car and truck traffic developed.

Meanwhile, emulsions, initially almost entirely of anionic type, have continued to progress. Hugh Alan MacKay filed a patent in 1922 on bitumen emulsion (3). This patent is regarded as the start of emulsion technology. It is reported in the literature (1) that by the end of 1926, the production of emulsion in the U.K., Germany, Austria, Denmark, and India reached 150,000 tons, which is not negligible. France was also an important producer with reference to 6000 tons of emulsion produced in 1925. Then, in 1951, cationic emulsions appeared, opening the emulsion market to high performance processes, in the sense that anionic emulsions break by evaporation of water, which takes time, while cationic emulsions present a chemical breaking behavior leading to much shorter delays between construction and trafficking as well as higher performance.

Aside from the advantage of working at ambient temperature, the interest of emulsifying bitumen is that, as a result of the surfactants used, bitumen maintains its adhesive properties toward minerals in the presence of water. This is particularly interesting in road construction, as crushed rock aggregates are stock piled in the open air and are therefore moist. Using bitumen in emulsion form eliminates the need to dry the aggregate, an essential step when working with molten bitumen. Drying aggregate requires a complex and energy intensive plant.

This chapter will first review briefly the nature of bitumen, the specificity of surfactants available to manufacture bitumen emulsion and the emulsification techniques. We will then cover important issues such as bitumen emulsion stability and breaking mechanisms in the different type of construction applications. Focus will be on road construction where most of the current emulsion developments are taking place.

## 11.2 BITUMEN

Bitumen is a semi-solid material, which can be produced from certain crude oils by distillation. It can also be found in nature as “natural asphalt.” It consists of a mixture of hydrocarbons of different sizes containing small amounts of heteroatoms like sulfur, nitrogen, and oxygen, as well as traces of metals like vanadium and nickel. Bitumen behaves as a visco-elastic thermoplastic solid at ambient temperature and turns into a viscous liquid at high temperature. It presents unique adhesive and waterproofing properties which make it ideal to manufacture asphalt for road construction as well as a wide range of industrial application, from waterproofing in construction to sound dampening in the car industry.

The term “bitumen” is not completely unambiguous since it has been given different meanings in different parts of the world. In Europe the term “bitumen” is defined as above, while in Canada, for example, the term “bitumen” is used for heavy crude oils. In the U.S.A. the term “asphalt” is used instead of bitumen. Sometimes bitumen is confused with tar, which is a product of completely different origin. Tar is produced by dry distillation of coal or wood.

The most common process for production of bitumen is by distillation under vacuum of properly selected crude oils. There are, however, a limited number of crude oils which permit

direct distillation to proper bitumen grades suitable for production of road asphalt. Although the reserves of such crude oils is very large worldwide, they are not primarily produced since they contain too small amounts of fuel, which is the most important and profitable product for refiners. A vacuum residue which is not directly suitable as a bitumen binder may be further processed by extraction or oxidation. The primary product from an extraction process using propane as solvent is heavy oil. There will also be a hard residue of bitumen remaining after the extraction process that is sometimes referred to as propane bitumen. Propane bitumen may be diluted with a distillate to give bitumen fulfilling the specification for a road binder. A process sometimes used to increase the stiffness of bitumen is oxidation. This can be achieved by blowing air through hot bitumen. The oxidation makes the bitumen harder at high temperatures while partly maintaining the soft properties at low temperatures.

The true chemical nature of bitumen is not completely known. Most books and papers on bitumen chemistry teach that bitumen is a colloidal dispersion of asphaltenes in maltenes. The dispersion is stabilized with resins. This statement is based on the well-known fact that when bitumen is diluted with certain hydrocarbon liquids, n-alkanes, a precipitate appears. If the hydrocarbon liquid is n-heptane, the precipitate is called "asphaltenes." It has been proposed that the "asphaltenes" are present in the bitumen in the form of micelles. The first author to introduce this concept was Nelensteyn in 1924 (4). The model was later refined by Pfeiffer and Saal (5). Other models, which question the existence of micelles, have also been proposed, for example by Park and Mansoori (6), and later as a result from the SHRP development program in the U.S.A. (7). Recent research has shown that the asphaltenes are soluble in the maltenes and thus no micelles can exist in the bitumen (8). To further investigate the chemistry of bitumen the maltenes are separated into different fractions using chromatographic techniques. A large number of different procedures have been described, for example gel permeation chromatography (GPC), ion exchange chromatography (IEC), high pressure liquid chromatography (HPLC), and others (9). The most common procedure is probably the SARA separation, which divides bitumen into four generic groups. In the first step the asphaltenes are precipitated by n-heptane, followed by separation of the maltenes with respect to polarity in three fractions: saturates, aromatics, and resins (10).

The functional properties of bitumen are usually related to its use as binder in asphalt for roads. Thus the most common properties are related to the rheology of bitumen. Since the road construction area is very conservative and bitumen has been used for about 100 years, most tests are empirical and have been used for a long time. Two of the most common tests are penetration at 25 °C and softening point Ring&Ball. The penetration gives a measure of the stiffness of the bitumen at most common service temperatures of a road, while the Ring&Ball gives the stiffness close to the highest expected temperature in the road. In Europe bitumens are graded according to their penetration at 25 °C, for example 50/70, where the two numbers give the highest and lowest limit for the particular grade. It is also common, particularly in the U.S.A., to use viscosity gradation based on viscosity at 60 °C. Bitumen is, however, a visco-elastic material with a complex rheology and thus can not be completely described by simple penetration and softening point. The development of modern and reliable rheometers, for example the dynamic shear rheometer (DSR), has made it possible to describe the full rheology of bitumen.

### 11.3 EMULSIFIERS

Most types of emulsifier have been used for emulsification of bitumen. In the early days anionic emulsifiers were the most common, but since the 1950s cationic emulsifiers have taken over more and more. One of the advantages of cationic emulsifiers is their good adhesion to acidic stone materials like granite, which also are good construction materials in roads. Another advantage is

the “active breaking” against the surface of acidic stones. The anionic emulsions have maintained some importance for certain industrial applications as well as for road construction using basic stones like limestone. Non-ionic emulsions and clay emulsions have occasionally been used for certain applications but are currently not produced in any substantial amounts.

### 11.3.1 ANIONIC EMULSIFIERS

During the early days of bitumen emulsions, anionic emulsifiers were the most common types. In principle, any type of long chain fatty acid or mixture of fatty acids can be used for emulsification of bitumen. The first type of emulsifier, which was reported for emulsification of bitumen, is oleic acid (Figure 11.1) potassium or sodium soap. In later years they were replaced by rosin soaps, for example Vinsol<sup>®</sup> resin and tall oil soaps. Tall oil is distilled from a byproduct of the paper pulp industry making use of the so-called “sulfate process.” The main constituents of tall oil are oleic acid, linoleic acid, and abietic acid. In 1960 about 95% of all bitumen emulsions used in the U.S.A. was of the anionic type (11).

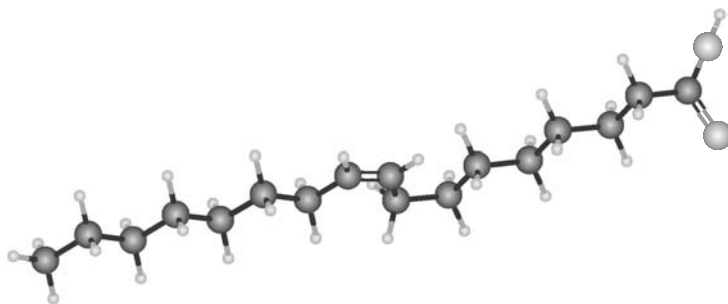
In spite of the dominance for cationic emulsifiers for bitumen many new anionic emulsifiers, tailor-made for bitumen, are available on the market. They are mainly derivatives of the same byproducts from the paper pulp industry, tall oil, tall oil rosin or lignin, as used in the early days.

A typical formulation of an anionic bitumen emulsion is:

Bitumen 160/220 65%  
Water 34.1%  
Tall oil (crude) 0.4%  
Vinsol<sup>®</sup> resin 0.4%  
Sodium hydroxide 0.09%

In the first manufacturing step the fatty acid is dispersed in water followed by addition of sodium hydroxide (or potassium hydroxide). Hot bitumen is then added to the soap solution under vigorous mixing. In full-scale production a colloid mill is usually used.

One disadvantage with carboxylic acid soaps is that most calcium salts of carboxylic fatty acids are insoluble in water. Since calcium ions are very common in tap water or water from natural wells, it is very important to keep careful control of the water quality when working with anionic emulsions based on fatty acids. Calcium salts of fatty acids remain in the soap solution as lumps, which might block filters and pipes.



**FIGURE 11.1** Oleic acid. Black is carbon, light gray is oxygen atoms.

One way of overcoming the disadvantage with calcium sensitivity is to use anionic emulsifier based on sulfonic acids or sulfates. These emulsifiers are very effective for emulsification of bitumen and they do not form insoluble calcium salts.

### 11.3.2 CATIONIC EMULSIFIERS

During the last 30 years the cationic emulsifiers have dominated in bitumen emulsions for road applications. The main advantage is the good adhesion to acidic stone materials which usually is preferred for road constructions due to their good mechanical properties.

A large variety of commercially available cationic emulsifiers are suitable for emulsification of bitumen. The most common is of the general type “fatty diamine.” In these emulsifiers the hydrocarbon part originates from fatty acids where the acid part has been replaced by some type of diamine or polyamine. The alkyl part commonly originates from fatty acids from tallow, which are more or less hydrogenated to increase their stability. The mixture of fatty acids varies slightly depending on origin of the tallow but a common figure for the hydrogenated tallow mixture is:

Tetradecanoic acid (myristic acid) 4%  
 Hexadecanoic acid (palmitic acid) 30%  
 Octadecanoic acid (stearic acid) 60%  
*cis*-9-Octadecanoic acid (oleic acid) 2%

Also the hydrocarbon part of tall oil and lignin from the paper and pulp industry are used to produce cationic emulsifiers. Tall oil also consists of a mixture of fatty acids while lignin has a completely different structure.

Perhaps the most common emulsifier for bitumen emulsification is *N*-tallow alkyltrimethylenediamine (Figure 11.2) but a variety of emulsifiers exist with different types of amino groups. For example, tallow amine ethoxylates, tallow polyamines, tallow amido amines, quaternized tallow diamines, imidazolines. Although alkyl chains originating from tallow are the most common for bitumen emulsifiers there are also a large variety of synthetic alkyl chains used to manufacture emulsifiers for bitumen.

A common formulation of a cationic bitumen emulsion is:

Water 33.6%  
*N*-tallow-1,3-propanediamine 0.2%  
 Hydrochloric acid (32%) 0.2%  
 Bitumen 66%

Commercial emulsifiers for bitumen often consist of mixtures of more than one emulsifier to give the optimal properties for a particular application. Recently, automatic plants where bitumen

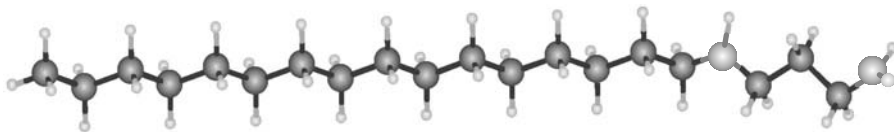


FIGURE 11.2 *N*-hexadecanoic-1,3-propanediamine. Black is carbon, light gray is nitrogen atoms.

emulsions are prepared in one continuous process have been developed. This requires emulsifiers which can be pumped at ambient temperature and thus the development of liquid emulsifiers has been important. This can be achieved by oxyalkylation of the *N*-tallow-diamines. One example is oxypropylation with a polypropylenoxide containing 1 to 4 propylenoxid units (12).

Before the fatty amines can be used as emulsifier they have to be acidified (except the quaternary amines). This is usually done with hydrochloric acid, making a soap solution in water. Sometimes other acids have been used, such as acetic acid or phosphoric acid. The latter acid should be used with care because, generally, fatty-amine phosphates are insoluble in water. The emulsion is produced by pumping the soap solution together with hot bitumen in a colloid mill.

### 11.3.3 NON-IONIC EMULSIFIERS

Non-ionic emulsifiers can also be used for emulsification of bitumen. These emulsifiers become less immobilized when in contact with soil and stone material which make the emulsions very stable. They have thus frequently been used in applications where the bitumen emulsion is supposed to penetrate through soil, dust, and even clay. The advantage is that the bitumen makes the soil less susceptible for water.

Typical emulsifiers used for bitumen belong to the group of alkyl ethoxylates. The previous most common emulsifier from this group is the nonyl phenol ethoxylates. This emulsifier has been suspected, however, of being harmful for the aquatic environment and is not recommended for bitumen emulsification any more, although up to the end of 2004 there has been no legislation restricting its use.

Non-ionic emulsifiers have also been used for emulsification of very heavy crude oils (Orimulsion) to facilitate pumping, storing, and transportation of the crude oil. These crude oils have such a high viscosity that they cannot be handled with conventional equipment for crude oil transportation (pipelines and tankers), not even at higher temperature. As emulsions they can be used, however, as fuel for industrial boilers without any further refining.

### 11.3.4 CLAY STABILIZERS

Bitumen can also be emulsified using colloidal clays as stabilizers. Most common are clays of the montmorillonite, kaolinite, and attapulgite type. One of the most common clays of the montmorillonite type is bentonite.

The most effective bitumen emulsifiers are clays which are readily wet in water and disperse as very fine particles ( $<1 \mu\text{m}$ ) having colloidal properties and which adhere to the surface of the bitumen with a contact angle less than  $90^\circ$ . If enough clay particles attach to the surface, the surface charge of the clay will create a repulsive energy, which prevents coalescence of the bitumen drops.

Clay emulsions are mainly used for house building purposes as protective coatings for roofs, metals, and masonry. They have also been used as adhesives for laminates and tiles as well as flooring mastics.

## 11.4 MANUFACTURING AND HANDLING

Bitumen emulsions are generally of the oil-in-water type of emulsions; thus most emulsifiers for bitumen emulsification are more soluble in the water phase than in the bitumen. Therefore it would be an advantage for the emulsification process if the emulsifier was added to the bitumen phase, since the migration of the emulsifier into the water phase will help the emulsification

process. In the production of bitumen emulsions, however, the bitumen is usually at temperatures between 120 °C and 180 °C to keep the viscosity at a suitable level for emulsification. At these temperatures most emulsifiers are not stable, or at least have a very short lifetime. Thus the common practice in bitumen emulsification is to mix the emulsifier into the water phase. The demand on thermal stability is then less, but it still requires the emulsifier to be stable up to 100 °C for several days.

### 11.4.1 COLLOID MILLS

The general process of emulsification involves controlled mixing of water, emulsifier, and bitumen. With the aid of high shear action, the bitumen is broken up into minute particles and dispersed in the water phase. The dispersion may be accomplished by use of simple mixers, centrifugal pumps, homogenizers, or colloid mills. The selection of the type of equipment is dependent on the expected volume of manufacture as well as plant investment considerations. For the manufacture of road emulsions, colloid mills are most commonly used. A colloid mill consists of a rapidly revolving conical disc, or rotor, which fits closely in a stationary part known as a stator. The bitumen, water, and emulsifier are forced through the narrow clearance between the rotor and the stator thus effecting dispersion (Figure 11.3). The capacity is usually between 10 and 40 ton/h.

The equipment for manufacturing anionic emulsions and cationic emulsions is principally very similar, so for the simplicity of the following discussion we will focus on cationic emulsions.

The first step in the emulsification process is to acidify the emulsifier. Most diamines and particularly *N*-tallow alkyltrimethylendiamine are supplied as slightly basic products. It is a paste-like semi-solid at room temperature. The *N*-tallow alkyltrimethylendiamine is dispersed in warm water followed by addition of hydrochloric acid until a pH of 2 to 4 is reached. By this process the diamine is protonized and the amine functionalities will carry a positive charge. In this state the *N*-tallow alkyltrimethylendiamine is a very effective emulsifier for bitumen. The manufacture

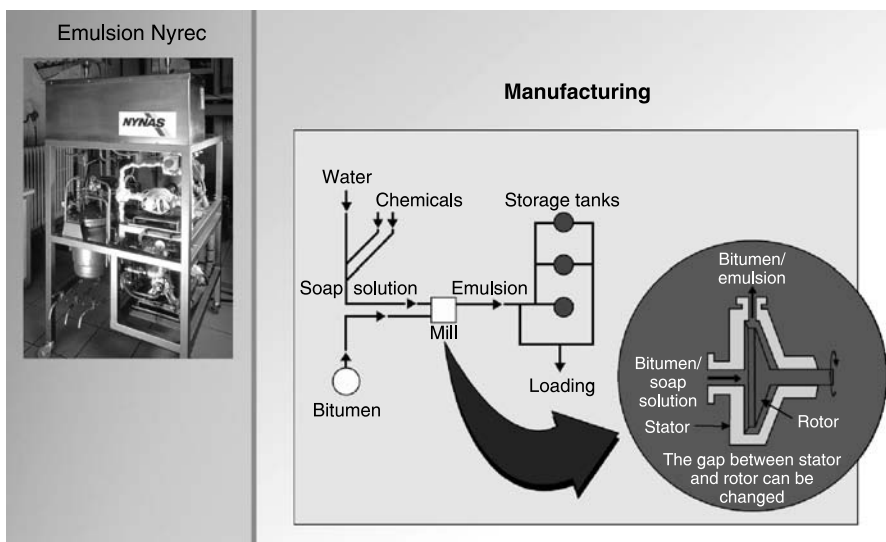


FIGURE 11.3 Schematic of a bitumen emulsion plant. Left: Laboratory plant.



of the soap solution is usually a batch process while the production of the emulsion in the colloid mill preferentially is made continuously. Therefore several batches of soap solution have to be made in parallel to maintain a continuous production in the mill.

During the last 20 years the development has been toward fully continuous emulsification plants, including the acidification process. The emulsifier, the water, and the acid are then mixed in line to make the soap solution. Sometimes a small container is located on the line before the mill to give enough time for the emulsifier to react with the acid, but this reaction is fast and no extensive reaction time is necessary. The key is to have access to special liquid emulsifiers or to install a heating system to handle the emulsifiers in a liquid state. Modern emulsion plants are built as fully mobile plants that can easily be transported in containers and be set up close to the work site.

Another important factor to take into consideration is that bitumen is too viscous at ambient temperature to be emulsified. Bitumen must therefore be brought to high temperature (above 100 °C) to reach a sufficiently low viscosity for emulsification to be possible. It is commonly agreed that the bitumen must be at a temperature corresponding to a viscosity of 200 cP or less for emulsification. The temperature of the bitumen and the aqueous phase should therefore be adjusted so that the resulting emulsion temperature does not exceed 100 °C. In some cases when hard bitumen (pen 50 and below) and polymer modified bitumen are emulsified it is not possible to keep the resulting temperature below 100 °C. If this is the case, a cooler must be fitted on the output of the emulsion mill to bring the emulsion below the boiling point of water.

Calculation of expected emulsion temperature can be achieved using the following equation:

$$(T_b - T_e) \cdot SH_b \cdot b = (T_e - T_w) \cdot SH_w \cdot w$$

where

$T_b$	=	bitumen temperature
$T_w$	=	water temperature
$T_e$	=	emulsion temperature
$b$	=	bitumen content, %
$w$	=	water content, %
$SH_b$	=	specific heat of bitumen (1.9 kJ/kg K)
$SH_w$	=	specific heat of water (4.2 kJ/kg K)

Note that the milling operation in itself generates an emulsion temperature increase of approximately 10 °C.

Sometimes it is desirable to add minor amounts (<2%) of light petroleum naphtha (kerosene) to the emulsion. The kerosene improves the wetting to stone surfaces as well as improves the coalescence once the emulsion is broken. The kerosene could either be added by an extra feeding line into the bitumen line before emulsification, or alternatively it could be added directly to the finished emulsion under gentle mixing.

#### 11.4.2 OTHER INDUSTRIAL EMULSIFICATION METHODS

Colloid mills are not ideal tools, however. Many emulsion formulators would very much like to be in full control of their emulsion particle size, which is far from being the case with colloid mills. Some mills have a possibility of adjusting rotor speed or rotor/stator gap supposedly to help control emulsion particle size. However, all colloid mills seem to produce polydisperse bitumen emulsions with particle size ranging from 1 to 100 microns. Several properties, in

particular viscosity and breaking characteristics, are affected by the particle size distribution of the emulsion and work is under way to develop potential methods to achieve monodispersed emulsions of adjustable median diameter (13).

Although homogenizers in association with a standard colloid mill would be an option the authors are not aware at the time this book was written that such a device has been used industrially for production of bitumen emulsions.

The only industrial alternative to the colloid mill seems to be the so-called SMEP process for static mixer emulsification process (14). This emulsification method has been applied at industrial scale in Europe. It is claimed that it is possible to reach monodispersed emulsions of controlled median diameter with this method.

### **11.4.3 STABILITY**

Bitumen emulsion stability is a critical issue due to the high viscosity of bitumen at ambient temperature. Once a bitumen emulsion is broken it is impossible to bring it back to the emulsified state again. An emulsion sufficiently unstable to cause coalescence and to break will cause major problems in the industry: storage tanks, pipes, pumps, and filter blockage which can be cleaned only by melting back the bitumen to liquid stage, i.e., above 150 °C; or through solvents. On the other hand, the aim of the bitumen is to act as glue between stones, which only can be achieved once the emulsion is broken. It is therefore necessary to formulate the emulsion to provide stability for storage and transportation but sufficiently unstable so it breaks once in the right place in the application.

#### **11.4.3.1 Different Aspects of Bitumen Emulsion Stability**

As many as five types of bitumen emulsion stability are recognized: chemical, storage, freezing, mechanical, and mixing. Some of these types are related to each other, whereas often there is no relationship between others. In this discussion we will focus on storage stability which is mainly due to sedimentation or creaming, and chemical stability which is more related to true breaking and coalescence of the emulsion. In the first case it is possible to restore the emulsion to its original state by simple stirring, but in the second case it is necessary to re-emulsify it.

Another aspect of stability is the emulsion's ability to break on contact with stone materials. Depending upon the type of application it can be desirable to have a very quick breaking, for example with surface dressing, slurry surfacing, or various types of sealing. In other applications it is desirable to have a very slow breaking, for example with mixing grade asphalt stored for later use for patching or pot hole filling. It is, however, common to all emulsions that once they are in place on the road they should break and cure as quickly as possible.

#### **11.4.3.2 Storage Stability**

Storage stability relates to "static" storage of the emulsion. Storage stability is usually solved in the industry by maintaining the emulsion under slow agitation in the storage tank. Agitation may, however, promote breaking if too intense. Bitumen emulsions can not always be stored in tanks with agitation, but are sometimes supplied in drums to smaller work sites. In these cases it is important to select emulsions with good storage stability or to have a procedure to stir or roll the drums before using the emulsion.

### 11.4.3.3 Properties that Control Storage Stability

#### 11.4.3.3.1 Bitumen Density

Creaming and sedimentation are mostly related to the density difference between the bitumen (from 0.95 to 1.10) and the water. Since the density of bitumen and water are very close and since the thermal expansion coefficients are different for water and bitumen it is often possible to find a temperature where the density is practically identical. This temperature is usually found around 70 °C. If the density of the bitumen is very high it can be an advantage to increase the density of the water by adding a salt, for example calcium chloride. It should be noted that the high temperature and high salt content decrease the chemical stability of the emulsion. High temperature facilitates coalescence by decreasing the viscosity of the bitumen while high salt content decreases the electrical double layer which decreases the repulsive force between bitumen particles.

#### 11.4.3.3.2 Bitumen Content

Bitumen emulsions containing high concentrations of bitumen (67 to 70%) generally have fewer problems with storage stability than emulsions with low bitumen content (40 to 60%). The reason is that in the 70% emulsions so much space is filled by the bitumen phase that there is practically no room for sedimentation or creaming to take place. For the 50% emulsions, however, the distance between the bitumen drops is so large that only Brownian movements can keep the emulsion stable, and these movements are too weak for particles larger than 10 µm; thus it is almost impossible to avoid sedimentation or creaming. Unfortunately, it is very common to supply 50% emulsions in drums which are stored at ambient temperature and thus severe separation always has to be expected, so these emulsions should be carefully stirred before use.

#### 11.4.3.3.3 Freezing

Freezing generally destroys oil-in-water emulsions, and this is also the case with bitumen emulsions. They should never be stored at temperatures below the freezing point of the continuous phase. A bitumen emulsion which is suspected of having been frozen should not be used for road applications. If, for some reason, bitumen emulsions are to be used below the freezing point, antifreeze liquids should be added. Examples are ethanol or ethylene glycol. None of these is soluble in bitumen and therefore will not destroy the bitumen properties.

#### 11.4.3.3.4 Maximum Particle Size

If the emulsion contains particles which are larger than approximately 10 µm it becomes more sensitive to mechanical stress. This results in increased risk for breaking during pumping, transport, and stirring of the emulsion. The expected storage time for such emulsions is also shorter due to Oswald ripening that consumes the smallest particles which coalesce into the largest ones.

### 11.4.3.4 Chemical Stability

With chemical stability we refer to the stability against breaking and coalescence. There are several factors which determine the chemical stability. Some of these are related to the formulation such as emulsifier type and amount, pH, and bitumen content. Other factors are related to handling of the emulsion, such as mechanical stress, pumping, stirring, and transportation. Another aspect

of emulsion stability is stability in contact with stone material. This is further discussed in Section 11.6.

#### *11.4.3.4.1 Emulsifier Type and Content*

Surfactant type and concentration in the water phase is a very important factor in bitumen emulsion stability. Generally speaking an increase of emulsifier content and an increase in acidity (lower pH) increase the stability of the emulsion. This statement is true within reasonable limits, such as an emulsifier content between 0.1 and 3% and from pH 2 to 5, but it is not generally valid. Some cationic emulsifiers are of the quarternary amines type. These emulsifiers do not lose their effect as emulsifiers when the pH is changed, and are thus not sensitive to pH changes.

It is usually easy to make very stable bitumen emulsions which can be stored for months and even years but many bitumen emulsions are formulated to have certain breaking characteristics when coming into contact with stone material, and are thus formulated to be on the borderline of stability. The selection of emulsifier type and amount is usually done on an empirical basis, with respect to the type of bitumen, type of emulsion mill, and type of stone material expected.

#### *11.4.3.4.2 Mixing of Bitumen Emulsions*

Mixing of bitumen emulsions made with emulsifiers of opposite charge, for example anionic and cationic, is not possible. Emulsions made with identical emulsifier can generally be mixed. In more unclear cases, mixing should be avoided since the exact effect of mixing can not easily be predicted. One possibility of using emulsion mixing is to have emulsions with the same type of emulsifier but different grades of bitumen. By mixing the emulsions, any bitumen grade between the two can be achieved in the final application when the emulsion is fully broken and the bitumen droplets have coalesced. Another advantage is the lower stiffness and the better coating of the stones in a cold asphalt mix prepared with mixed emulsions (15).

## **11.5 PROPERTIES OF BITUMEN EMULSIONS**

Properties of bitumen emulsions for roads are specified in many standards. Each country usually has a national standard, although there are many similarities among the different countries. It is obvious that the national standardization bodies have to some extent copied each other. In Europe a harmonized standard will soon be launched which will make all national standards in Europe obsolete. Examples of standards on bitumen emulsions are ASTM D-977 in the U.S.A., EN 13808 in Europe and JIS K 2208 in Japan. All standards specify only very basic properties and it is usually not possible to determine from the specification whether the emulsion will perform well in a particular road application or not. The performance as a construction material can only be determined from the properties of the binder as retained after full breaking and coalescence of the emulsion. The most common properties of bitumen emulsions specified are given in Sections 11.5.1 to 11.5.10.

### **11.5.1 CHARGE ON EMULSION PARTICLES**

This is a test to distinguish anionic and cationic emulsions. It is included in most specifications for bitumen emulsions, but is rarely performed in any laboratory. Usually the type of emulsion is known, or as is the case in many countries, only cationic emulsions are used.

### 11.5.2 VISCOSITY

The viscosity of the bitumen emulsion is important for pumping and transportation. In some applications, for example surface dressing, bitumen emulsion is sprayed on the road followed by a thin layer of stone material. In this case the viscosity is critical. It should be low enough to permit even spraying but at the same time high enough to prevent run-off, once it is sprayed on the road.

In most standards the viscosity is determined by some kind of efflux viscometer, for example in the European EN 12846 which makes use of a STV (standard tar viscometer). The value given is an efflux time rather than a viscosity and should more correctly be named pseudoviscosity. It has been proposed that modern rheometers are used to specify the true viscosity of bitumen emulsions. There are, however, problems with the non-Newtonian behavior and further complications due to breaking of the emulsion against metal surfaces in the rheometers which so far have prevented standardization.

The viscosity is mainly controlled by the binder content, but also by type of emulsifier, particle size distribution, and salt content in the bitumen. The latter might give an osmotic effect which will drag water inside the bitumen drops, resulting in expansion of the drops and a decrease in continuous water phase which will be seen as an increase in viscosity (16). The effect could be overcome by adding small amounts of a salt, for example calcium chloride, to the water phase. The increased salt content in the water phase will decrease the osmotic pressure for the water into the bitumen droplets.

### 11.5.3 BREAKING BEHAVIOR

This test is used to classify bitumen emulsions into slow breaking, medium breaking, and fast breaking. Most tests for breaking behavior make use of some kind of mineral filler additive which is added to the emulsion until it breaks. The amount of additive is a measure of the stability. The European specification EN 13075 makes use of standard filler which is added until the emulsion is completely broken. The breaking speed in real applications may, however, be completely different since the reaction against fines varies a lot with different minerals.

### 11.5.4 MIXING STABILITY WITH CEMENT

A special test used for identification of so-called “over stabilized emulsions” is the mixing stability with cement. Since Portland cement is very reactive against most emulsifiers and has very high specific surface area, it breaks most cationic and anionic emulsions immediately. Over-stabilized emulsions are characterized by very high stability and should not break even after mixing with cement. These emulsions are generally formulated with nonionic emulsifiers or sometimes with anionic emulsifiers to make them very stable even in contact with soil and clay. They are mainly used for soil stabilization and to make soil less water sensitive when the soil contains relatively large amounts of clay and fines. The presence of clay also causes very stable emulsions to break.

### 11.5.5 RESIDUE ON A SIEVE

This test is mainly used for quality control. The test determines the amount of bitumen which is present in the emulsion as larger particles or lumps. The test consists of simple pouring of the emulsion through a sieve with relatively low mesh size. The amount of material which is collected on the sieve should not exceed a certain value. In the European specification there are

several options with two mesh sizes (0.500 mm and 0.160 mm) and different levels of acceptance for retained material on the sieve from 0.1 to 0.5%.

A special case of the sieve test is a storage stability test, where the emulsion is stored for several days (usually 7) followed by a second sieve test. If the amount of material collected on the sieve is higher than the specified amount the emulsion is deemed not to be stable enough to sustain storage for a certain time. In this test the collected material is considered to be broken and it is thus not possible to restore the emulsion by simple stirring.

### 11.5.6 SETTLING TENDENCY

In this test the settling or the creaming tendency of bitumen emulsion is determined. The test is part of the European standards and the principle is to hold the emulsion for 7 days in a cylinder and then measure the binder content in the top and bottom of the cylinder. If the binder content has increased in the top part of the cylinder, the emulsion is “creaming,” while an increase of binder content at the bottom of the cylinder indicates a tendency of the emulsion for “sedimentation.” This property is particularly important for emulsions containing less than 60% bitumen and which are stored in drums or tanks without stirring. An emulsion that has settled can usually be restored by careful stirring provided that no breaking has occurred.

### 11.5.7 COATING AND ADHESION

These are two of the very few tests which are related to performance of the bitumen emulsion in road applications. Most coating tests are empirical and make use of a mixing procedure with stone material followed by a visual inspection of the degree of coating. If the inspection takes place after full breaking and curing of the emulsion it is sometimes referred to as adhesion. For practical purpose it is not advisable to specify a coating test with standard stones since the behavior is very much dependent on the mineralogy of the stone. The test should preferably be performed with the local stone material and is consequently more a test of the stone material rather than the emulsion.

### 11.5.8 RECOVERY OF BITUMEN

Strictly speaking this is not a property of the emulsion, but in most standards for bitumen emulsion a process for recovery of the bitumen from the emulsion is included. This is to give the user a standard test to recover the material that gives the functional properties to the finished asphalt. In the European standard EN 13808 two methods have been included. The first method consists of a distillation procedure as specified in ASTM D-244 or EN 1431. In this test the water and solvents, if present, are distilled and collected in such a way that the solvent content can easily be determined. The bitumen content is determined by weighing and the recovered bitumen can also be subjected to further testing. The high temperature used during the distillation (260 °C) may, however, have slightly changed the properties of the binder. Caution should then be applied to the validity of further testing on recovered bitumen. This is particularly important when testing emulsions of polymer modified binders which are more sensitive to high temperatures. When further testing of polymer modified binder is needed the use of a milder test to recover the binder without too much heating should be considered. In EN 13074, the second European method for recovery of binder, the water is evaporated at maximum 50 °C. In this method, a residue of solvent might still remain in the binder, changing its original properties.

### 11.5.9 BINDER CONTENT

A basic property of a bitumen emulsion is the bitumen content. The bitumen content may be calculated based on the result from any of the methods for recovery of bitumen above. If, however, the emulsion contains solvent with high volatility (kerosene) the two methods will give different values. In the U.S.A. it has been decided to use the residue after distillation as the binder content. In Europe it has been decided to consider everything which is not water as “binder content.” Therefore a method for determination of water content according to Dean and Stark has been approved as European standard (EN 1428). Thus if solvent is present in the emulsion it will be considered as part of the binder. In most cases the solvent content is low (<2%) and the difference between the two methods for recovery of binder will be of minor importance for the practitioner.

### 11.5.10 PARTICLE SIZE

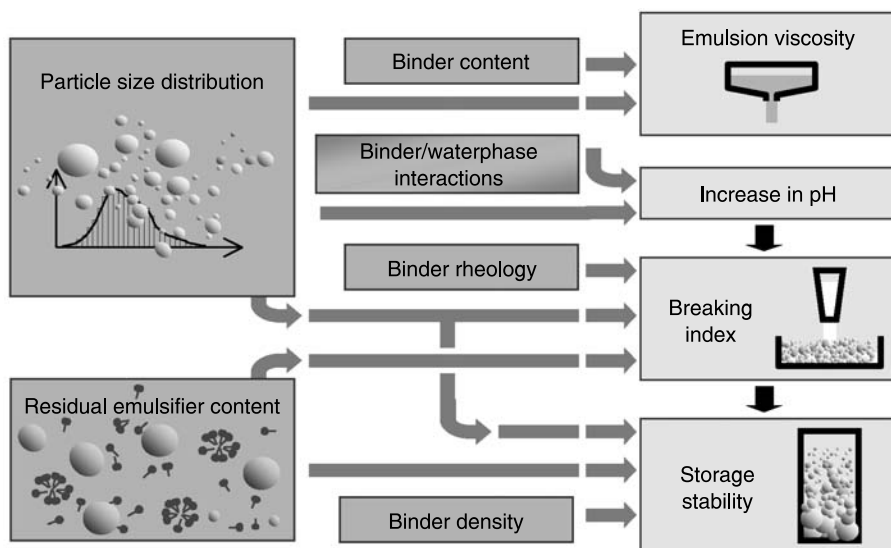
One of the most important factors determining the properties of a bitumen emulsion is the particle size and the size distribution of the bitumen droplets. This is never specified, but many producers of bitumen emulsion include measurement of particle size in their quality control system. The most common technique is laser scattering and many practical commercial instruments are available on the market. Particle size distribution is partly determined by the formulation of the emulsion, but the manufacturing conditions are also of vital importance for the size distribution. Some examples are:

- The temperature difference between bitumen and aqueous phases
- The viscosity of the bitumen
- The gap between the rotor and stator in the emulsion mill
- The rotation speed of the mill
- The contacting configuration between the soap and the bitumen

In fact, it is known that different emulsion mills give products with different properties although identical formulations of bitumen emulsions are applied. An attempt to relate particle size to other properties is illustrated in [Figure 11.4](#) (17).

## 11.6 BREAKING AND ADHESION

The main purpose of bitumen in asphalt is to act as a glue to bind the stones together. The emulsification of bitumen should be considered as a way of transportation of the binder (bitumen) to the right place between the stones in the asphalt. Once the bitumen is in the right place it should separate from the water followed by wetting the stone surface and gluing the stones together. We may call this process the “breaking of the emulsion” although in reality it consists of a number of different processes. It is, however, not enough to make the water separate from the bitumen; we also need a good adhesion to the surface of the stone. This is also a complication since the surface of the stone is generally more hydrophilic than hydrophobic. This means that the affinity for water is higher than the affinity for the bitumen. Thus the full strength of the adhesion between the bitumen and the stone surface will not be achieved until the stone surface is completely dry, which sometimes can take a very long time. Here a proper selection of surfactant could improve the situation, since certain cationic emulsifiers could displace the water from the stone surface and promote good adhesion between the bitumen and the stone. In these aspects



**FIGURE 11.4** Proposed relation between the formulation of a bitumen emulsion and its properties (17).

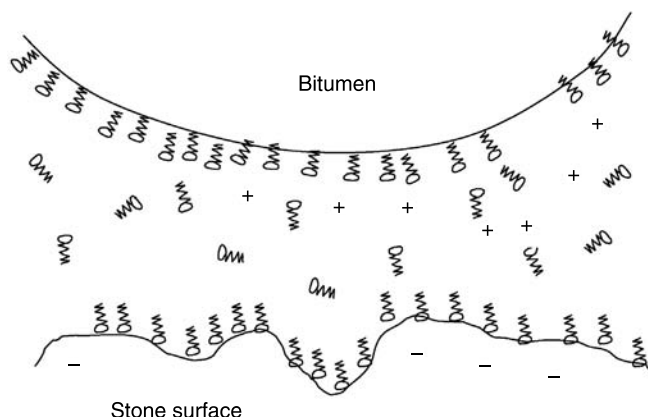
cationic emulsifiers are preferred for acidic stone surfaces, while anionic emulsifiers are preferred for basic stones.

Depending on type of application the desired breaking process is different. In some applications a fast breaking is preferred while in others a delayed process is preferred. The conditions could also be very different, as for example in some applications the stone material could be dry or wet as well as clean or dusty. For example in surface dressing applications (see below) the breaking should be as fast as possible as well as having good adhesion of the stones. In cold asphalt mix applications on the other hand the breaking process must be delayed to permit enough time for transportation, laying, and compaction after the aggregates have been mixed with the bitumen emulsion. After compaction the breaking should take place as quickly as possible to achieve good strength in the new road to be able to sustain traffic as soon as possible, preferably within hours rather than days.

The breaking mechanism is mainly of two types, breaking under influence of added stone material or breaking due to evaporation of the water (drying). In the case of pH sensitive emulsifiers it is also possible to cause breaking by changing the pH of the emulsion. This will be further discussed under “breaking additives.” It is preferred to select an emulsifier that adsorbs strongly to the stone surface because then the breaking will mainly be controlled by the addition of the aggregate. The breaking mechanism itself is rather complicated and can be divided into different steps. The exact nature of these steps is not completely known in detail but basically they consist of the following:

- Destabilization of the emulsion due to adsorption of emulsifiers on the added stone material
- Agglomeration of the emulsion particles forming a solid but nontacky and brittle material (cheesy state)
- Coalescence of the bitumen droplets to give back the tackiness and stiffness of the bitumen
- Complete evaporation of water giving full adhesion to the aggregate surface and full strength of the asphalt





**FIGURE 11.5** Situation when bitumen emulsion has been contacted with stone material.

A hypothetical process for fast breaking bitumen emulsions is illustrated in Figure 11.5. It is assumed that the concentration of emulsifier is below the critical micelle concentration (CMC) in the water phase and that the surface of the stone material is negatively charged. The emulsifiers are adsorbed on the surface of the stone, and consequently if the surface of the stone material is large enough the emulsion becomes destabilized. At the same time the layer of emulsifier sticking to the stone will make the surface hydrophobic, promoting the wetting of the aggregate by the hydrophobic bitumen. At the same time the emulsifier will act as an anti-stripping agent.

If the emulsifier content in the emulsion is increased to a concentration higher than the CMC, the excess emulsifier will form micelles in the water phase. When mixing this type of emulsion with stone material, the excess emulsifier might coat the stones without destabilization of the emulsion. The breaking of the emulsion then becomes much slower and may even not take place until the water has evaporated.

It is evident that the breaking speed is dependent on the amount of emulsifier, but the amount of stone surface is equally important. The aggregates used in road construction are usually crushed stones, which may contain various amounts of fines. The fines have a very high specific surface area (surface per gram) and the breaking will thus be very sensitive to the filler content in the stone material. The third important step in the breaking process is coalescence, which is heavily dependent on the viscosity of the bitumen. At low temperatures the bitumen droplets can be considered more as solids rather than liquids. Under these conditions the coalescence can take a very long time. A common way of improving the coalescence is to add a small amount of light petroleum liquid, for example kerosene. If the coalescence is not complete the binder may stay in a state where full strength has not been achieved (cheesy state) for days and even weeks. When the road is opened for traffic the kneading action will easily make the coalescence complete.

### 11.6.1 BREAKING ADDITIVES

One way of increasing the flexibility of bitumen emulsions is to have good breaking additives to control the breaking rather than to be dependent on the fines in the stone material or evaporation of the water. Due to the different nature of cationic and anionic emulsions, different approaches have to be applied for breaking of the different types of emulsions.

### 11.6.1.1 Anionic Emulsions

Anionic emulsions based on fatty acids can easily be destabilized by adding a salt solution containing a divalent metal ion, for example calcium ions. They will form an insoluble salt with the fatty acid, which will precipitate out of the water phase. This principle has been exploited in systems for waterproofing where the bitumen emulsion and the breaking additive are sprayed on surfaces using specially designed spray guns with two nozzles. One nozzle sprays a polymer modified bitumen emulsion and the other nozzle the breaking agent which usually consists of a water solution of calcium chloride. When the droplets hit a solid wall the emulsion breaks instantly forming a layer of bitumen on the wall and thus a layer up to 1 cm thick can be sprayed in one operation without requiring drying in between. The use of polymer modified bitumen will further improve the quality of the layer.

### 11.6.1.2 Cationic Emulsions

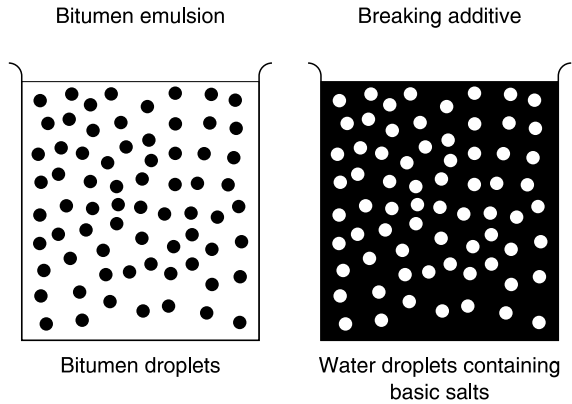
Cationic emulsions may be destabilized by increasing the pH, which usually leads to destabilization and consecutive breaking of the emulsion. The reason for the breaking is that the amine group loses its positive charge and becomes a less effective emulsifier. This technique may be used by spraying an alkaline water solution on top of a bitumen emulsion. The breaking will start, however, on the surface forming a bitumen skin on top of unbroken emulsion. This will prevent further evaporation of water, resulting in a delayed breaking instead of the desired accelerated breaking.

Several techniques have been presented to solve this problem. One solution is to use two spray bars spraying the emulsion and the additive simultaneously when the stones are applied (18). The technique is limited, however, to surface dressings where the bitumen emulsion is sprayed on top of an already existing road. But in cold mix applications the stone material and the emulsion have to be mixed before laying and compaction. In these applications it is very important that the emulsion does not break immediately, since the workability of the mix has to be good enough to permit laying and compaction before breaking takes place. The breaking additive thus has to be given a delayed effect. One solution is to encapsulate the breaking additive, as has been presented in some patents (19–21). Another technique, which has successfully been applied in several road constructions in Sweden, is to emulsify a basic water-soluble material in oil making a W/O emulsion (22–24) (Figure 11.6). If this W/O breaking additive emulsion is added to the O/W bitumen emulsion the situation illustrated in Figure 11.7 is obtained.

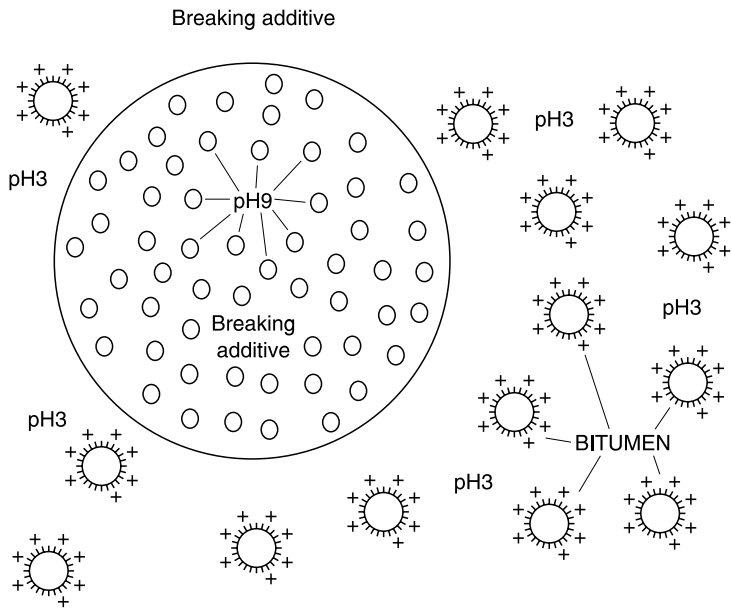
The alkaline breaking additive is dispersed in oil, preventing the alkaline material to neutralize the acid in the bitumen emulsion. After a certain time the breaking additive diffuses into the water phase of the bitumen emulsion causing neutralization of the acid. When the cationic emulsifier loses its positive charge it also loses its ability as emulsifier and the emulsion breaks. The time for breaking is mainly determined by the viscosity of the oil and the agitation of the emulsion.

## 11.7 APPLICATIONS

The use of bitumen emulsions may be divided into two main construction areas: roads and other industrial applications. The largest volumes of bitumen emulsions are by far those used in road applications. It is also in this area that research and development is most intense as a result of environmental constraints towards less solvent, better work environment, and lower energy consumption. The phrase “industrial applications” covers a variety of different applications of which waterproofing can be considered as one of the most important. Road applications using



**FIGURE 11.6** Bitumen O/W emulsion and W/O breaking additive.



**FIGURE 11.7** Bitumen emulsion immediately after addition of breaking additive.

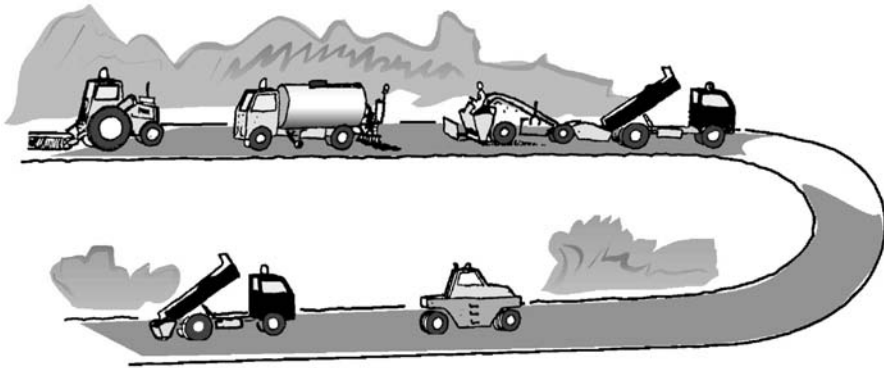
bitumen emulsion can be classified into two main techniques: sprayed applications and cold mix asphalt. There are several basic differences in the requirements of emulsions for spraying and mixing. Spraying emulsions are usually formulated to break rather fast on the road and since they are going to be sprayed, viscosity is also usually an important property. Mixing grade emulsions are usually formulated to be rather stable to permit contact with stone material without premature breaking.

## 11.7.1 SPRAYING TECHNIQUES

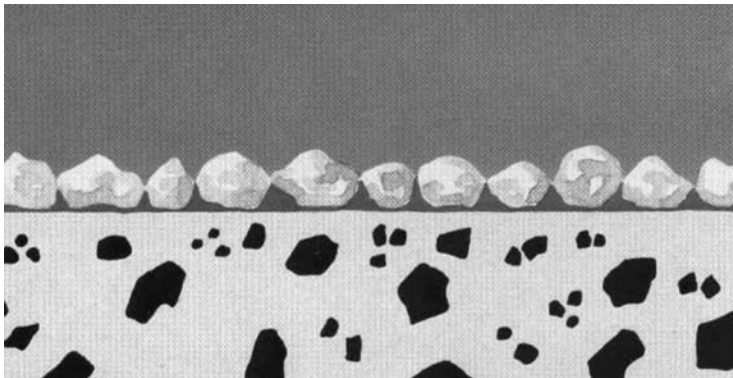
### 11.7.1.1 Surface Dressing

Surface dressing, or chip seal, is a maintenance technique for old roads which can restore the surface by sealing microcracks as well as give the road a new wearing layer. The technique is attractive because many square meters can be laid each day for a relatively low price (Figure 11.8). In principle the technique consists of applying approximately 2 mm film of emulsion on the existing pavement surface which is immediately covered with a layer of crushed rock of selected gradation (Figure 11.9). Grain interlock between aggregate chippings and adhesive effect of bitumen must provide sufficient cohesion to the system to allow traffic directly after construction. The performances expected from the emulsion cover:

- Sufficient emulsion viscosity to avoid emulsion run-off during spraying on sloped surface (road crown, grade).
- Good reactivity, which is a combination of break and adhesion as soon as the emulsion is in contact with the mineral aggregate. Reactivity is a phenomenon occurring before



**FIGURE 11.8** The organization of a surface dressing operation.



**FIGURE 11.9** Cross-section of a single layer surface dressing.

the emulsion has had time to lose water and is related to the adsorption of the emulsifier on the surface of the stones. At this point it is important to note that the emulsion must not break too fast, since there should be enough time to wet the stone before breaking takes place.

- Fast coalescence. It is expected from the emulsion film that it loses water by evaporation quickly. Coalescence and reactivity are the two main phenomena involved in the breaking of the emulsion in this technique.

Emulsions for surface dressing usually have high binder content (68 to 71%) in order to have a high viscosity and a minimum amount of water to evaporate. They are also generally formulated to be very fast breaking. Formulations making use of polymer modified binders are becoming more and more popular and make up a considerable part of the use today.

Surface dressings come in several different variations. Some include double application of emulsion and stone material, sometimes referred to as sandwich technique. In such applications the requirement on high viscosity of the emulsion is not so strong. It is also common to consecutively apply two different gradations of stone material, first large stones, and then smaller stones expected to “lock in” the large stones. This system is sometimes referred to as “racked in system.”

#### 11.7.1.1.1 Evaporation Filtration Test

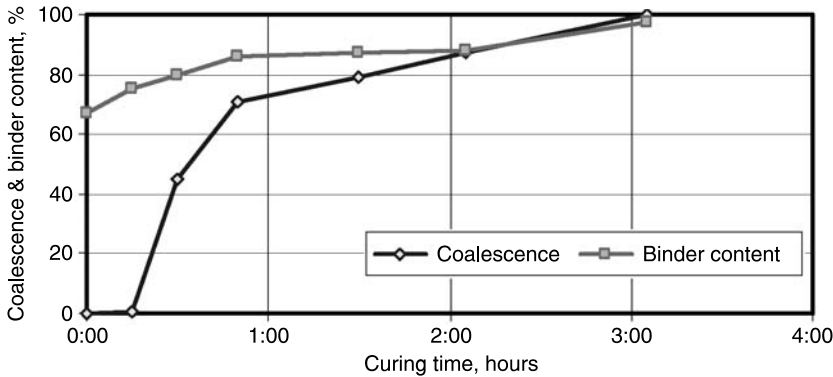
This is a test which has been proven useful for characterization of surface dressing emulsion. In surface dressing applications where a thin film of bitumen emulsion is sprayed on the road and covered with aggregate chipping, two phenomena contribute to the break of the emulsion:

- Break in contact with minerals, referred to as reactivity
- Break due to increasing emulsion binder content as water evaporates until the emulsion becomes unstable and breaks

The evaporation filtration test has been developed to follow the second phenomenon (25). This test follows the evolution with time of thin emulsion films placed in standard dishes. The evaporation rate is obtained by weighing the samples at regular time intervals. Coalescence is estimated by washing the film with soap solution whilst stirring with a glass rod through a 160-micron sieve. Coalesced binder will either adhere to the dish or be retained on the sieve. Noncoalesced emulsion is washed away.

The details of the test are as follows. A complete test requires a total of six samples. Approximately 13.58 g of emulsion is placed in a 100 mm diameter dish (emulsion film thickness 1.5 mm) and placed in an environmental chamber at 40 °C. Each sample is weighed regularly until it reaches 75, 80, 85, 90, and 95% binder content. When the desired binder content is reached, the time is recorded and the sample is washed. Usually a test takes approximately 2 to 4 h. The sixth sample is kept in the environmental chamber for 24 h and its binder content measured as an indication of how much water remains trapped in the fully coalesced film.

Results are expressed in terms of coalescence versus binder content and time versus binder content (evaporation rate). [Figure 11.10](#) presents a typical result for a surface dressing emulsion. The rapid change in coalescence between 75 and 85% binder indicates that phase inversion may be occurring without any real effect on evaporation. When 86% binder is reached the change in evaporation rate is quite dramatic indicating that water is now trapped in the system and finding it more difficult to escape.



**FIGURE 11.10** Evaporation filtration test result for a typical surface dressing emulsion.

### 11.7.1.2 Tack Coat (or Bond Coat)

Tack coats are a thin emulsion film sprayed onto the existing pavement surface before applying a new asphalt layer. The purpose of tack coats is to get good adhesion between successive pavement layers. This is of fundamental importance for the strength and the durability of roads consisting of several asphalt layers and even more important when thin layers are applied as wearing courses. As this new layer is usually applied hot (minimum of 140 °C), breaking of the tack coat emulsion is expected to occur during compaction under the heat of the new layer. The major characteristics expected from a tack coat emulsion are storage stability and proper viscosity. Viscosity must be sufficiently low to insure good wetting of the existing surface and also have ability to penetrate through remaining layers of dust or fines on the old surface.

## 11.7.2 TECHNIQUES FOR COLD MIX ASPHALT

Potentially cold mix asphalt can replace hot mix asphalt in most constructions. There are, however, a number of limitations with cold mix asphalt which so far have limited their extensive use. Part of the limitation is conservatism by road constructors and specifiers, but there are also technical limitations which need to be overcome. Three of the major factors which are particularly important when working with emulsion mixes are:

- Workability (stiffness of the mix)
- Void content in the stone material
- Breaking and curing combined with release of water

Workability is related to the stiffness of the uncompacted cold mix. A good workability is needed to secure a smooth paving and proper compaction of the mix. The main reason for poor workability is that the emulsion starts breaking immediately when contacted with the stone material. This is particularly difficult to avoid if the stone material contains large amounts of fines. There are many ways of achieving good workability, but many solutions are also associated with some disadvantages. One of the most common solutions is to make the binder soft enough to permit laying and compaction, even if broken. This can be done by using a soft binder or alternatively using a solvent which will soften the binder during mixing, laying, and compaction and then eventually evaporate and give full strength to the pavement. Another solution is to use

**TABLE 11.1**  
**Emulsion Cold Mix Workability**

Broken Systems		Nonbroken System, Slow Set Emulsion
Soft Binder	Solvent Fluxed Binder	
<ul style="list-style-type: none"><li>• Soft paving</li><li>• Flexible paving</li><li>• Self-healing</li><li>• Easy to lay</li><li>• Easy to make</li></ul>	<ul style="list-style-type: none"><li>• High VOC emission</li><li>• Improve strength with time</li></ul>	<ul style="list-style-type: none"><li>• Long curing time</li><li>• Good strength after curing</li><li>• Very sensitive after laying</li></ul>

a very stable emulsion which does not break in contact with the stones. The disadvantage is that it may take a very long time to achieve full strength of the road. Table 11.1 summarizes the different approaches for achieving good workability on cold mix asphalt.

The second factor is void content. Crushed stone material used for road construction consists of a mixture of aggregates with different size or different gradations. The amount of space between the mineral aggregates is called the “volume of voids in mineral aggregate.” In dense graded hot mix asphalt the void content in the aggregate should be slightly higher than the volume of the bitumen. The air void in the compacted asphalt sample should be as small as possible, but the air voids must never be completely filled with bitumen, since this will cause the asphalt to be unstable and very sensitive to deformation and bleeding. This makes it impossible to use the same gradation with emulsion mixes since we must always allow for additional 35% water from the emulsion. This makes it very difficult to make a truly dense graded cold asphalt mix using bitumen emulsions.

The third factor is breaking and curing. After paving and compaction of the cold mix asphalt, breaking and curing should take place as quickly as possible. This contradicts the desire to have as stable emulsion as possible to have good workability. A further complication is the necessity to remove the water as soon as possible. In wet climatic conditions this could take a very long time. In open graded mixes water could drain out of the paving but in dense graded mixes the water has to evaporate out of the paving unless a water consuming additive like cement is added.

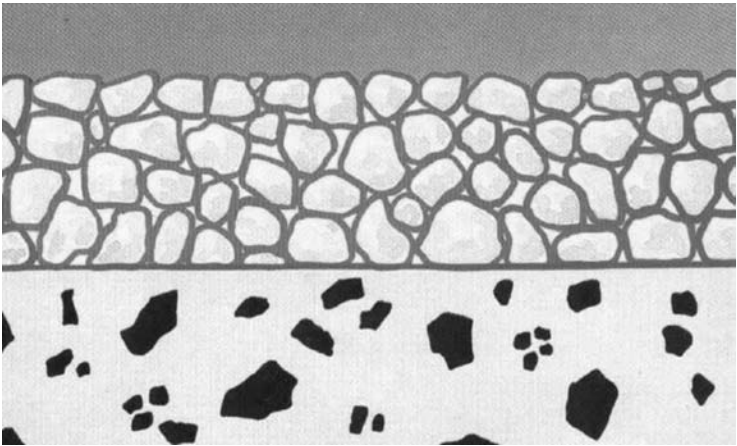
The choice of emulsion type for a certain application is heavily dependent on the amount of fines in the stone material since the fines are very reactive towards the emulsion. Too much fines can cause premature breaking, while too little fines could cause “run off” of the emulsion from the mix. Thus we may classify different applications according to the type and amount of fines (defined as particles less than 80 microns) present in the minerals to be coated (Table 11.2).

**11.7.2.1 Open Graded Emulsion Mixes**

In this technique an open gradation of stone material is selected. This means that there is plenty of space between the stones to allow for binder and water. Figure 11.11 illustrates the internal structure of this type of mix. The open gradation usually contains very little fines making premature breaking less probable and thus the mix workability is usually good. On the other hand the retention of the emulsion in the mix becomes very critical. A high amount of binder is desired to have good durability and good strength. If, however, too much emulsion is added it will simply run off the aggregates and leave just a thin layer of binder on the stone surface. This is sometimes referred to as “run off.” The retention of emulsion can be improved by thickening additives. Open graded mixes are mainly used as base courses since the open structure makes the asphalt

**TABLE 11.2**  
**Application and Emulsion Type with Respect to Filler Content**

	Construction Method			
	Sprayed	Mixed		
Type of fines	None	Crushed aggregate		Silt/clay
Fines content	<1%	<2%	2 to 10%	≤10%
Application	<ul style="list-style-type: none"><li>• Surface dressing</li><li>• Tack coats</li></ul>	<ul style="list-style-type: none"><li>• Cold recycling</li><li>• Open graded emulsion mixes</li></ul>	<ul style="list-style-type: none"><li>• Dense graded emulsion mixes</li><li>• Slurry seal</li><li>• Microsurfacing</li></ul>	Soil stabilization
Emulsion type	Cationic/anionic Formulated to pass storage and transportation requirements Fast break upon contact with road and chipping required	Cationic/anionic Sufficiently stable to allow coating of aggregate	Cationic/anionic Sufficiently stable to allow coating of fines  Quick set after construction usually required	Anionic High stability required to allow mixing in presence of silt/clay particles



**FIGURE 11.11** Cross-section of an open graded emulsion mix layer (the top part).

sensitive to aging and penetration of water and thus less suitable for top layers. If open graded mix is used as top layer it is advisable to seal the asphalt with a surface dressing or a slurry seal to guarantee durability. The emulsion used must be able to coat the aggregate and have a break time after mixing adapted to the construction methods. When mixing and construction are carried out with little delay, emulsion break times similar to surface dressing can be required in order



to have a quick cohesion build-up after compaction. Requirements for this type of technique include:

- Aggregate must be moist for best results (about 2 to 6% water content).
- Emulsion must have sufficient viscosity to avoid emulsion run-off after mixing (particularly true in the case of open graded emulsion mixes, where thick bitumen film is needed).
- Emulsion binder content depends on the moisture content of the aggregate; it is best to work with low bitumen content (60 to 65%) when working with relatively dry aggregate. If the aggregate is wet, it is possible to work with higher binder content emulsions (65 to 70%).

As in the case of surface dressing, reactivity is an important phenomenon. The mix, however, does not depend as strongly as surface dressing on coalescence, since compaction has an important role in the break of the emulsion. An example of paving so-called semi-dense cold mix asphalt is illustrated in Figure 11.12.



**FIGURE 11.12** Paving of semi-dense cold mix asphalt.

### 11.7.2.2 Dense Graded Emulsion Mixes

Cold dense graded mixes may be compared to hot mixes. They are characterized by a high fine content and a dense gradation leaving minimum amount of voids. This is the most challenging type of mix for the emulsion formulator in a sense that he must both design for fines coating and coarse aggregate coating. In most cases, the fine coating criterion is critical and the emulsion is formulated for high stability. However, by increasing stability, reactivity is decreased and there may be difficulties achieving 100% coating of the larger aggregate particles. This has been solved by coating the fine fraction and the coarse fraction separately in the cold mix plant, followed by mixing the two fractions before laying.

In any case stone gradations used in emulsion mixes can not be identical to the gradations used in hot mixes. There must always be space for at least 35% water present in the emulsion. In reality there is usually even more water in the mix, coming from natural moisture in the aggregate piles. It might also be necessary to add extra water to secure even coating and good workability. If more liquid is added, than the available voids, the emulsion will be squeezed out at compaction, and the mix will contain less binder than designed. The emulsion water on the surface will also cause a disaster by sticking to vehicles, persons, and tools around the work site. To give enough space for the water in the cold mix we need to use a gradation with more voids than normally used in hot mix design. The result is that when the emulsion is fully cured and the water is evaporated, we have more voids in the asphalt than with the corresponding hot mix. All this taken together makes it impossible to produce a true dense graded cold mix asphalt, but experience has proven that cold mix asphalt with void content of 7% will perform as well as a hot mix asphalt with void content of 3%.

So far, many commercial dense graded cold laid mixes have been made with very soft binder or hard binder being fluxed with solvent to become soft enough to permit paving and compaction even if the emulsion is broken. These soft systems are also subjected to after compaction which will make the void content more comparable to hot mix asphalt but also sensitive to deformations.

### 11.7.2.3 Slurry Seal and Microsurfacing

Slurry seal and microsurfacing are special types of dense graded mixes and are often viewed as the top of the scale of complexity in bitumen emulsion techniques. In the U.S.A. they are frequently used to seal and improve skid resistance on highways as well as for maintenance of local roads in urban areas with very little traffic. Sealing on top of an old road can extend the lifetime of the road by 10 years or more. While ordinarily dense mixes form a relatively stiff mix before compaction, slurry seal and, to a large extent, microsurfacing form a slurry composed of:

- Fine aggregate gradation (usually up to 5 mm for slurry seal and 10 mm for microsurfacing)
- Water
- Break control additives dispersed in the water
- Emulsion
- Cement

Slurry seals and microsurfacing are always applied directly after blending in one continuous operation, with machines which are specially designed to lay microsurfacing. They are equipped with an individual dosing system to adjust the balance between the components listed above. A skilled technician may adjust the formulation to have more or less immediate breaking once the material is laid on the road. The breaking speed is very much dependent on the type of aggregate

and the type of emulsion used. Thus the formulation of the slurry should be individually optimized for each work site using proper selection of additives and cement. Microsurfacing systems make use of particular types of emulsifiers, of which di-quaternary fatty amine is one example, but many other excellent types are available on the market. The breaking in such systems is a true chemical break in which both chemical nature of the aggregate and the emulsifier play a major role. Slurry seal is applied in thin layers not exceeding 5 mm while microsurfacing systems usually build thicker layers and use polymer modified binders. Once the emulsion breaks, it is expected that the system rejects the water. Compaction and traffic help in this process. Set is completed once the mix is dry.

#### **11.7.2.4 Recycling**

Recycling of old asphalt pavements is becoming more and more important. Today most old asphalt is recycled. Cold recycling is preferred because most of the operations can be made close to the work site without extensive transportation and heating. The mix is composed of reclaimed asphalt pavement (RAP) issued from cold milling of asphalt materials which are mixed with a suitable bitumen emulsion. The RAP for cold recycling already contains 4 to 6% aged bitumen and usually comes in relatively open gradations with very little fines. One of the difficulties with cold recycling is the lack of control over the material entering the process. The existing binder can be of different types and the stone material can be of different type of mineral as well as different gradations. Sometimes small amount of virgin stone material (up to 20%) is added to adjust the gradation and to improve the quality.

The selection of binder follows generally two lines. One is that a soft binder should be used to rejuvenate the old binder. The viscosity of the added binder is selected to give a suitable stiffness when the new and the old binder have been completely mixed. The other line considers the old binder as a part of the stone, and the new added binder should have the desired stiffness for the road. Experience has shown that using hard binder gives much better initial strength (modulus) to the new road.

Although it is sometimes expected that coated stones and lack of fines guarantee low reactivity of the RAP, this is not always the case. To secure an even coating of all RAP by the new binder, the emulsion should be rather stable. The addition of new binder has a maximum of approximately 3%. Too much binder gives a risk for permanent deformation (rutting) or bleeding, while too little binder decreases the durability of the road considerably.

#### **11.7.3 OTHER ROAD APPLICATIONS**

Bitumen emulsions are also used in many other road applications, but it is outside the scope of this chapter to go into details of all these, but just to mention a few:

- Soil stabilization
- Penetration macadam
- Grave emulsion (particularly France)
- Prime coat
- Dust binding

#### **11.7.4 INDUSTRIAL APPLICATIONS**

Bitumen emulsions have also proven to be very useful in many applications other than road building. In most cases anionic emulsions or clay emulsions are used in these applications

although sometimes cationic emulsions are also used. The producers of cationic emulsions for road applications generally do not like to produce anionic or clay emulsions due to the consequences if the two types are accidentally mixed. Instead the emulsions for industrial applications are produced in small plants specially designed for the particular product. Some examples of applications are:

- Paint
- Roofing mastic
- Protective cover for freshly seeded areas
- Mulch treatment
- Metal and masonry coating
- Spray coating for water proofing
- Grout mastic for vibration dampening
- Adhesives
- Tile cement
- Laminant
- Fiber board sizing

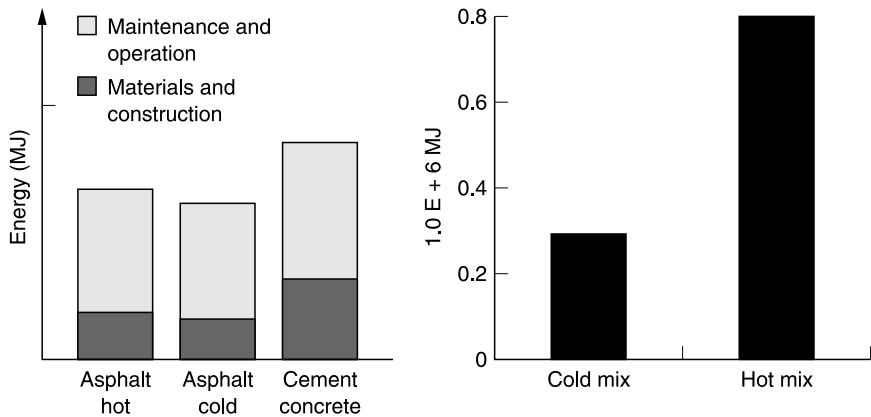
## 11.8 THE FUTURE FOR BITUMEN EMULSIONS

Even 80 years ago it was predicted that within 10 years bitumen emulsions would dominate as binders in the road construction industry. It has not happened yet, although we are convinced that sooner or later they will, although we do not expect this to happen within 10 or even 20 years. On the contrary, during the last 10 years we have seen a slight decline in the use of bitumen emulsions, reflecting the general trend of declining road construction and maintenance work on public roads. The ratio of emulsions to hot mix asphalt has been maintained, however, or even slightly increased during the same period.

Today bitumen emulsions dominate in some construction applications, such as where spraying is required (surface dressing in roads, waterproofing in construction), because it is possible with emulsions to work at ambient temperature on wet surfaces and reduce almost entirely the need for solvents. However, usage of bitumen emulsions remains secondary to hot bitumen for several technical and economic reasons. On the technical side, emulsion behavior is more complex to master than hot bitumen. Engineers generally feel more comfortable with hot bitumen. In the hot process, there is no water to eliminate and hardening is achieved simply by cooling instead of being achieved through the coalescence and setting phenomena as in the case of emulsions. On the economics side, the cost of emulsification always needs to be justified. The economical advantages of emulsions are real, however, and related to the savings in energy from working directly with moist minerals and therefore avoiding the drying stage of minerals. Also, emulsions give the possibility of working on site with lighter equipment than in the case of hot techniques.

Continuous research into emulsion and emulsion mixes is still on-going, identifying more and more areas where emulsions present clear advantages or where molten bitumen would not be applicable, such as most on-site techniques. Finally, the need to reduce the use of volatile solvents is an important reason for using emulsions in sprayed applications.

During recent years bitumen emulsion technology has sometimes been presented as the “green” alternative to hot mix asphalt. A comparison between hot mix asphalt and cold mix asphalt is, however, rather complicated and several factors should be taken into consideration. Cold mix has without doubt several advantages over hot mix, but we should be careful about presenting cold mix as the “green” alternative without any reservations. Let us take a look at some factors related to cold mix as an environmentally preferred product.



**FIGURE 11.13** Comparison of energy consumption using hot mix asphalt and cold mix asphalt. The right diagram refers to production only.

Cold mix technology can lead to energy savings. Since this technology does not require heating of the stone material, which makes up 94% of the asphalt, there is considerable saving in energy. Cold mix technology also makes use of less sophisticated and cheaper production equipment. Usually cold asphalt mix plants are mobile and can easily be placed close to the work site, considerably reducing transportation. If all these factors are taken together, cold mix gives a considerable saving in energy compared to hot mix (Figure 11.13).

Consider also the health and safety aspect. A historical success story showing the advantage with bitumen emulsions is the reduction in volatile organic compounds (VOCs) when surface dressings previously produced with cut back bitumen (bitumen and kerosene) were replaced by bitumen emulsions. This change took place between 1975 and 1990 and considerably reduced the amount of VOCs released to the atmosphere. It is also clear that the working environment when laying cold mix asphalt completely eliminates all problems with fuming from hot bitumen and also reduces the risk of burns from hot asphalt.

Everything is not “green,” however, with bitumen emulsions. There is still a large number of formulations, containing small amounts of kerosene or other solvents, which eventually evaporates to the atmosphere, although not to the extent of cutbacks in the 1970s. There has also been concern that the emulsifier may be washed out from the asphalt by rain and could possibly contaminate ground water, particularly since most cationic emulsifiers are considered as hazardous to the environment. On the other hand, investigations have shown that after breaking of the emulsion the cationic emulsifiers are irreversibly captured by the soil and would not be released until they are completely degraded by micro-organisms (26).

The main reason why road construction and maintenance technology are based on hot mix asphalt is mainly due to the fact that most countries, particularly in Europe, have an infrastructure adapted for hot mix asphalt. The available specifications and practices are also more adapted to hot mix asphalt rather than cold mix asphalt. There is an excess of hot mix plants covering the most densely populated areas of the Western countries. These plants represent considerable capital employed and it is important for the owners to use the plants for production of hot mix asphalt.

The most important advantages with cold mix technology over hot mix are the inexpensive equipment required for production, giving high flexibility for production of cold mix asphalt close

to the work site. Another advantage is the relatively low energy consumption due to the lack of heating of the stone material.

The disadvantages are mainly that the binder becomes more expensive, since an additional operation is needed to produce the emulsion. On top of that the addition of chemicals (emulsifiers and acid) gives further additional cost. After emulsification the volume of binder is increased by approximately 30% due to the water content in the emulsion, which means that larger volumes of binder have to be transported to the work site. However, taking account of all economic factors, including the capital cost and the operation expenses for a hot mix plant, emulsion technology is, without doubt, more economical compared to hot mix.

The fact that the use of bitumen emulsion varies greatly in different countries implies that the choice of material for road construction is not completely rational. France is the largest user, with more than 25% of all bitumen for road constructions used as emulsions, while in Germany, for example, with mainly the same environmental conditions, only 3% of the bitumen is used as emulsion. Currently, the E.E.C. and U.S.A. each consume approximately 2 million tons of emulsion, representing on average, respectively, 12% and 7% of the annual bitumen consumption. There is, however, no doubt that bitumen emulsions will become more and more important, particularly for maintenance of our road network in the future.

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