Asphalt Emulsions (Chemistry and Concepts)

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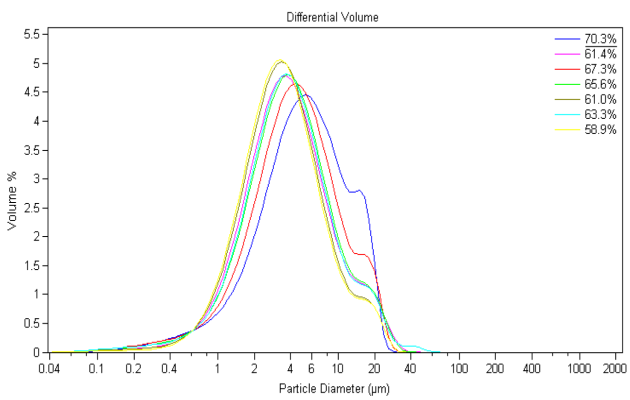
Emulsion - Definition

An emulsion is a dispersion of small droplets of one liquid in another liquid. Typical examples include such everyday products as milk, mayonnaise, and cosmetic creams. Emulsions can be formed by any two immiscible liquids but in most emulsions one of the phases is water. Oil-in-water (O/W) emulsions are those in which the continuous phase is water and the disperse (droplet) phase is an 'oily' liquid. Water-in-oil (W/O) "inverted" emulsions are those in which the continuous phase is an oil and the disperse phase water. More complex structures are possible such as water-in-oil-in-water (W/O/W) emulsions in which the oil droplets themselves contain smaller droplets of water.

Bitumen (asphalt) emulsions are normally of the O/W type and contain from 40 to 75% bitumen, 0.1-2.5% emulsifier, 25-60% water plus some minor components which are described below. They are brown liquids with consistencies from that of milk to double cream which depend mostly on the bitumen content and the particle size. The bitumen droplets range from 0.1-20 micron in diameter and some drops may contain smaller water droplets within them so are better described as W/O/W emulsions. This 'trapped' water can influence the physical properties of the emulsion.



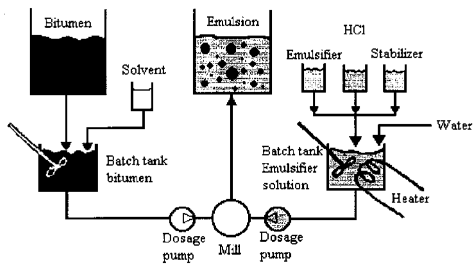
Typical particle size distribution of bitumen emulsions with different bitumen contents. Measured on a Coulter LS230 Particle Sizer [1]

Classification of Bitumen Emulsions

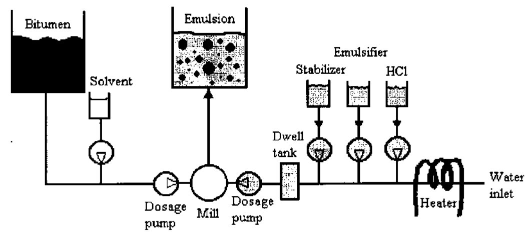
Bitumen emulsions are classified according to the charge on the droplets and according to their reactivity. *Cationic* emulsions have droplets which carry a positive charge. *Anionic* emulsions have negatively-charged droplets. *Rapid-setting* emulsions set quickly in contact with clean aggregates of low surface area such as the chippings used in chipseals (surface dressings). *Medium-setting* emulsions set sufficiently less quickly that they can be mixed with aggregates of low surface area such as those used in open graded mixes. *Slow-setting* emulsions will mix with aggregates of high surface area. In the naming of emulsions according to the ASTM standards, cationic rapid-, medium- and slow-setting emulsions are denoted by the codes CRS, CMS and CSS, whereas anionic emulsions are called RS, MS, and SS.

Manufacture of Bitumen Emulsions

Emulsions are made by mixing hot bitumen with water containing emulsifying agents and applying mechanical energy sufficient to break up the bitumen into droplets. Bitumen emulsions are usually made using a colloid mill where energy is applied to the system by passing the mixture of hot bitumen and water between a rotor and a stator. The disc or cone-shaped rotor may be grooved or have teeth in order to create a turbulent flow.



Batch Emulsion Plant

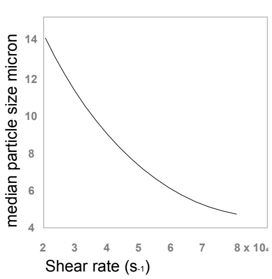


Continuous Emulsion Plant

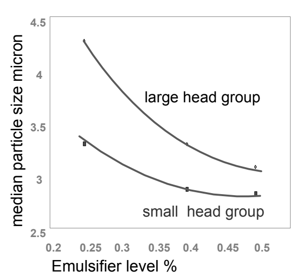
Emulsification is opposed by the internal cohesion and viscosity of the bitumen and the surface tension of the droplet which resists the creation of new interface. Smaller droplets are favored by a high energy input, a low bitumen viscosity and by the choice and concentration of emulsifier (which reduces the interfacial tension)[2].

The highest practical temperature is used to prepare the emulsion in order to reduce the bitumen viscosity. Bitumen is generally heated to 110-160ºC until it has a viscosity of 500mPa.s or less for pumping into the mill and the water phase may also be heated to 30-70^{o}C to dissolve the emulsifiers. Hot asphalt and water mix in the mill and temperature equilibration occurs rapidly. The temperature which determines the particle size is this temperature after mixing (=the exit temperature) and is limited to 100ºC in unpressurized systems to avoid boiling of the emulsion but can reach 120ºC or more in modern pressurized plant.

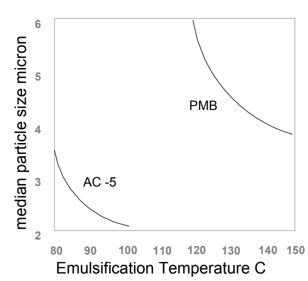
Droplets have a tendency to rejoin (coalescence) and it is necessary not only to create small drops but also to prevent their coalescence by the design of the equipment and the choice of emulsifier. Coalescence is more difficult to prevent in emulsions of high solids content because the droplets are closer together, and as a result these emulsions tend to have higher average particle size (see first figure).



Droplet size vs. shear rate[2]



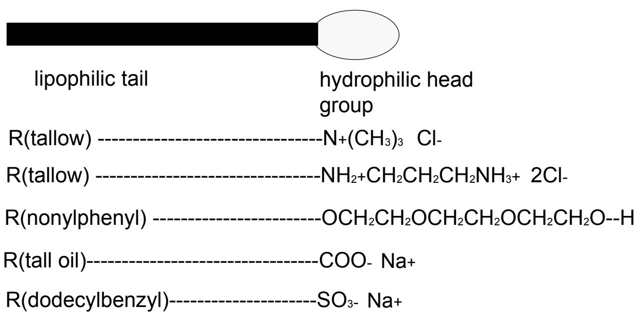
vs. emulsifier concentration



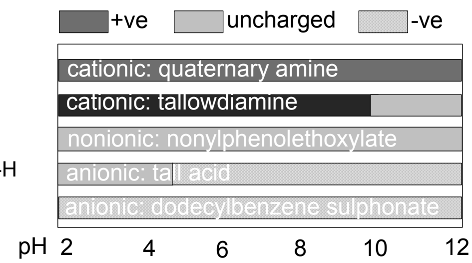
vs. production temperature

Chemical Nature of Emulsifiers

Most bitumen emulsifiers are made from renewable resources such as natural fats and oils and wood. Because they have both hydrophilic (water loving) and lipophilic (oil-loving) portions in their molecules they concentrate at the interface between water and bitumen. This both reduces the energy required to emulsify the bitumen and prevents coalescence of the droplets once formed. A typical emulsifier has a hydrophilic 'head' group and lipophilic 'tail' comprising 12-18 carbon atoms. Emulsifiers are classified into anionic, cationic, and nonionic types depending on the charge their head groups adopt in water, although this charge may depend on pH. The emulsifier head groups are associated with counterions such as chloride or sodium. Diffusion of the counterions into the water phase leaves behind a small net charge on the asphalt droplets and the charge on the emulsifier



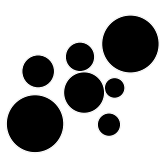
Typical emulsifier structures



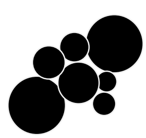
Emulsifier head charge depends on pH

head group largely determines the charge on the asphalt droplets. The size and sign of the charge on the droplets can be measured and is expressed as the 'zeta potential' of the droplet and there is a tendency for emulsions containing droplets with low zeta potentials (positive or negative) to be less reactive [3].

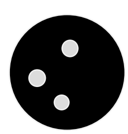
Repulsion of like-charged droplets helps prevent close approach which could lead to flocculation and eventually to coalescence. The film of emulsifier at the interface also helps prevent coalescence. Nonionic emulsifiers provide a steric barrier to close approach.



Emulsion Droplets



Flocculation



Coalescence

Generally more emulsifier is required to provide good stability and the right performance properties to the emulsion than is necessary to fill the interface, so bitumen emulsions will contain some 'free' emulsifier present in the water phase which acts as a reservoir helping to prevent coalescence during emulsification and storage and transport.

Formulation of the Emulsion

Emulsifiers are often supplied in a water-insoluble form and need to be neutralized with acid or alkali to generate the anionic or cationic soluble form. The choice of acid or alkali and the final pH of the emulsion influence the emulsion properties. Cationic emulsions are acid and anionic emulsions alkaline.

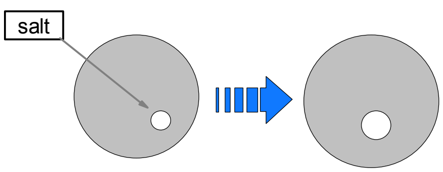
RNH_2 + HCl = RNH_3^+ + Cl^-
insoluble form *water-soluble cationic form*

$RCOOH$ + $NaOH$ = $RCOO^-$ + Na^+ + H_2O
insoluble form *water-soluble anionic form*

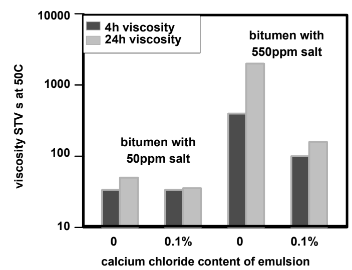
Other components of the emulsion and their function

Calcium Chloride

Bitumen contains a small amount of salt, which can lead to an osmotic swelling of the droplets in an emulsion which results in an increase in emulsion viscosity, often followed by a decrease as the salt slowly escapes from the bitumen. Calcium chloride is included in cationic emulsions to reduce the osmosis of water into the bitumen and minimize the changes in viscosity [4].



bitumen emulsion droplet swells due to osmosis



calcium chloride reduces viscosity changes

Calcium chloride can also reduce the settlement of emulsions by increasing the water phase density.

Sodium tripolyphosphate

Anionic emulsions may be sensitive to hard water. Addition of sodium tripolyphosphate to the formula acts as a water softener and improves emulsion quality.

Thickeners

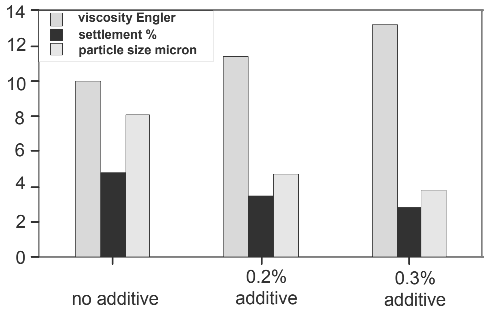
Water soluble thickeners used at 0.02-0.2% can increase emulsion viscosity, helping to meet national standards or to reduce emulsion run off in open graded mixes.

Adhesion promoters

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

Asphalt peptizers

The emusifiability of bitumens varies. Emulsion quality can sometimes be improved by treating the bitumen with an asphalt peptizer. The particle size of the emulsion droplets is reduced and this leads to reduced settlement, higher emulsion viscosity, higher reactivity and improved adhesion



Benefits of asphalt peptizers in CRS emulsions

Solvent
Solvents may be included in the emulsion to improve emulsification, to reduce settlement, improve setting rate at low temperatures or to provide the right binder viscosity after setting.
Latex
Polymer modification can improve the properties of bitumen in terms of cohesion, resistance to cracking at low temperatures and resistance to flow at high temperatures. Latex is a water based dispersion of polymer which is particularly suited to the modification of emulsions. Latex comes in anionic, nonionic and anionic forms and its important that the latex type should be compatible with the emulsion.

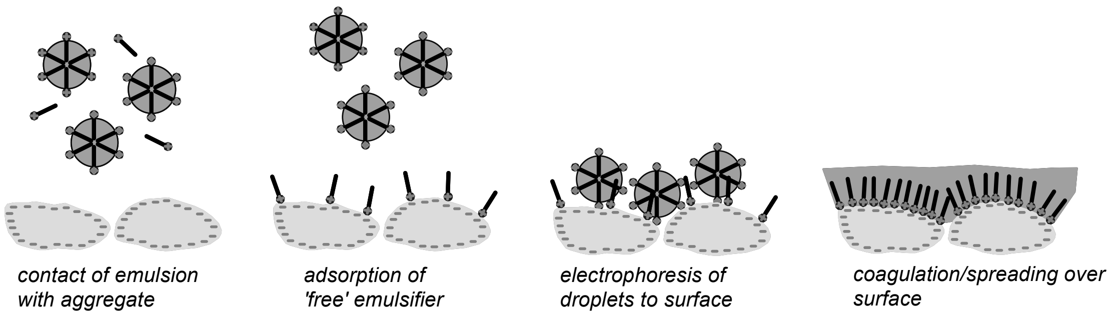
The setting (or 'breaking') process
Bitumen emulsions must revert to a continuous bitumen film in order to fulfil their role as a cement in road materials. This involves flocculation and coalescence of the droplets and removal of the water. The speed of this setting and curing process depends on the reactivity of the emulsion, the reactivity of the aggregate and environmental factors such as temperature, humidity, wind speed, and mechanical action. It may take a few hours in the case of a chipseal to several weeks in the case of a dense cold mix for the full strength of the road material to be reached.

Aggregates take up a characteristic surface charge in water which depends on the nature of the minerals, the pH and the presence of soluble salts. So-called 'acid' aggregates high in silica tend to take up a negative charge, whereas basic aggregates like limestones can take a positive charge. Generally speaking cationic emulsions react faster with an aggregate with negative surface charge and the final adhesion is better.

The setting of an emulsion is a complex process, not fully understood, and more than one factor is responsible for the break. Some aggregates like carbonates and fillers like cement may neutralize acid in cationic emulsions causing the pH to rise and the emulsion to be destabilized.

As water leaves the system by evaporation, the droplets are concentrated eventually leading to coalescence. The coalescence process is a type of 'inversion' in which the emulsion turns from an oil-in-water type to a water-in oil type. The emulsifier type can influence the amount of water which must be lost before inversion takes place and the bitumen can no longer be re-emulsified. Evaporation may be the main breaking mechanism for very slow-setting emulsions.

Mechanical action such as compaction or traffic may squeeze the droplets together, promoting coalescence and squeezing water out of the coalesced film.



Possible stages in the setting of a cationic emulsion

Meeting the requirements of national specifications

National standards generally specify bitumen content, particle charge, emulsion viscosity, storage stability (settlement), particle size (sieve residue), the setting properties of the emulsion and the properties of the residue after the water has been removed. An understanding of the factors influencing these properties allows emulsions to be designed meeting the specifications.

References

[1] Specifying Slurry Surfacing Emulsion Quality : Particle Size and Size Distribution, M Engman, A James, D. Needham, and T. Ng , ISSA 36th Annual Meeting, 1998 San Diego.
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