



**Universitat de Lleida**  
Escola Politècnica Superior

EN CIÈNCIES APLICADES A LA ENGINYERIA  
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Universitat de Lleida  
Escola Politècnica Superior  
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Treball final de màster

**Highly concentrated bitumen emulsions**  
**A state of the art, review of experimental results**

Autor/s: Núria Querol Solà  
Director/s: Dr. Luisa F. Cabeza  
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## Acknowledgments

*To SORIGUE*

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# 1.Introduction

## 1.1 *History of bitumen emulsions*

Historically, although we could find references of emulsions or tar water dispersions used to the road paving in the early 20<sup>th</sup> century, it was not until 1922 when the first patent bitumen emulsion appeared and emulsions factories were known in United States, France, England, Germany, etc. It is estimated that the word emulsion production was 150.000tn in 1926. (1)

The objective pursued by using emulsion is being able to move a hydrocarbon binder at ambient temperature. These types of emulsions were firstly anionic.

In 1951, when they appeared in the market, cationic emulsions became almost universally used at any time. With this product aggregates could be used at whatever weather condition, worked correctly fine, so bitumen emulsions reached their full development.

In Spain, the development of emulsions was produced with certain delay behind other countries, but nowadays Spain is one of the first world emulsion producers behind United States and France, which are in this order the first ones. Spain is also the second largest country, behind France, producer of cold techniques (emulsion) against hot techniques (pure bitumen) (2).

The world emulsion production is estimated to be around 12 million tones, of which around 30% are manufactured in United States and 10% in France. In Spain the annual production is around 400.000 ton/year.

Although bitumen emulsions find applications in different fields from road, for example waterproofing covers, painting, etc., we could estimate that the percentage for the roads could exceed 95% of the global production.

## 1.2 *General Concepts*

In the nature there are different aqueous dispersions types: suspensions (dispersion of a solid in a liquid), emulsions (dispersions of one liquid in another liquid), and foams (dispersions of a gas in a liquid). (1)

Among them, emulsions constitute a very large group. A very typical example close to human days is milk. Milk is an emulsion which basically consists of fat particles dispersed in an aqueous medium. There are also numerous emulsions products from industry like food, cosmetic, pharmaceutical and chemistry products.

### *1.2.1 Emulsion Definition*

A simple definition of emulsion is a dispersion of a liquid (dispersed phase) as tiny particles within another non-miscible liquid (continuous phase). There are many precise definitions referring to the size of the particles of the dispersed phase, the number of phases or the specific properties, such as stability.

Probably one of the most accurate and complete definitions from the scientific point of view is proposed by P. Becher: "An emulsion is a heterogeneous system thermodynamically unstable formed by at least two immiscible liquid phases, where one is dispersed in the other in form of little droplets (beads) whose diameter is generally higher than  $0.1\mu\text{m}$ . Such a system has a minimum stability which could be improved by addition of appropriate agents, such as surfactants, or finely solid divided".  
(3)

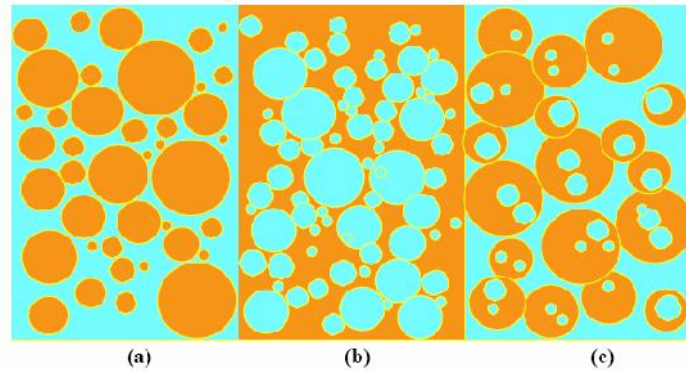
### *1.2.2 Classification*

#### *i) By Type*

The more extended classification of an emulsion is those referenced to the type of emulsion. So, they are classified as direct, inverse or multiple.

#### *i.1) Direct Emulsions*

Direct emulsions are those in which the dispersed phase is a lipophilic substance (fat or oil) and the continuous phase is hydrophilic (typically water). These emulsions are called L/H or O/W. As examples we could say: bituminous emulsions, milk, mayonnaise, some paints, and many other products and pesticides. (4)



**Figure 1:** (a) O/W emulsion, (b) W/O emulsion; (c) multiple W/O/W

### *i.2) Inverse Emulsions*

Inverse emulsions, by contrast, are those where the dispersed phase is a hydrophilic substance while the continuous phase is the lipophilic one. These emulsions are denominated with the abbreviation H/L or W/O. As examples we could name margarines, hydraulic fluids, and most cosmetic creams. (4)

### *i.3) Multiple Emulsions*

Finally, multiple emulsions are those which have an inverse emulsion like a dispersed phase while the continuous phase is an aqueous liquid. These emulsions are called H/L/O or W/O/W. These emulsions are used primarily in pharmacy, because they allow obtaining a delayed release medicine.

### *ii) By diameter particle size*

Other classifications are referred to the diameter particle size which constitute the dispersed phase, thus we could difference between emulsions, microemulsions and nanoemulsions. Although there is not yet an official definition for nanoemulsions, these usually have a diameter particle size generally lower than 0.5  $\mu\text{m}$  (500nm) and could measure up to a few tens of nanometers. In contrast, the emulsions which have a higher diameter size are called macroemulsions. There are also microemulsions but they are not really emulsions. Clearly, this kind of classification often creates confusion but has remained for historical reasons, as the word “microemulsion” appeared in the

1950s, so much earlier than the word “nanoemulsion”. Now we know that microemulsions differ from emulsions because they create a stable system (1):

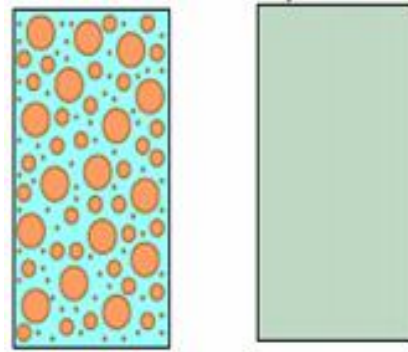


Figure 2:    **EMULSIONS**                      **MICROEMULSIONS**  
                           $\varnothing = 10^{-6}\text{m}$                        $\varnothing = 10^{-8}\text{m}$

*iii) By the sign of the charge on the droplets*

Bitumen emulsions are classified according to the sign of the charge on the droplets in (4):

*Cationic:* emulsions have droplets which carry a positive charge.

*Anionic:* emulsions have negatively charged droplets.

*iv) By their reactivity:*

Bitumen emulsions are classified according to their reactivity in:

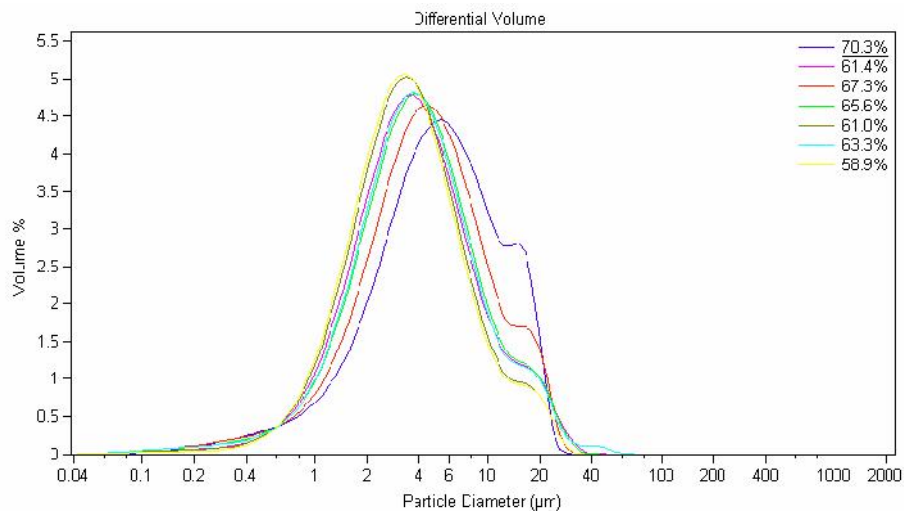
*Rapid-setting (RS):* emulsions set quickly in contact with clean aggregates of low- surface area, such as the chippings used in chip seals (surface dressings).

*Medium-setting (MS):* emulsions set sufficiently less quickly that they can be mixed with aggregates of low surface area, such as those used in open-graded mixes.

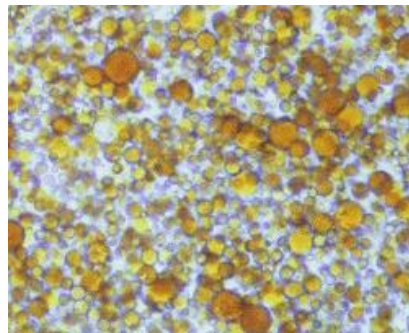
*Slow-setting (SS)* emulsions will mix with reactive aggregates of high surface area. RS emulsions are reactive and are used with unreactive aggregates; SS emulsions are unreactive and are used with reactive aggregates. The actual setting and curing time in the field will depend on the technique and materials being used as well as the environmental conditions.

Standard bitumen (asphalt) emulsions are normally considered to be of the O/W type and contain from 40% to 75% bitumen, 0.1% to 2.5% emulsifier, 25% to 60% water plus some minor components which are described later. The bitumen droplets range from 0.1–20 micron in diameter. Emulsions with particle sizes in this range are sometimes referred as macroemulsions. (4)

They are brown liquids with consistencies from that of milk to double cream, which depend mostly on the bitumen content and the particle size. Some bitumen droplets may contain smaller water droplets within them; a better description of asphalt emulsion would be a W/O/W multiple emulsion. The viscosity of the emulsion and especially changes in the viscosity of the emulsion during storage are strongly influenced by this internal water phase. There is a distribution of particle sizes in the emulsion, and this distribution is influenced by the emulsion recipe and the mechanics and operating conditions of the emulsion manufacturing plant.



(a)



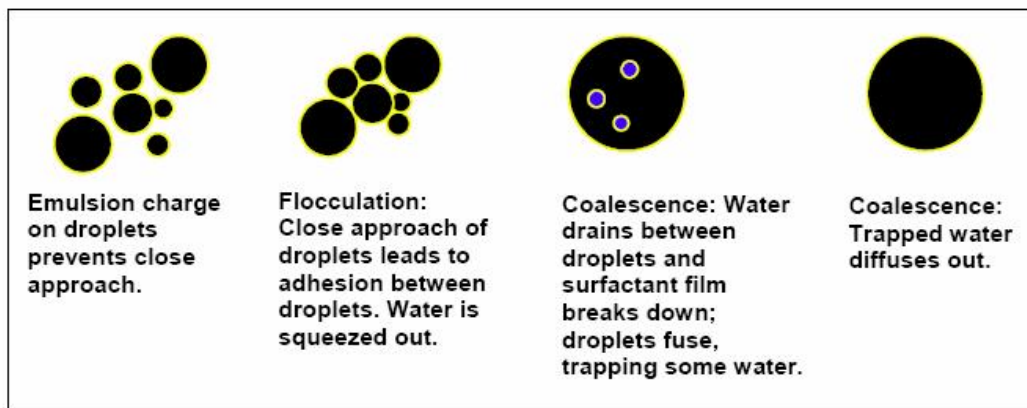
(b)

**Figure 3:** (a) Typical particle size distributions of asphalt emulsions with different asphalt contents and (b) micrograph of asphalt emulsion.



The particle size and the particle size distribution of the emulsion droplets strongly influence the physical properties of the emulsion, such as viscosity and storage stability; larger average particle size leads to lower emulsion viscosity, as does broad or bimodal particle size distribution. Particle size also influences the performance of emulsion. In general, smaller particle size leads to improved performance in both mix and spray applications. Some recent developments in asphalt emulsion technology have focused on the ability to control the particle size and size distribution of the emulsion during the emulsification process, and consequently to influence the emulsion properties.

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



**Figure 4:** Stages in the breakdown of emulsions

The asphalt droplets in the emulsion have a small charge. The source of the charge is the emulsifier, as well as ionisable components in the asphalt itself. These small charges on the droplets normally provide an electrostatic barrier to their close approach to each other (like charges repel). However, when two droplets do achieve enough energy to overcome this barrier and approach closely then they adhere to each other (flocculate). This flocculation may sometimes be reversed by agitation, dilution, or addition of more emulsifier. Over a period of time the water layer between droplets in the floccules will thin and the droplets will coalesce. The coalescence cannot be reversed. Factors which force the droplets together such as settlement under gravity, evaporation of the water, shear or freezing will accelerate the flocculation and coalescence process, as does anything which reduces the charge on the droplets.

Lower viscosity asphalts coalesce more rapidly than high viscosity asphalts. Of course, eventually we want the emulsion droplets to coalesce after the asphalt emulsion has come in contact with the aggregate and been placed on the roadway. Setting and curing of emulsion are discussed in more detail below. (4)

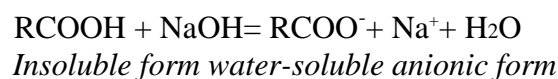
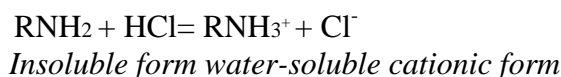
### ***1.3 Formulation of emulsion components***

Emulsions are made by mixing hot bitumen with water containing emulsifying agents and applying mechanical energy sufficient to break up the bitumen into droplets. The manufacturing system of the emulsion could influence the emulsion itself. It is clear that the manufacturing process may not only affect the physical properties of the emulsion but also affects the performance of the emulsion. (4)

Emulsification is opposed by the internal cohesion and viscosity of the bitumen and the surface tension of the droplet which resists the creation of new interface. Smaller droplets are favored by a high energy input, a low bitumen viscosity at the emulsification temperature and by the choice and concentration of emulsifier (which reduces the interfacial tension). In the most common process, the emulsifier is dissolved in the water phase of the emulsion, and this water solution or “soap” is mixed with the hot liquid asphalt in a colloid mill.

Emulsifiers are often supplied in a water-insoluble form to the emulsion producer and need to be neutralized with acid or alkali by the emulsion manufacturer to generate the anionic or cationic water-soluble form used to prepare the soap solution. The choice of the acid or alkali and the final pH of the emulsion influence the emulsion properties.

Hydrochloric acid and occasionally phosphoric acid are the acids used, and sodium and potassium hydroxide are the most common alkalis. Cationic emulsions are usually acid and anionic emulsions are typically alkaline (Table 1):



Some emulsifier types, like quaternary ammonium compounds and alkylbenzenesulphonates, have permanent head group charges and do not need to react with acids or alkalis (Table 2).

These products, as well as non-ionic emulsifiers, allow the formulation of emulsions which are neutral in pH.

Increasing emulsifier concentration decreases the reactivity of the emulsion. MS emulsions are generally formulated with the same emulsifiers as RS grades but at higher concentration (0.4%–0.8%). The emulsion producer can adapt the emulsion recipe to cope with reactive aggregates or high temperatures, generally by increasing the emulsifier concentration or blending emulsifiers of lower reactivity.

A wide range of chemistries have been used for asphalt emulsifiers. In addition to cationic, non-ionic, and anionic emulsifiers, there are products with amphoteric head group character which may adopt positive or negative charges depending on pH. (4)

CRS		CSS		Anionic RS		Anionic SS	
Asphalt	65	Asphalt	60	Asphalt	65	Asphalt	60
Tallowdiamine	0.2	Tallow diquaternary ammonium chloride	0.6	Tall Oil	0.3	Ethoxylated nonyl phenol	0.5
Hydrochloric acid, 35%	0.15			Sodium hydroxide	0.2	Lignins	0.5
Soap pH	1.5–2.5	Soap pH	3–7	Soap pH	11–12	Soap pH	10–12
Water	to 100	Water	to 100	Water	to 100	Water	to 100

**Table 1:** Typical emulsion recipes

Lipophilic Portion	Head Group	Counterion	Head Group Charge, pH2	Head Group Charge, pH11
Tallowalkyl-	$[-NH_2CH_2CH_2CH_2NH_3]^{2+}$	2 $Cl^-$	Positive	Neutral
Tallowalkyl-	$[-N(CH_3)_3]^+$	$Cl^-$	Positive	Positive
Nonylphenyl-	$[-O(CH_2CH_2O)_{100}H]$	None	Neutral	Nonionic
Tall oil-	$[-COO]^-$	$Na^+$	Neutral	Negative
Alkylbenzene	$[-SO_3]^-$	$Na^+$	Negative	Negative

**Table 2:** Chemistry of Asphalt Emulsifiers

## ***1.4 Advantages of uses of emulsions***

With viscosities in the range 0.5–10 Poise at 60°C, asphalt emulsions is of considerably lower viscosity than asphalt itself (100–4,000 Poise), allowing it to be used at lower temperature. Low temperature techniques for construction and maintenance reduce emissions, reduce energy consumption, avoid oxidation of the asphalt are less hazardous than techniques using hot asphalt. They are also more economical and environmentally friendly than cold techniques using cut back asphalts. (4)

The environmental benefit of asphalt emulsion is particularly positive when used for in-place or on-site techniques which avoid the energy usage and emissions associated with heating, drying, and haulage of aggregate. The construction of a roadway with cold techniques has been calculated to consume approximately half the energy of one of similar bearing capacity made with hot-mix asphalt (HMA). An environmental impact analysis (EIA) technique called “eco-efficiency” has been applied to emulsion maintenance techniques (microsurfacing and chip seal) and it was concluded that the emulsion system had less environmental impact than a thin hot-mix overlay.

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

## ***1.5 The setting process***

Emulsified asphalt must revert to a continuous asphalt film in order to act as cement in road materials. This involves flocculation and coalescence of the droplets and removal of the water (Figure 4). Evaporation and absorption of water by the aggregate may be the main breaking mechanism for very slow-setting emulsions, but in most cases chemical reactions between the aggregate and the emulsion contribute to the emulsion setting and it is not necessary for all the water to evaporate before curing takes place. (4)

The strength of the reaction of emulsion with aggregate is in many cases sufficient to squeeze the water from the system. Clean water can be seen separating from the mixture. The speed of these setting and curing processes depends on the reactivity of the emulsion, the reactivity of the aggregate and environmental factors, such as temperature, humidity, wind speed, and mechanical action. Less viscous asphalts tend to give faster coalescence. It may take a few hours in the case of a chip seal to several weeks in the case of a dense cold mix for the full strength of the road material to be reached.

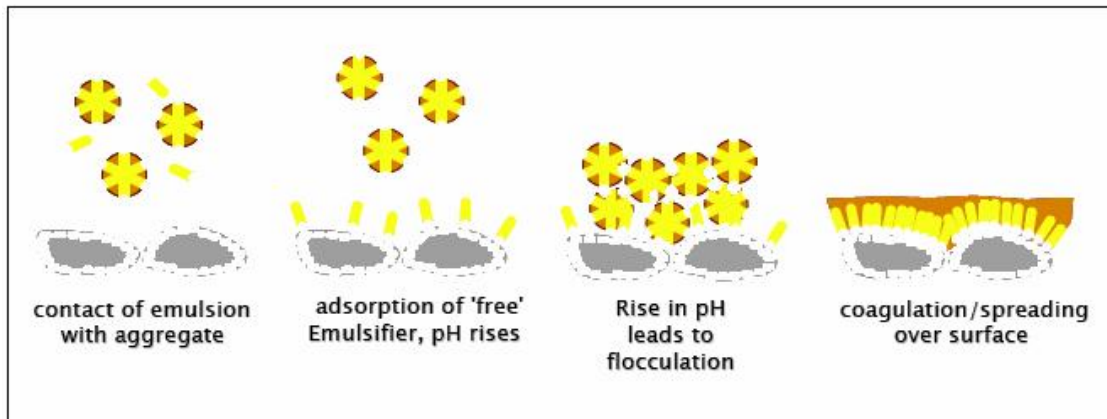
Important factors are changes in pH caused by reaction of the aggregate with acids in the emulsion, adsorption of free emulsifier onto the aggregate surface, and flocculation of the emulsion droplets with the fines. The relative timescale of flocculation (setting) and coalescence (curing) depends on the system, but in general flocculation is the more rapid process in which some water can be expelled from the system and some cohesive strength develops, followed by a slower coalescence process which results in a continuous asphalt phase. This asphalt phase must also adhere to the aggregate.

Coalescence is an inversion process; the O/W emulsion is transformed into a W/O type which then slowly loses its internal water phase. This inversion process is favored as the ratio of asphalt to water in the system increases. The tendency for an emulsion to invert can be determined in laboratory tests and has been related to curing behavior in the field.

Aggregates take up a characteristic surface charge in water which depends on the nature of the minerals, the pH, and the presence of soluble salts. So-called “acid” aggregates high in silica tend to take up a negative charge. Some aggregates, like carbonates, and fillers, like cement, may neutralize acid in cationic emulsions causing the pH to rise and the emulsion to be destabilized. Anionic emulsions may be destabilized by soluble multivalent ions. We can consider two extreme cases of emulsion breaking. In the case where the charge on the emulsion droplets is quickly destroyed by pH changes, for example, then the emulsion very quickly flocculates and coalescence begins to occur at a slower rate. This rate is dependent on the viscosity of the binder, as well as environmental conditions; coalescence is slower with high viscosity asphalts and lower temperatures. At the other extreme where the emulsion droplets remain charged, loss of water, either by evaporation or by absorption of water into porous aggregate, eventually forces the droplets close enough for attractive forces to predominate, forcing out water and starting the coalescence process. The attractive

forces between the droplets can generate significant cohesion even before coalescence occurs.

In a simplified process (Figure 5) of the setting of a RS cationic emulsion where the aggregate does not contain significant fines; important stages in the setting process can be considered as follows:



**Figure 5:** Possible stages in the setting of a cationic emulsion

1. Free emulsifier adsorbs onto the (oppositely charged) mineral surface, which neutralizes some charge on the surface while at the same time making the surface somewhat lipophilic. Too high a free emulsifier concentration in relation to the surface area of the aggregate can actually reverse the charge on the minerals and so inhibit the setting of the emulsion.
2. Minerals neutralize acids in the emulsion, causing loss of charge on the emulsion droplets, leading first to flocculation of the asphalt droplets and then to a slower coalescence of the droplets.
3. Water is absorbed by the mineral, as well as evaporates from the system.
4. Droplets in contact with the mineral spread on the surface, especially that surface made lipophilic by adsorbed emulsifier, eventually displacing the water film on the aggregate surface. In the breaking of SS grades, where the aggregate contain high content of fines, hetero flocculation of the droplets of asphalt and the oppositely charged fines may occur, which is sufficiently strong to squeeze out water and form an asphalt mastic. A similar situation is achieved in

microsurfacing where filler is intentionally added to initiate setting. Mechanical action, such as compaction or traffic, may squeeze the droplets together, promoting coalescence and squeezing water out of the coalesced film. In practical situations too early coalescence of the asphalt droplets can hinder final curing by skin formation reducing the evaporation of water. Coalescence throughout the asphalt emulsion film, before water is trapped in the system, is promoted by smaller asphalt droplets with narrow size distribution. Too early coalescence of asphalt droplets in some systems can interfere with the formation of a composite binder formed from latex and asphalt, which depends on latex curing before asphalt.

## ***1.6 Components of an emulsion***

The components of an asphalt emulsion include the following. (4)

### ***1.6.1 Asphalt***

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

### ***1.6.2 Diluents and Fluxes***

Other refinery products that may be blended with basic asphalts without altering their properties include, but are not limited to raffinates, vacuum residuum, asphaltenes, and petroleum resins. The addition of any refinery streams or products other than these, and all no refinery products introduced into asphalt in significant



quantities, may affect asphalt properties and should be considered prior to emulsion manufacture.

### **1.6.3 Water**

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

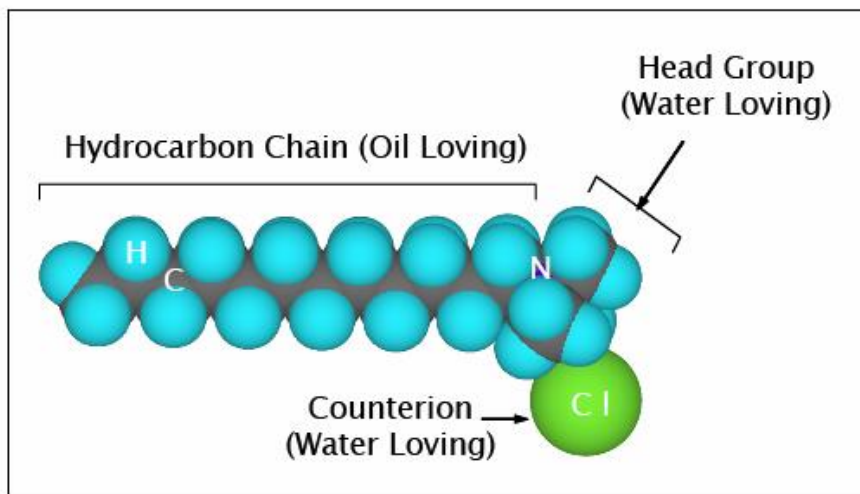
### **1.6.4 Surfactants**

Surface active agents (surfactants), also known as emulsifiers or emulsifying agents, are needed to provide the stability required over time. The stability of the emulsion determines its appropriate use. Surfactants are chemical compounds with a surface activity which, when dissolved in a liquid, especially water, lowers its interfacial or surface tension by preferential adsorption at the vapor/liquid surface or other interfaces. (4)

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

The surfactants are characterized by possessing two different parts in the molecule, one fatty molecule, lipophilic or non-polar with a large bitumen affinity and other hydrophilic or polar; with have a high affinity for the water. This double characteristic allows it to place in the interphase water-bitumen with the lipophilic part integrated into the bitumen and the polar one in the water (figure 6):



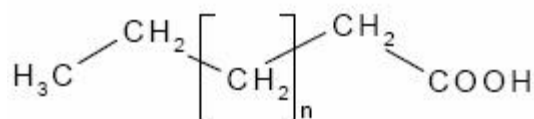


**Figure 6:** Cationic emulsifier molecule

Emulsions are classified as depending on the charge given by the surfactant that provides cationic or anionic charge to the emulsion. Their properties are different and also their ability to employment. Today, 95% of the emulsions produced in Spain are cationic and only 5% are anionic. (2)

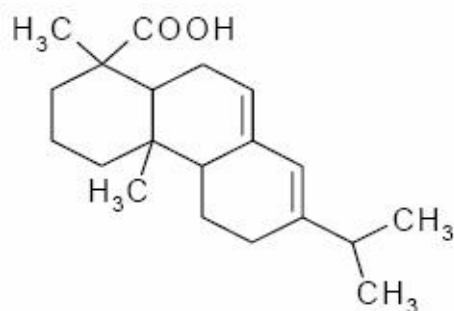
Anionic emulsifiers are those which have polar part negatively charged. They are usually sodium or potassium fatty acids (steering) or resinous (tall oils). Sometimes organic acids precedents from synthesis or other precedents from wood like lignin are also used.

The stearins or fatty acids are precedent from the hydrolysis of animal fats (tallow or fish oils) or vegetable one (palm oil, palm kernel or pomace). They are molecules with acid radicals and chains from 12 to 22 carbon atoms, either saturated or unsaturated.



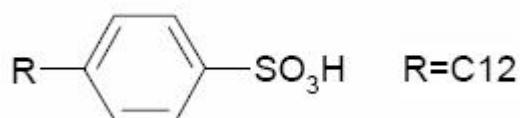
**Figure 7:** stearin molecule

Resin acids are derived from wood distillation. They present mixtures from cyclic compounds with double links and a carboxylic group. The principal compound is the abethic acid.



**Figure 8:** resin acid molecule

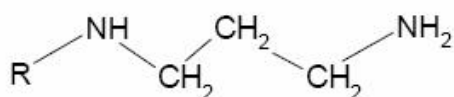
Acid derived synthesis types usually are dodecylbenzenesulfonate acid.



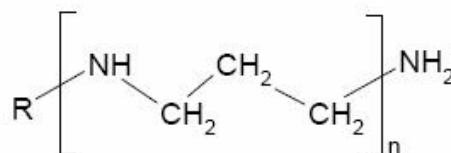
**Figure 9:** dodecylbenzenesulfonate acid

The emulsifiers which have positive charge are called cationic emulsifiers. They are primarily fatty polyamine and diamins (in some cases also amidoamins or imidazolins) and ammonium quaternary salts, salinized in great majority cases with hydrochlorhidric acid.

The fatty polyamine and diamins are synthesized by the reaction of a fatty acid (usually tallow beef) with ammonium. This reaction gives a primary amine that posteriorly is condensed with acrylonitrile and after that hydrogenated to obtain a diamina. If the process is repeated different times we obtain polyamines.



**Figure 10:** Diamine molecule



**Figure 11:** Polyamine molecule

Amidoamins and imidazolins are obtained by the reaction of a synthetic fatty acid with short chain polyamines such as diethylamin or triethylamin.

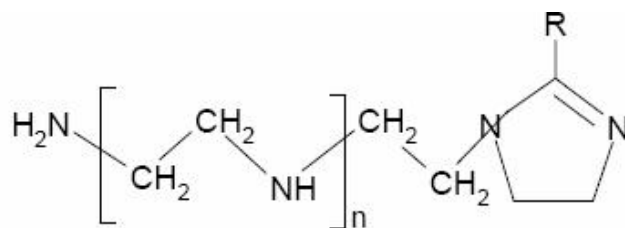


Figure 12: amidoamins molecule

Quaternary ammonium salts are obtained by reaction of an amine with a methylating agent (methyl chloride or dimethyl sulfate).

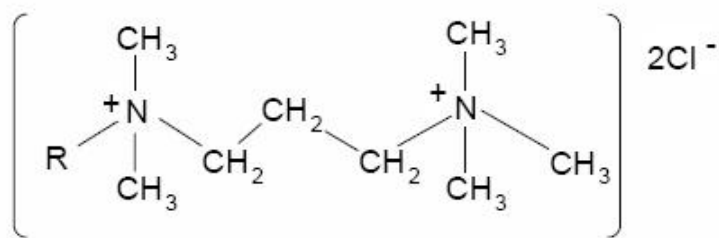


Figure 13: quaternary ammonium salts

In all cases, except for the quaternary ammonium salts, the emulsifiers, as we indicated above, must be hydrolyzed, the anion ones with a base (sodium or potassium) and the cationic ones with an acid (typically hydrochloric or acetic).

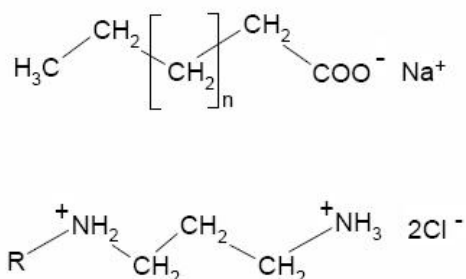
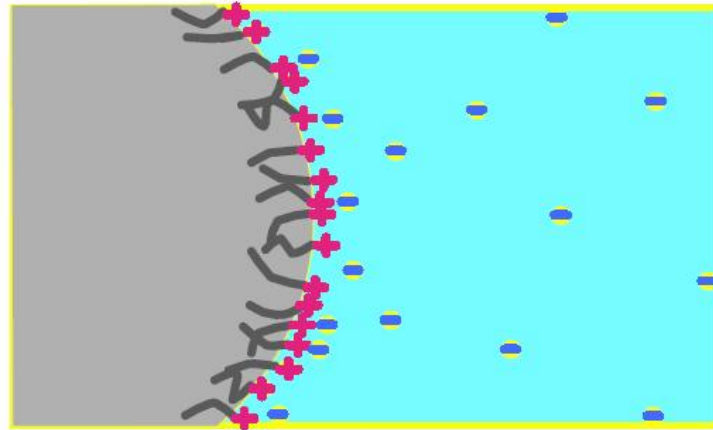


Figure 14: Quaternary ammonium salts hydrolysis

It is then, after the formation of the salt, when the emulsifier is active and can perform its function. The lipophilic (its hydrocarbon chain) is introduced in the bitumen, while its hydrophilic part (the polar group) is oriented towards outside of bitumen, to the water.



**Figure 15:** Origin of charge on asphalt droplets. Emulsifier concentrates at the interface.

### 1.6.5 Acid

As emulsifiers are insoluble in water, it is necessary to convert them into salts so as to dissolve them in the dispersing phase. This is generally done by reacting with acid, most often hydrochloric acid in a 20°C to 22°C solution. Acid dosing is the regulatory factor which determines final emulsion pH. (4)

## 1.7 Manufacturing parameters

The parameters to consider in the manufacture of asphalt emulsions are outlined below. (4)

### 1.7.1 Dispersion Energy

Emulsion dispersion is caused by mechanical energy and physicochemical energy. The mechanical energy (provided by the mill) divides the asphalt into fine particles and

the emulsion fineness increases with fractioning capacity (mill capabilities). The physicochemical energy is provided by the emulsifier and must:

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

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

### ***1.7.2 Particle Size Distribution***

Particle size and particle size distribution are important variables and are controllable with formulation, raw materials, and the equipment used to manufacture the emulsion. Many of the processes of breaking and curing are directly dependent on the particle size and the particle size distribution. The importance of particle size in emulsions has been discussed in many papers that we are going to comment later. It is a determinant of emulsion stability, coating, break rate, and cure rate. Methods to improve particle sizing of emulsions by formulation and adjustment of asphalt chemistry are studied nowadays by different authors. These methods usually involve improvement of the dispersing phase, doping of asphalt with surfactants, and tailoring asphalt composition and optimization of manufacturing conditions. The intention is to improve formation and dispersion of asphalt particles by the mill and stabilize the resulting emulsion. The mill and milling process are the main determinants of initial particles size for a given asphalt–emulsifier system as particle size is determined by the shear in the mill and mill residence time. The relationship of the milling process to particle size can be expressed by:

$$\text{Shear rate} = (2\pi \quad RV / 60 \text{ E}) \quad \text{Eq.1}$$

Where,

R = colloid mill radius (rotor and stator combination);

V = velocity of rotation or rotation speed (rpm); and

E = gap dimension.

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

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

$$\text{Shear rate} = (2\pi \text{ RV} / 60 \text{ E}) \text{ Mf} \quad \text{Eq.2}$$

Where

Mf = mill factor, and the mill factor is the increase or decrease in shear created by the mill configuration and tooling.

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

### ***1.7.3 Component Viscosity and Temperature***

Often the mechanical energy required providing asphalt particles with the correct size and concentration is aided by increases in the temperature of the hydrocarbon phase (asphalt). In other words, in order to enable the asphalt binder to properly disperse in the aqueous phase, it is necessary that its viscosity be relatively low. From practical colloidal mill experience, the optimal viscosity is 200 centipoises, which is obtained by maintaining the asphalt at a temperature that yields this viscosity; it is called the equiviscous temperature (EVT). The EVT of some common asphalts are given in Table 3: (4)

Asphalt Grade	Approximate EVT
AC-5	140°C (284°F)
AC-10	150°C (302°F)
AC-30	160°C (320°F)
7–9 dmm	185°C (365°F)

**Table 3:** Equiviscous temperature of common asphalts

The EVT limit of 200 centipoises is obtained from practical experience. In actual practice we know this works because emulsions from the asphalts listed above are typically produced at these temperatures. If these temperatures are significantly exceeded, unwanted and undesirable effects may occur. In fact, if the emulsion at the mill outlet is at a temperature higher than 100°C (212°F) the emulsion aqueous phase will boil, as water typically has a boiling point of 100°C (212°F). At higher altitudes the boiling point of water will be lower. A good rule of thumb for emulsion manufacturing purposes is to not exceed 95°C (203°F) at the mill outlet.

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

#### 1.7.4 Emulsion Temperature

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

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

Eq.3

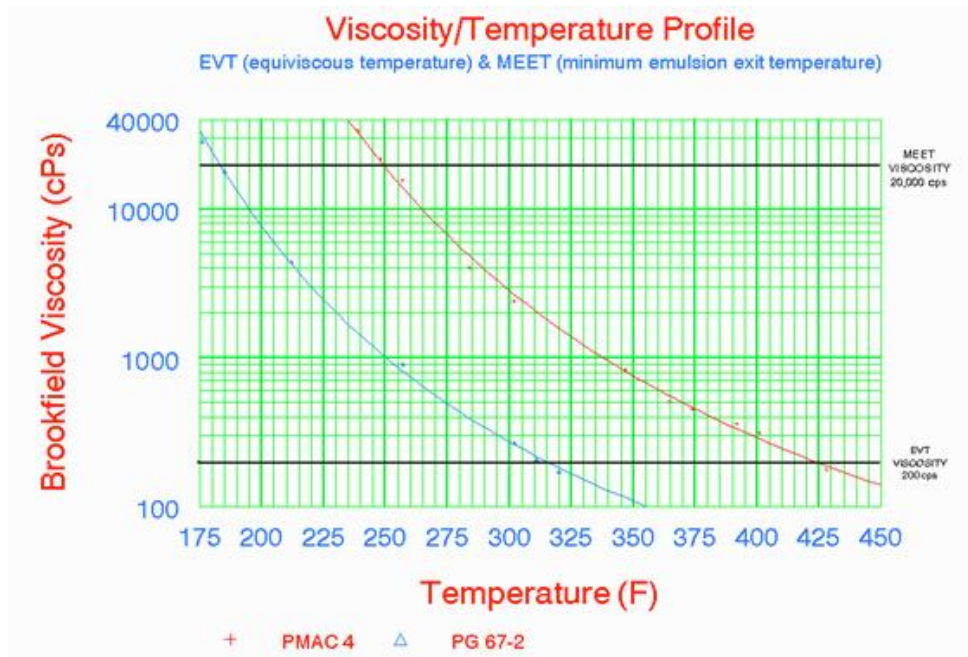
As the boiling point of water varies directly with respect to decreases and increases in pressure of its environment, the boiling point of water can be increased by increasing the pressure of its environment. That is, if a certain amount of pressure is maintained on the emulsion, until the temperature is below its boiling point, boiling of the emulsion can be prevented. Therefore, if temperature requirements dictate, e.g., minimum soap temperature and asphalt EVT, the emulsion can be manufactured under pressure without fear of boiling the emulsion. (4)

#### **1.7.5 Pressurized Manufacturing**

If a colloidal mill is used with relatively high Emulsion Viscosity Temperature value, EVTs, of some asphalt binders or minimum soap temperatures the conventional manufacture system require that the emulsions must be manufactured under a pressure of a few bars (30–60 psi) to satisfy the mandatory parameters corresponding to these components and simultaneously prevent boiling of the emulsion. The EVT of asphalt and its importance in the manufacture of asphalt emulsions has been presented. It is obvious that another important emulsion manufacturing parameter is the emulsion exit temperature or what is defined as the minimum emulsion exit temperature (MEET). MEET is considered to be equivalent to the temperature of the asphalt where the viscosity is approximately equal to 20,000 centipoises. As with EVT this limit is obtained from practical experience. It is a common belief that if the emulsion outlet temperature is maintained at or above the MEET, emulsion stability is improved during manufacturing, cooling, and storage. (4)

The EVT and MEET can be obtained from a viscosity profile of the asphalt. An example of rotational viscosity profiles of a neat AC-30 (PG 67-22) and a 4.0% styrene-butadiene-styrene (SBS) -modified asphalt (PMAC-4) are given in figure 16:

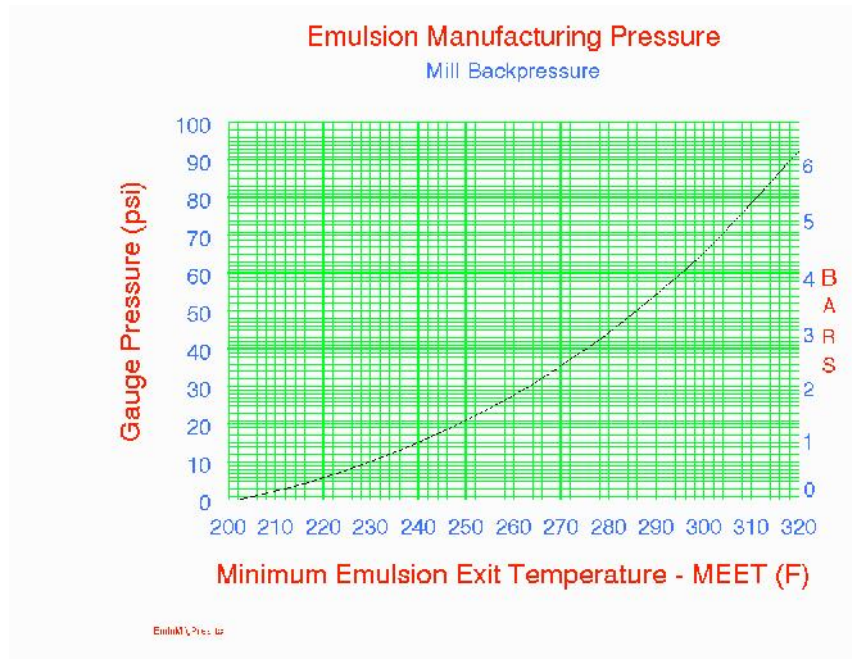




**Figure 16:** Viscosity/temperature profile with EVT and MEET of two different asphalts.

From Figure 16, the MEET can be obtained as the point where the viscosity of the asphalt is equal to 20,000 centipoises; for the PG 67-22, the MEET equals 82°C, and for the 4.0% SBS-modified asphalt, the MEET equals 118°C. The EVT can be obtained as the point where the viscosity of the asphalt is equal to 200 centipoises; for the PG 67-22, the EVT equals 177°C, and for the 4.0% SBS modified asphalt, the EVT = 218°C (425°F). (Note: Often it may be necessary to actually heat asphalt to about 6°C higher than the EVT to ensure that the asphalt is at EVT at the milling surfaces.)

An emulsion manufactured from the PG 67-22 represented in Figure 16 could be manufactured under normal atmospheric conditions, while an emulsion manufactured from the 4% SBS asphalt must be manufactured under pressure if we use colloidal mills. As a general rule, if the MEET is greater than 95°C the emulsion will have to be produced under pressure. The amount of pressure required can be obtained by consulting steam data temperature tables using the absolute pressure value plus 20%. It should be noted that this pressure is absolute pressure and not gauge pressure; gauge pressure would be equivalent to absolute pressure less 1 bar (14.5 psi). For demonstration purposes, consider the SBS-modified asphalt presented in Figure 16. The manufacturing pressure of the SBS-modified asphalt emulsion based on the MEET of 118°C can be obtained from figure 17:



**Figure 17:** Pressure versus temperature curve for determination of mill back pressure.

From Figure 17 it can be seen that the emulsion manufacturing pressure for the MEET of 118°C is approximately 1.3 bars (19 psi) gauge pressure. At this point, it is important to note that the actual emulsion exit temperature for this asphalt may be higher than 118°C depending on the soap temperature requirements and the recommended asphalt temperature of 218°C based on EVT. The mill outlet temperature may also be slightly higher than calculated from Figure 16 as the milling process, mill resonance time and pressure effects will contribute to the final emulsion outlet temperature.

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

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

**Eq4**

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

### **1.7.6 Component dosing**

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

Understanding this, consider a 65% residue emulsion with the 218°C EVT asphalt from Figure 16 and a soap temperature of 60°C. This emulsion would have an emulsion exit temperature of 136°C, from Equation 3, which would require an emulsion manufacturing gauge pressure of 2.8 bars (Figure 17). Note that the actual outlet temperature could possibly be 10–15 °C higher due to milling energy and pressure effects.

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

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

## **1.8 Concentrated bitumen emulsions**

Highly concentrated or high-internal-phase-ratio emulsions are characterized by disperse phase volume fractions,  $\phi$ , higher than the critical value  $\phi_c = 0.74$ , for the most compact arrangement of uniform spherical droplets. At this critical volume fraction an emulsion is expected to invert. However, emulsions can retain the original oil-in-water (O/W) or water-in-oil (W/O) structure at volume fractions exceeding the critical

value because of two phenomena: polydispersity and droplet deformation. Consequently, the structure of this type of emulsions consists of polyhedral droplets, with typical radii of a few microns, separated by thin films of continuous phase, a structure resembling gas-liquid foams. Their rheological properties range from elastic (solid like) to viscoelastic depending on the system components, composition variables and temperature, having a gel appearance. (6)

In concentrated emulsions, dispersed droplets are very close one of each other, separated only for a very narrow film of continuous phase. (6)

Each interfacial film is subjected to a compression pressure which is counteracted by pressure of disunity due to:

- Attraction forces of Van der Vals
- Repulsion electrostatic forces
- Short-range forces

The balance of these forces depends on the stability of the emulsion.

### 1.8.1 Theoretical considerations

We could define the free Gibbs Energy during the formation of an emulsion as:

$$\Delta G (f) = \sigma \Delta A - T \Delta S (conf) \quad \text{Eq. 5}$$

Where:

$\sigma$  = *Interfacial tension*

$\Delta A$  = *increase interfacial area*

$T$  = *Absolute temperature*

$\Delta S (conf)$  = *change conformational entropy of the system*

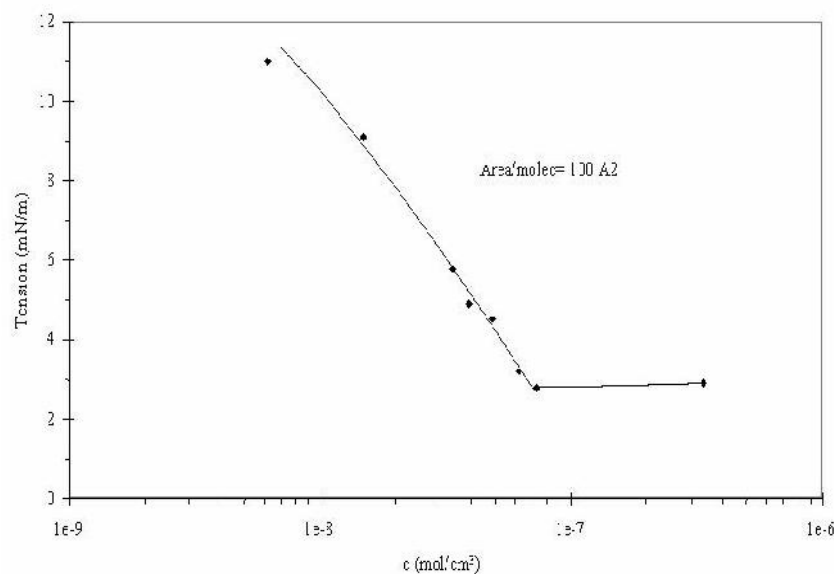
$\sigma \Delta A$  Is the work we have to give to the system in order to expand the interface during the emulsification process. If the interfacial tension decreases the energy necessary for the process is fewer. And the presence of a surfactant in the process decreases this interfacial tension.

**$T\Delta S$  (conf)** Represent the increase of the entropy as a result to convert one component in a lot of droplets.

If the  $\sigma\Delta A$  is higher than  $T\Delta S$ ;  $\Delta G$  (?) is higher than 0, so, the process is **no spontaneous**, so the stability of the emulsion is determinate by kinetic effects.

It is observed that the interfacial tension ( $\sigma$ ) decreases with surfactant concentration due to the adsorption of it at the interface. Eventually, we could reach a surfactant concentration, from which  $\sigma$  remains constant. This concentration is known as critical micelle concentration (CMC) and corresponds to the concentration at which the interface is saturated with the surfactant and it begins to form aggregates or micelles in the aqueous phase. (6)

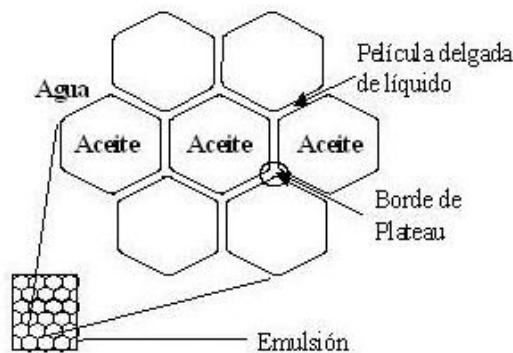
In Figure 18 the interfacial tension of a bitumen/water system, as a function of the water phase concentration, from a surfactant polyethoxylated nonylphenol type containing 17 units of ethylene oxide (UOE) per molecule can be seen. It is observed that the interfacial tension ( $\sigma$ ) decreases with surfactant concentration due to the adsorption of it at the interface.



**Figure 18:** Interfacial tension ( $\sigma$ ) for the bitumen/water system as a function of the concentration (C) of polyethoxylated in the water phase.

### 1.8.2 Polyhedral structure of concentrated emulsions

The highly concentrated emulsions are characterized by fractions of disperse phase volumes greater than 0.74, which corresponds to the maximum packing of monodispersed spheres. Therefore dispersed droplets are very close to each other, separated by a very thin film continuous phase formed at each point where the drops are touched. (6)



**Figure 19:** Polyhedral structure of a concentrated emulsion

Each interfacial film is subjected to a compression pressure, which is counteracted by a pressure deboning, generated within the interfacial film, due to the existence of attractive forces of Van der Waals, electrostatic repulsion forces. The balance between these forces depends on the stability of an emulsion. The presence of a monolayer of surfactant adsorbed on the surface of dispersed droplets in the emulsion is responsible for imparting proper magnitude deboning pressure and thus maintains stability and other properties of these systems.

In emulsions, it is of fundamental importance to control the stability and rheological properties during the formation process and thereafter during storage and transport. By careful control of the nature and magnitude of the forces of interaction between drops, it is possible to control the properties of these systems.

The stability of an emulsion can be measured by determining the time between its formation and the complete separation of the phases.

Ideally, the concentrated emulsions (more than 70% internal phase) consists of an agglomeration of polyhedral droplets separated by a very thin film continuous phase (Figure 19). Three interfacial films converge in Plateau border. The curvature of the

surface of the droplet at the edge of Plateau generates a pressure difference between the liquid film and the interfacial Plateau edge, causing a flow of continuous phase from the liquid film to the edges of interfacial Plateau. Thus, the interfacial liquid film becomes increasingly thinner with time and can eventually break down, at which time the emulsion becomes unstable.

Thus, the stability of an emulsion depends on the stability of the interfacial film of liquid, which in turn depends on the pressure deboning. Deboning pressure is a hydrostatic pressure inside the liquid film interface, which acts perpendicular to the surface of the droplets. This pressure is opposed to the contact between the droplets and therefore their coalescence. In other words, the pressure deboning is a force per unit area which is opposed to the drain of the continuous phase liquid contained in the interfacial film.

The main forces acting within the liquid interfacial film which contribute significantly to the pressure of disunity are: London forces, Van der Waals and electrostatic repulsion forces.

These forces, whose magnitudes are substantially modified by the presence of a surfactant adsorbed on the dispersed droplets surface, achieve their maximum efficiency, when the thickness of the liquid film interfacial is equal to or less than about 1000 Å.

The rheological properties of concentrated oil in water emulsions play an important role in determining their suitability for a particular application. In general, oil in water emulsions shows a very typical rheological behavior. Thus, at low volume fractions of the dispersed phase, emulsions behave as Newtonian fluids.

However, when the volume fraction of the dispersed phase is increased, this behavior turns pseudo plastic, showing viscoelasticity in some cases. In order to design and manufacture emulsion- based materials that are capable of exhibiting this wide range of rheological characteristics, it is necessary to understand the factors that determine emulsion rheology.

In highly concentrated emulsions, the dispersed droplets are very close to each other, and separated by thin films of continuous phase, formed at each point where droplets touch. Each film is under a compressive pressure, counteracted by a disjoining pressure that is developed within the film, as a result of the existing attractive van der Waals forces, as well as electrostatic, stearic or other repulsive forces, so that equilibrium is maintained.



The presence of a surfactant layer, adsorbed on the surfaces of dispersed droplets in the emulsions, is responsible for conferring a sufficiently strong disjoining pressure, and for controlling the stability and the rheological properties of such systems.

The formation of stable emulsions that can be stored for long periods of time, without deterioration, is an important issue in many industrial activities. Unfortunately, this task is rather difficult, since emulsions are thermodynamically unstable systems that break down over time through a variety of physicochemical instability mechanisms, such as: gravitational separation, coalescence, flocculation, inversion, and Ostwald ripening, among others. These destabilizing effects promote changes in the mean droplet diameter and in the droplet diameter distribution, which may cause significant alteration of the emulsion rheology. Thus, an adequate formulation is of paramount importance for achieving long term stability in emulsions and for preserving their rheological properties.

One of the most powerful methods of investigating interaction between droplets in concentrated emulsions is the measurement of the viscoelastic properties of these systems. By measuring the viscoelasticity as a function of dispersed phase volume fraction or as a function of some other parameters, it is possible to gather information that can be interpreted in terms of the interactions between droplets. By modifying these interactions, bulk rheological properties of emulsions can be modified too.

Over the last 20 years, increasing interest has been focused on highly concentrated bitumen in water emulsions, due to the potential use of these systems, as vehicles for handling those extremely viscous hydrocarbons.



## 2. State of the art.

Bitumen emulsions are a little studied field, let alone the highly concentrated bitumen emulsions one's.

We have found very few papers related with this kind of products. Most of the information found is patents related with the manufacture systems. There are very few papers related with the influence of the raw materials in the final product, the stability of the emulsions formulated, the final characteristics of the emulsions, or the viscosity behavior. And almost nothing related with the influence of the main product (bitumen) in the formulation powder or final properties, ergo which is the best bitumen we could use to formulate highly concentrated bitumen emulsions, which are the bitumen chemical characteristics which influence more to obtain a good emulsion, etc.

Most of the papers and patents find are focused on the physical parameters focused on how could manufacture process: flow rate, rotor speed, emulsification temperature, surfactant concentration, etc. influence on the main diameter particle size.

We have organized this state of the art in a chronological order. We have organized the information found related with the HIPR method which is the aim of our work.

In order to understand the best as possible the emulsion field we have introduced the conventional manufacture method, explaining the benefits and the limitations of this method, so it will be easier to understand the benefits and the necessary to find another manufacture method, HIPR one.

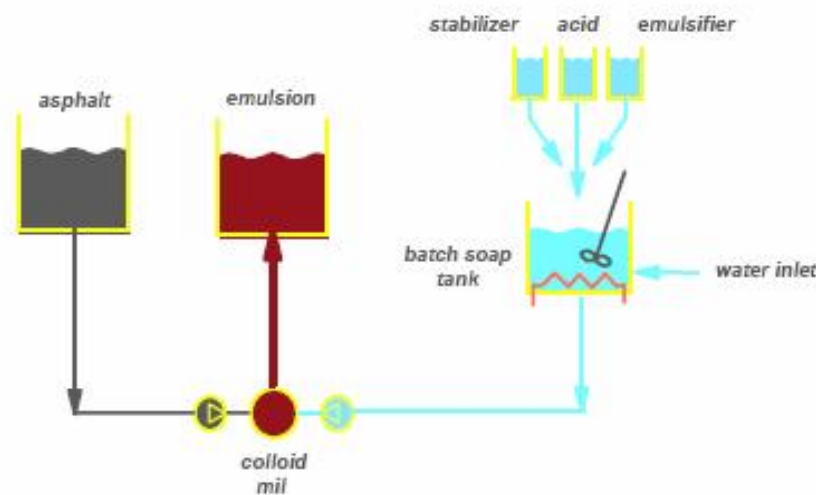
### 2.1 *Traditional method:*

Traditionally, bitumen emulsions have been obtained by both continuous and batch processes in colloid mills, rotor-stators and homogenizers as described in patents DE3818453 (7) and US4773883 (8). In these equipments, both the oil phase (bitumen) and the water phase are added at the same time (all at once) and are passed through a high-speed agitation chamber. This method is known as "direct emulsification" due to the high shear and in general particle size is reduced by increasing the energy of agitation. Thus the corresponding emulsions are currently prepared by hot injection. (9)

Generally, the bitumen is heated up to a temperature over 120 °C while the continuous phase, usually water, is also heated to approximately 60 °C. The mixture of bitumen and the aqueous phase are injected into a turbine under a very high rate of

agitation, of the order of 5,000 revolutions per minute and under a pressure that can reach up to 3 atmospheres.

As a consequence of this type of treatment, bitumen emulsions generally have a concentration that does not exceed 70% in weight of bitumen, a significant average particle size (typically over 5  $\mu\text{m}$ ) and also high polydispersivity. Emulsions obtained in this way, with a broad particle size distribution, and therefore with a high number of large sized drops ("distribution tail") have limited storage stability.



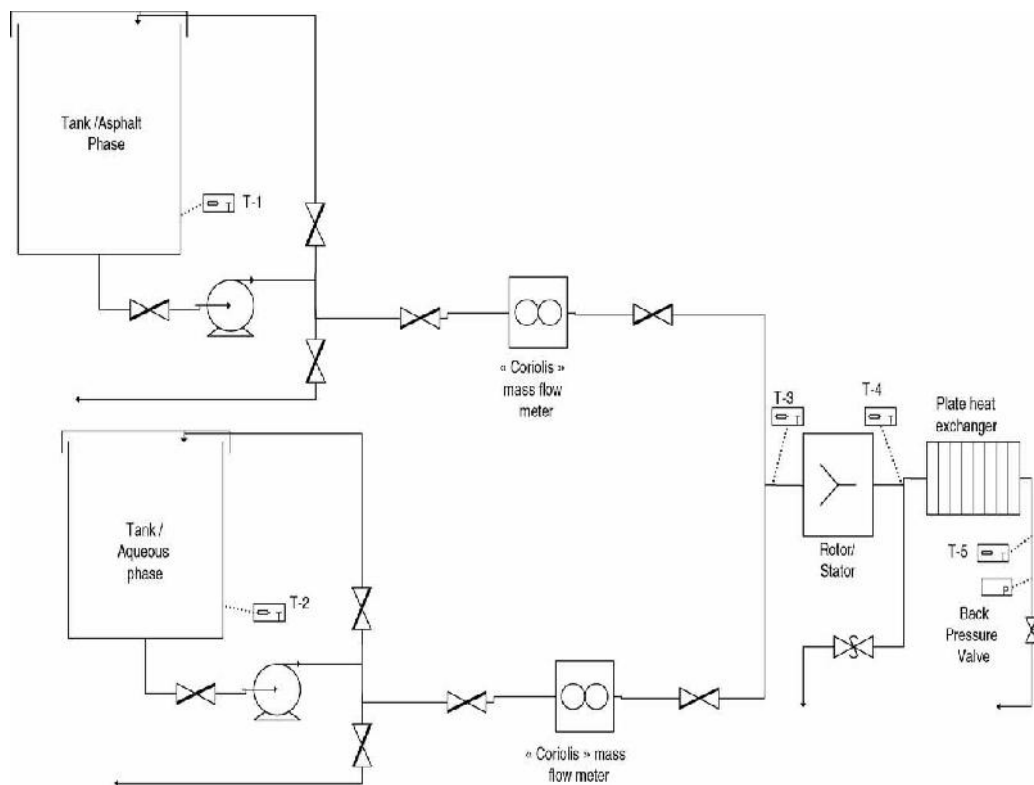
**Figure 20:** colloidal mill plant

Summarizing, this procedure therefore has several drawbacks:

- It does not allow concentrated emulsions prepared with residual bitumen content above 70%.
- There are not satisfactory results in terms of monodispersity.
- The average droplet size in the emulsion is generally bigger than 5  $\mu\text{m}$  and it's very heterogeneous.
- The storage stability and breaking index of such emulsions are difficult to control under the manufacturing conditions.

All this parameters are very well studied and summarized in Gringras et al. paper. (10). In 2005 Gringras et al. present a very interesting paper about the effects of process parameters on bitumen emulsions. The authors made the experiments in a continuous pilot scale rotor-stator. Gringras et al. have studied the effects of the following parameters: temperature of the aqueous phase and bitumen, the rotor speed, the dispersed phase content, the bitumen grade and the emulsion flow rate. They also compared the Sauter diameter ( $d_{32}$ ) with those available in the literature of emulsification.

The continuous emulsification process rig used in the work is shown in figure 21. In the experiments, the emulsification temperature was set by regulating independently the temperature of the bitumen and the continuous phase in their respective tank. The emulsification temperature is monitored at the outlet of the inline mixer. The pressure was adjusted manually with a back pressure valve between 0 and 6 barg. The flow rate in each line was controlled in feedback mode with a control loop between the pump and the mass flow meter. The emulsification was performed with a rotor-stator machine (Silverson) composed of a four flat blades agitator (rotor) and a cylindrical perforated plate (stator) with 800  $\mu$ m round holes. The rotor diameter is 5 cm and its speed was adjusted between 0 and 5200 rpm. (10)



**Figure 21:** Process flow diagram of the emulsification rig.

The continuous phase was composed of tapwater, cationic surfactant and HCl. The acid was added to solubilize the surfactant in water and to polarize positively the “head” of the surfactant molecule in order to obtain a cationic emulsion. The pH was set at  $2 \pm 0.05$ . The surfactant concentration was set at 13.9 ml of surfactant per liter of tapwater. With this procedure, if the dispersed phase content is modified, the surfactant concentration in the emulsion also changes. Hard and soft bitumen grades were used in the dispersed phase with a penetrability of 160/220 (soft bitumen) and 10/20 (hard bitumen). The penetrability of the bitumen was obtained with a standard test (ASTM D-5). Emulsion samples were taken when a steady state operation was reached (steady bitumen and aqueous phase flowrates, constant rotor-stator outlet temperature). The droplet size distribution and  $d_{32}$  were measured with a laser granulometer (MastersizerS, Malvern Instruments). Table 4 summarizes the process and formulation parameters considered in the work. (10)

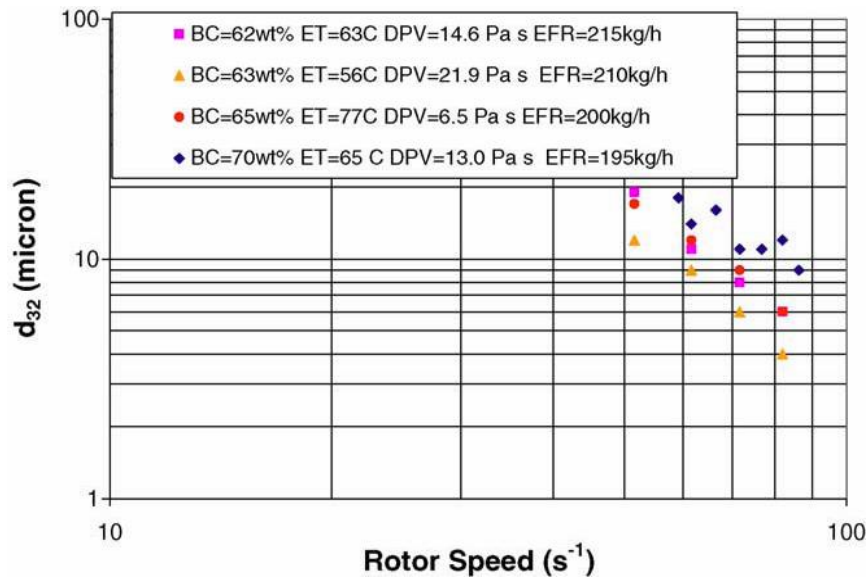
Process parameters investigated

Process parameters	Unit	Range
Rotor speed	s <sup>-1</sup>	52–87
Emulsion mass flow rate	kg/h	90–400
Bitumen temperature	C	70–140
Aqueous phase temperature	C	30–90
Bitumen content or dispersed phase content	wt. %	55–75
Bitumen grade	1/10mm	10/20, 160/220

**Table 4:** Process and formulation used in Gingras work.

1. Effect of the rotor speed on the droplet diameter size:

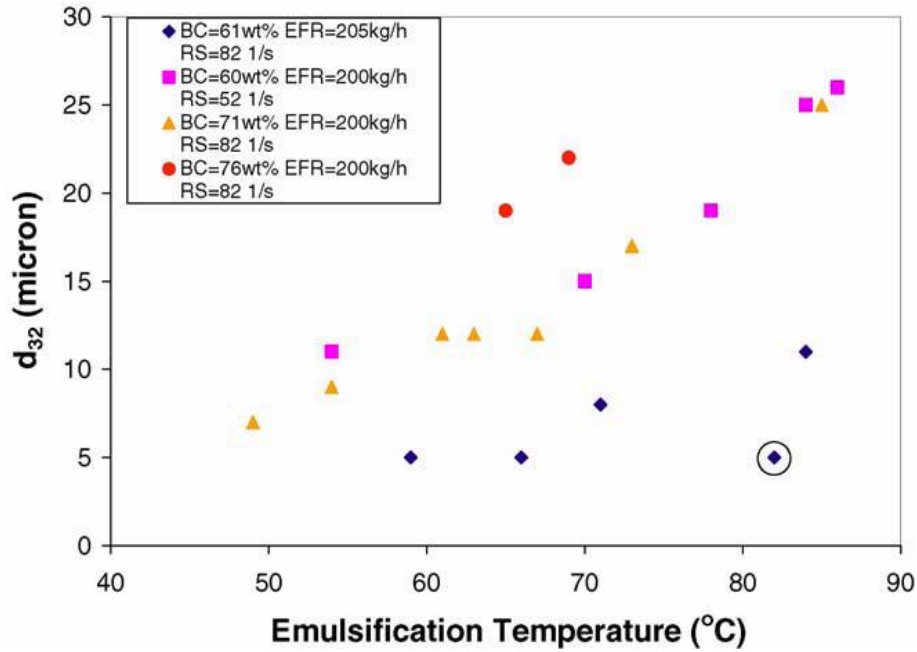
It can be seen that the droplet size decreases linearly (on a log–log-plot) with respect to the rotation speed. We could understand BC as Bitumen Concentration or dispersed phase content, ET as emulsification temperature, DPV as dispersed phase viscosity and EFR as emulsion flow rate in the graphic.



**Figure 22:** Effect of the rotor speed on the droplet size for 160/220 bitumen grades.

## 2. Effect of the temperature of the aqueous phase and bitumen:

Fig. 23 shows the effect of the emulsification temperature on the Sauter diameter. It can be seen that the droplet size increases with the emulsification temperature. The viscosity of the bitumen varies significantly in the range of the emulsification temperature tested. For a cationic emulsion as used in this work, changing the emulsification temperature is equivalent to modify the dispersed phase viscosity. Harder bitumen was emulsified to verify the influence of  $\mu_d$ . Many difficulties were encountered to emulsify highly viscous bitumen. The bitumen grade emulsified for the circle lozenge is 10/20. And BC is the bitumen concentration or the dispersed phase content; EFR is the emulsification flow rate and finally RS is the rotor speed.



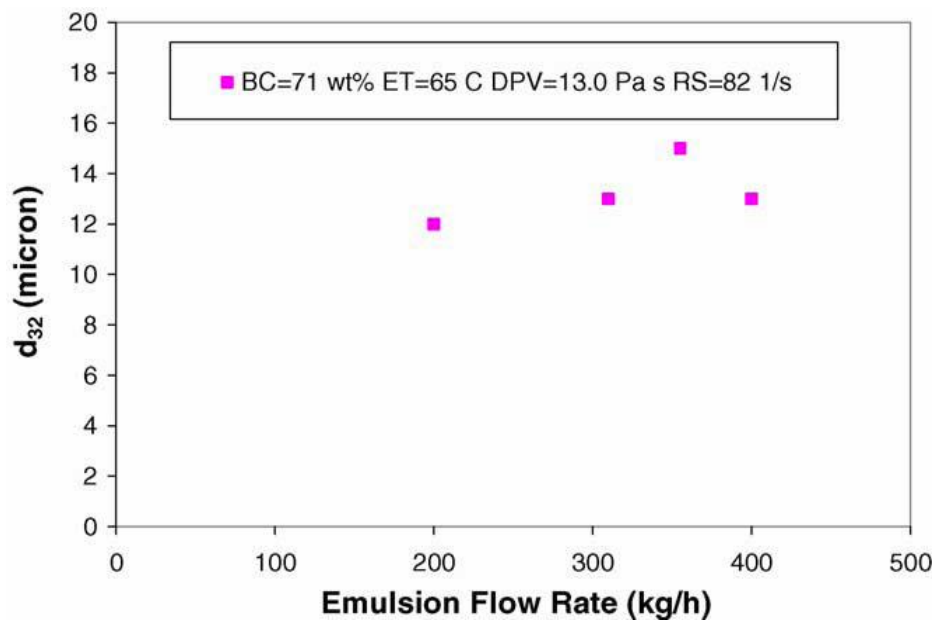
**Figure 23:** Effect of emulsification temperature on droplet size for 160/220 and 10/20 bitumen.

Nevertheless, emulsification of 10/20 grade bitumen has been carried out successfully on the rig (see circle dot in figure 23). The viscosity of the 10/20 bitumen at 80 °C is approximately one order of magnitude higher than 160/220 bitumen. This run with hard bitumen confirms that smaller droplets are obtained with a more viscous dispersed phase.

As it can be seen in figures 22 and 23, as the bitumen content increased, the drop size increases. The dispersed phase content has also an effect on the surfactant concentration in the emulsion, because the surfactant quantity is maintained at a constant level with respect to the tap water volume in the aqueous phase. It was assumed that this dosage was sufficient to ensure an excess of surfactant in the emulsion.

### 3. Effect of the emulsion Flow rate:

Limited experiments were performed to study the relation between the emulsion flow rate and the average size of the droplet in the emulsion (Figure. 24), because many difficulties were encountered to run the rig with an emulsion flow rate higher than 400 kg/h. For the range of emulsion flow rate tested, it is difficult to see a clear effect of the emulsion flow rate on the droplet size. BC is the bitumen concentration or dispersed phase content; ET is the emulsification temperature,, DPV is the dispersed phase viscosity and RS is the rotor speed.

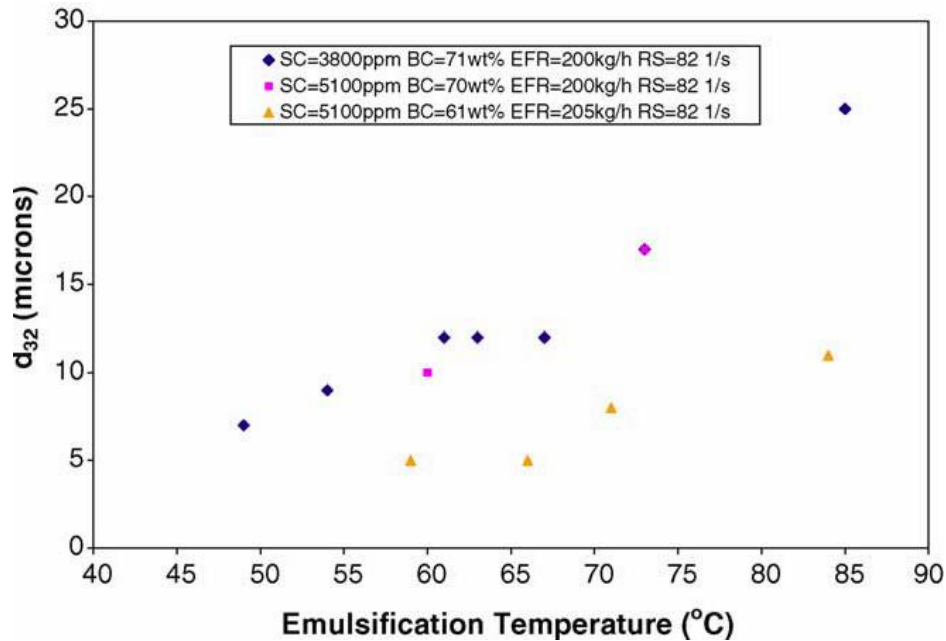


**Figure 24:** Effect of emulsion flow rate on the drop size for 160/220 bitumen grade

### 4. Effect of the surfactant concentration:

Figure 25, shows that the effect of surfactant concentration in the emulsion is insignificant in comparison with other effects studied in this work. The authors studied the effect of the surfactant concentration and dispersed phase content on droplet size. In the graphic showed SC is the surfactant concentration, BC is the bitumen

concentration or the dispersed phase content, EFR is the emulsification flow rate and RS is the rotation speed of the rotor.



**Figure 25:** Effect of surfactant concentration and dispersed phase content on droplet size for 160/220 bitumen grade

To summarize, the droplet size in bitumen emulsions produced in continuous mode by rotor-stator geometry are influenced by the process parameters. Experimental results presented by the authors indicate that the average droplet size decreases as the rotor speed increases or as the emulsification temperature, the bitumen grade or the bitumen concentration decrease. The numerous models based on the balance of forces acting on the droplets in turbulent or laminar flow do not follow this experimental results presented before. It is possible to explain this discrepancy by the high decalescence rate and the complexity of the flow during the emulsification of high viscosity ratio in a rotor-stator machine. The choice of a rotor-stator mixer is generally based on the specific energy. This strategy for inline bitumen emulsification can lead to the production of emulsion out of the specifications required for the application. To avoid this situation, the residence time in the dispersing zone has to be considered as a design criteria especially when surfactants with long adsorption time are used.



## 2.2 HIPR method

High Internal Phase Ratio (HIPR) method requires initial dispersion to be carried out at packing fractions greater than the critical. This facilitates the formation of highly concentrated emulsions with a very narrow droplet diameter distribution. According to this method it is possible to control with the formulation and the manufacture conditions the final morphology of the emulsion.

Emulsified systems containing >70% internal phase are known as HIPR emulsions. HIPR emulsions are normally prepared by dispersing increasing amounts of the dispersed phase into the continuous phase until the internal phase volumes exceeds 70%. Clearly, for very high internal phase volume, e.g. above 80%, the systems cannot contain discrete spherical dispersed phase droplets; rather, they will consist of highly distorted droplets, separated by thin aqueous films.

One of the foremost workers in the areas of HIPE's is K.J. Lissant of the Petrolite Corporation, St. Louis, Missouri, who has published numerous papers in this field and who held numerous patents related to HIPE technology. He has more than 25 patents related with this technology.

Despite that, we are not going to pay much attention to Lissant because his work is related with emulsions in general such as fuels, oil exploration, industrial cleaning, cosmetics, transport of solids, fire extinguishers, etc.... and our review is focused on asphalt emulsion technology.

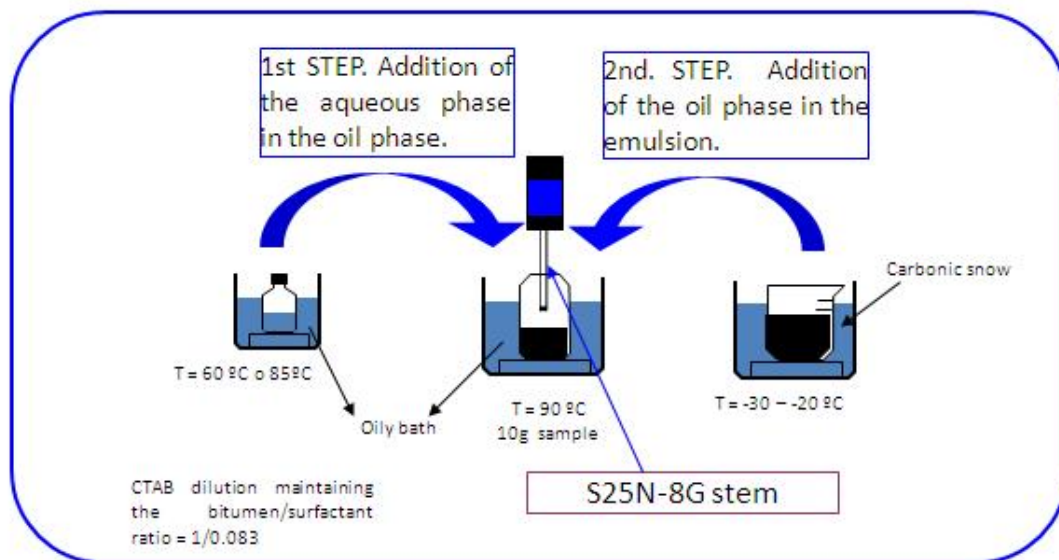
In the Canadian patent High Internal Phase emulsions, 1982, (11) Aronson Michael P. et al., makes a review of the high internal phase emulsion production. In this patent there are a lot of mentions to the work of Lissant. The patent is focused on an exhaustive description of the different parameters related with the emulsions manufacture such as surfactants, oil, aqueous phase, different additives, moisturizers, etc. It is focused to improve the emulsion stability and they make different test measuring the emulsion storage stability in accelerate room temperature aging them via centrifugation, high temperature stability, room temperature stability and freeze-thaw stability.

We are not either pay so much attention to this other patent because it don't talk about bitumen emulsions which is the principal aim of our work.

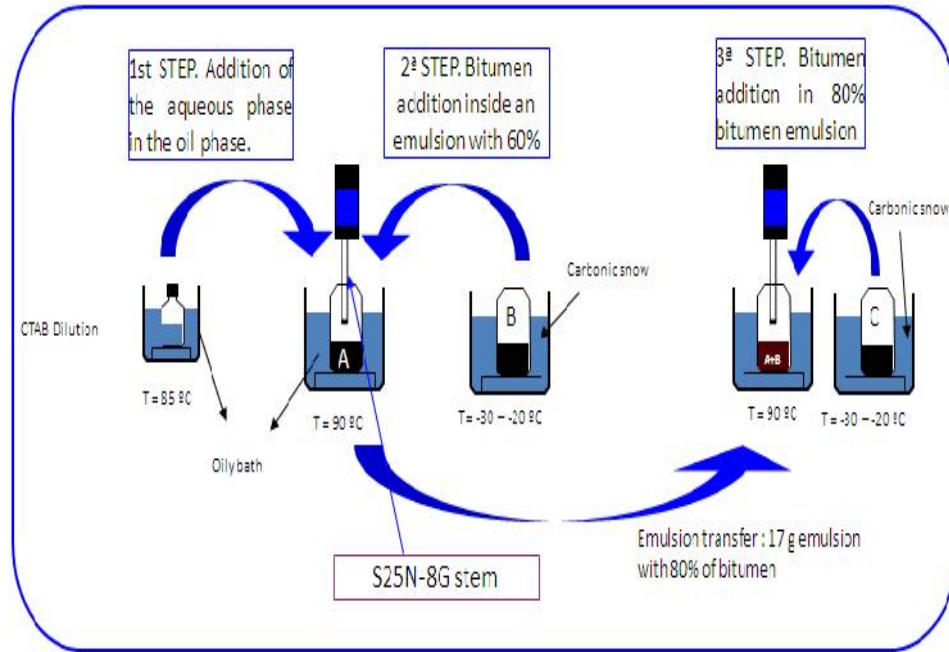
M.L. Chirinos et al. (12) proposed a method to manufacture this kind of emulsions in 1995. In this patent they propose HIPR method for the manufacture of bitumen in water emulsions. In this patent an HIPR bitumen emulsion in water is prepared by a method which comprises directly mixing 70% to 98% by volume of bitumen having a

viscosity in the range 200 to 500,000 m Pa·s at the mixing temperature with 30 to 2% by volume of an aqueous solution of an emulsifying surfactant, percentages being expressed as percentages by volume of the total mixture. Mixing is effected under low shear conditions in the range 10 to 1.000 reciprocal seconds in such manner that an emulsion is formed comprising highly distorted bitumen droplets having mean droplet diameters in the range 2 to 50 micron separated by thin films of water.

Depending on the final concentration of the emulsion we could prepare it in one step or two steps. If we do it in only one step all the oily phase is put it inside all the aqueous phase. It is also possible to do it in two steps, where we introduce partial of the bitumen in the water phase and once the emulsion is made we increase the final concentration by adding higher quantities of bitumen until we reach the concentration desired.



**Figure 26:** schematic representation of HIPR emulsion preparation in two steps.



**Figure 27:** schematic representation of HIPR emulsion preparation in three steps.

M.L.Chirinos et al. (12) state in the background of the invention that bitumen is a highly viscous material which is useful in road making and for other purposes. Because of its high viscosity it is difficult to use it in the cold or in a untreated condition. One method of reducing the viscosity is by heating the material and using it hot. Another is by adding a light petroleum distillate as diluents. This would thin the bitumen and allow its application at lower temperature. However, they thought, the distillate would subsequently be lost by evaporation and may increase environmental problems. A third method they presented is, with which their invention is concerned, by forming an emulsion of bitumen in water. Emulsions have lower viscosities than the starting bitumen and can be used at lower temperatures for spraying or mixing purposes.

Moreover the authors claim that however the method of forming an emulsion, the dispersion of bitumen in a medium of much lower viscosity such as water is an unfavorable process on hydrodynamic grounds. This problem is further complicated by the desirability in certain applications to utilize emulsions containing relatively high bitumen phase volumes without sacrificing emulsion fluidity. In the case of systems comprising dispersed spheres of equal size, the maximum internal phase volume occupied by hexagonally close-packed arrangement is a 74%. In practice, emulsions

are rarely monodispersed and it is therefore possible to increase the packing density slightly beyond 74% without causing appreciable droplet distortion. They thought that attempts to increase further the internal phase volume beyond these second level results in greater droplet deformation and, because of the larger interfacial area created, instability arises, and this culminates in either phase inversion or emulsion breaking. They affirm that only under exceptional circumstances, it is possible to create dispersions containing as high as 98% disperse phase volume without inversion or breaking.

Furthermore M.L. Chirinos et al. (12) discovered an improved method for the preparation of HIPR bitumen emulsions in which the emulsions are directly prepared from a feedstock initially containing a high volume ratio of bitumen to water using low energy mixing as opposed to high energy dispensing.

According to Chirinos et al. they have a HIPR emulsification method which comprises directly mixing 70 to 98% by weight of bitumen having a viscosity range 200 to 500.000 m Pa.s at the mixing temperature with 30 to 2% by weight of an aqueous solution or an emulsifying surfactant. The mixing is being held under low shear conditions in range 10 to 1.000 reciprocal seconds in such manner than an emulsion is formed comprising distorted bitumen droplets having mean droplets diameters in the range 2 to 50 micron separated by thin films of water. The HIPR emulsions as prepared by Chirinos et al. are stable and can be diluted with aqueous surfactant solution or water to produce stable emulsions of lower bitumen phase volume showing high degrees of monodispersity. Their emulsions may be diluted to a required viscosity without adversely affecting stability. Because the narrow size distribution is maintained upon dilution the resulting emulsion shows little tendency to creaming. This in turn reduces the risk of phase separation.

In order to provide bitumen having the appropriate characteristics, authors say that it will usually be necessary to heat the bitumen to a temperatures that not exceed 100°C. Nevertheless, this temperature is significantly lower than that to which bitumen is generally heated in the manufacture of conventional bitumen emulsions. Current methods for producing bitumen emulsions with a cationic surfactant involve emulsification at a temperature range 120° to 140°C under high shear conditions ( e.g. in a colloid mill) in order to attain the required droplet size. High shear mechanical dispersing can lead to the formation of polydisperse emulsions having some relatively large size particles or multiple emulsions, both of which are undesirable features.

This method presented by Chirinos et alters hard bitumens which could not be emulsified by conventional methods are suitable for emulsification by this one. Such

bitumens could be treated only with difficulty in the past because of the excessively high temperatures required to reduce the viscosity of the bitumen to a level at which it could be worked.

For the mixture the authors used equipment known to be suitable for mixing viscous fluids. The surfactant is employed in amount 0.1 to 5 % by weight, based on the total weight of the emulsion. Suitable surfactants they used include anionic surfactants, mixtures of anionic and non-ionic surfactants, cationic surfactants and mixtures of cationic and non-ionic surfactants. Non-ionic surfactants include ethoxylated alkyl phenols, ethoxylated alcohols and ethoxylated sorbitan esters. Cationic surfactants include the hydrochlorides of fatty diamines, imidazolines, ethoxylated amines, amidoamines and quaternary ammonium compounds. And anionic surfactants include long chain carboxylic and sulphonic acids.

Using HIPR method, Chirinos et al. prepare stable emulsions having high contents of bitumen. After prepared they can be diluted with aqueous surfactant solution or water to produce stable emulsions of lower bitumen phase volume showing high degrees of monodispersity.

As examples Chirinos et al. give different laboratory experiences:

#### *EXAMPLE 1:*

A 90% HIPR emulsion was prepared by adding a 90g sample of 200 pen grade Cyrus bitumen to a 250 ml beaker containing 10 g of 3.0% aqueous non-ionic surfactant solution. The surfactant was an alkyl aromatic ethoxylated solution. This was then mixed at 90 °C using a twin-beater hand-held domestic mixer operating for one minute at 1000 rpm followed by a further one minute period at 1200 rpm under low shear conditions ( a few hundred reciprocal seconds ).

During the mixing process, films of aqueous surfactant are stretched out and folded through the bitumen, ultimately leading to a complex film structure. Dilution of the HIPR emulsion with additional water releases the bitumen from its constraining framework and spherical droplets separate.

Subsequent dilution of this 90% bitumen emulsion with 1% surfactant solution at 90 °C enabled the formation of emulsions of lower bitumen contents; i.e. 70/30; 60/40; and 50/50. After 18 months storage at room temperature, these diluted emulsions showed no signs of coalescence. Although the viscosity of the emulsions increased with increasing bitumen content, it was evident that even at room temperature, the 70% bitumen emulsion still exhibited a reasonable degree of fluidity and would therefore be

suitable for pumping. Further dilution permitted microscopic examination of the emulsions and revealed a good degree of monodispersity and a mean droplet diameter of approximately 15  $\mu\text{m}$ .

It is a very good manufacture emulsion method, but due to using a high concentration of surfactant they don't reach a very narrow diameter size. They don't say anything about the stability, they mention that after 18 storage months there is no coalescence signal, but we did not know if they measure of if it is a visual observation. They neither say how they made the mean droplet size measure.

#### *EXAMPLE 2-7:*

In the following examples presented by the authors emulsions of bitumen in water were prepared by the following technique:

0.8g of the hydrochloride of that fatty amine sold under the trade name Dinoram-S was placed in a 500 ml beaker, water (24 ml) added and then the solution warmed to 40-50°C to dissolve the surfactant. Bitumen was heated to 90°C and 240 g added to the aqueous phase. The beaker containing the bitumen and aqueous phase was placed in a water bath at 90°C for 5 minutes. The bitumen and aqueous phase were then mixed for 30 seconds using a domestic mixer to give a 90% emulsion. An aqueous solution (76.5 ml) containing 1% by weight emulsifier was then added over a period of 30 seconds with mixing to dilute the emulsion to lower bitumen content. Following dilution, mixing was continued for a further 60 seconds to ensure a thoroughly homogenized product.

The storage stability of the emulsions was assessed by a subjective procedure comprising a visual examination of the emulsions after 1, 5, 24 and 48 hours. Signs of instability were indicated by skin formation and agglomeration which gave a granular appearance with a resulting reduction in viscosity.

Example	Bitumen Penetration Grade	Viscosity at 90° C. (mPa · s)	Temperature of Mixing (°C.)	Bitumen Content of Emulsion (% wt)	Surfactant Content Total Emulsion (% wt)	Stability (Hours)	Mean Particle Size Diameter (μ)
2	Cyrus 200 pen	4,300	90	70	0.52	>48	8.1
3	Kuwait 200 pen	3,600	90	70	0.52	>48	9.5
4				80	0.34	>48	7.7
5	Kuwait 100 pen	5,800	90	70	.52	>48	—
6				80	.52	>48	7.2
7	Kuwait 70 pen	10,000	90	70	0.52	>48	11.0

Table 5: Summary of the results set out obtained in example 1.

The surfactant concentration used in these examples is lower than the used in example 1. The results obtained are not very good results at least in stability terms. The mean diameter particle size obtained is not very narrow, not fewer than 8 μm. The stability parameters are not measured, they are only visual observation, there's no laboratory test used to measure the stability.

The authors also say that they have used similar procedures to prepare emulsions from three bitumens derived from atmospheric distillation of two Venezuelan crude oils.

The results and conditions used are summarized in the table 6:

Example	Bitumen Source	Penetration	Temperature of Mixing (°C.)	Bitumen Content of Emulsion (% wt)	Stability (Hours)	Mean Particle Size Diameter (μ)
8	Morichal	200	70	75	>48	9.8
9	Morichal	65	92	80	>48	7
10	Cerro Negro	92	90	90	>48	4

Table 6: Summary of the results obtained from example 2 to 7.

In table 5, the authors don't say what is the surfactant concentration used. There no mention to the stability, we suppose that they have made a visual evaluation and the values presented in the table 6 don't correspond to any laboratory test. Another question is what happens with harder bitumen, with a penetration grade lower than 65.



Another paper very interesting related with the formation of bitumen in water emulsions in the one by Gutierrez et al., 2002, (6). The paper describes the most relevant issues associated with the development of a technology of the formation of highly concentrated bitumen in water emulsions. The authors have found that viscosity values for bitumen in water emulsions containing between 70 and 85% (v/v) of bitumen have been found to be several order of magnitude lower than the viscosity of the hydrocarbon itself. Thus, the authors thought, these emulsions have potential applications in the processes of production, transportation, handling and commercialization of these extremely highly viscous hydrocarbons. The emulsions, the properties of which are discussed in the paper, were stabilized with mixtures of nonionic and natural surfactants and formed using HIPR technique. They give the information on the conditions required to produce emulsions with very narrow droplet diameter distribution is given. According to the authors the results indicate that the mean droplet diameter, the droplet diameter distribution and the bitumen volume fraction, significantly modify the rheological behavior. They measure the emulsion stability by following changes in the mean droplet diameter and in the rheological parameters with storage time.

Gutierrez et al. have used Cerro Negro bitumen to manufacture the emulsions. They have stabilized it with ethoxylated alcohol compounds at 60°C. The characteristics of the bitumen used are shown in the next table 7:

Aromatics % (w/w)	35.6
Resins % (w/w)	18.9
Asphaltenes % (w/w)	16.1
Acidity index (mg KOH/g)	3.02
Carbon % (w/w)	80.3
Hydrogen % (w/w)	9.9
Nitrogen (ppm)	6188
Sulphur % (w/w)	3.7
Vanadium (ppm)	367.4
Nickel (ppm)	95.5
Sodium (ppm)	11.8
Conradson carbon % (w/w)	17.2
Water % (w/w)	0.1

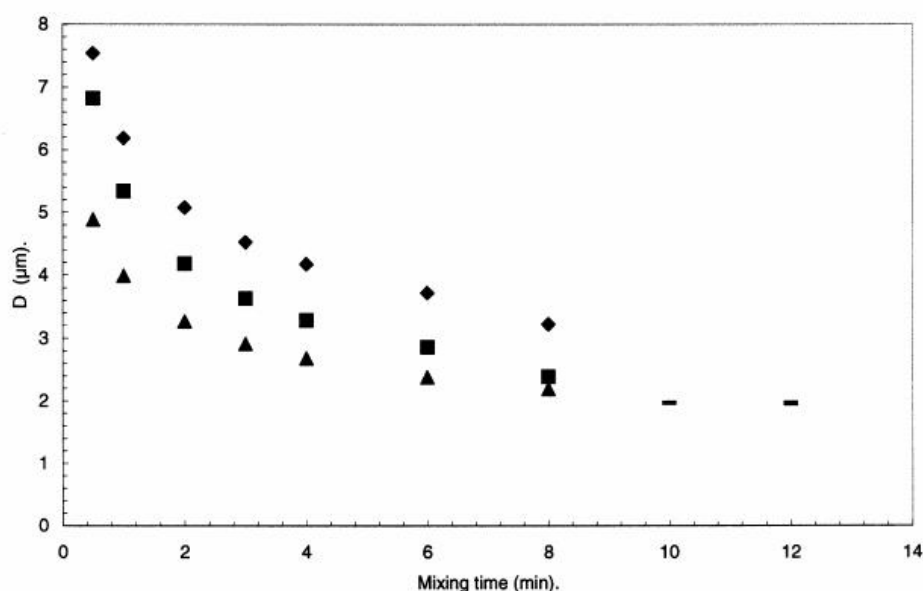
**Table 7:** Physico-Chemical Properties of Cerro Negro Bitumen



Emulsions were prepared following the HIPR method, which as we have explained before, requires the initial dispersion to be carried out at a packing fraction higher than critical. The emulsion obtained had a bitumen fraction of 0.90 and a surfactant concentration of 3000 ppm. The bitumen and water mixture is stirred for several minutes with a Rushton paddle mixer, until the required mean droplet size is attained. During the homogenization process, the mixing vessel was immersed in a 60 °C water bath. Emulsions are then diluted with water until the final bitumen volume fraction (ranging from 0.60 to 0.85) is attained. After preparation, emulsions were stored at 25 and 45°C in sealed containers and analyzed for their mean droplet diameter and size distribution by means of a laser light scattering instrument. These measurements allowed the monitoring of emulsion stability.

The authors said that the effect of the volume fraction, mixing speed and mixing time on the degree of emulsification was assessed by withdrawing emulsion samples at various intervals during the mixing process and by measuring the mean diameter and size distribution of the bitumen droplets.

Gutierrez et al. have studied firstly the effect of the mean droplet diameter size as a function of the mixing time. A representative plot showing the change in the droplet size distribution with mixing time and different mixing speed is shown in the figure 28. This emulsion contains a 0.90 bitumen volume fraction:

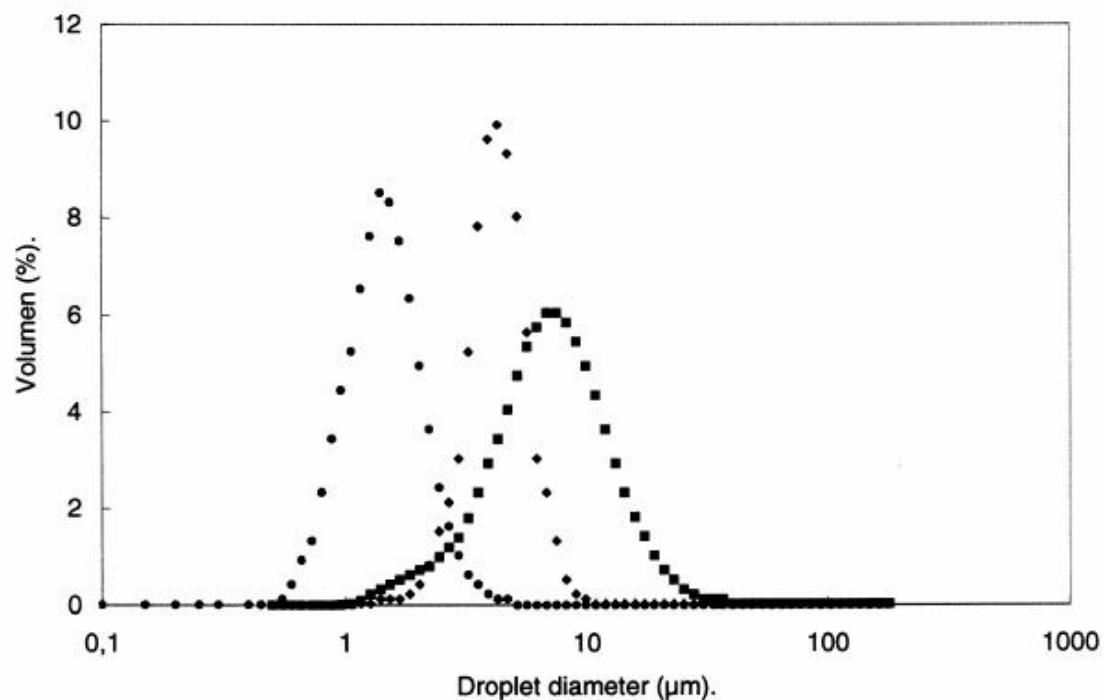


**Figure 28:** Mean droplet diameter ( $D$ ) as a function of mixing time, at 60°C for bitumen-in-water emulsions; having a bitumen volume fraction of 0.90: Mixing speed —◆— 1500 rpm; 2000 rpm; 2500 rpm

It can be seen from the representative data in the figure 27 that the droplet diameter distribution changes significantly, but uniformly with mixing time. This would suggest that the creation of interfacial area occurs in a well controlled manner, allowing in principle the production of emulsions with any given mean droplet diameter. The authors comment that the application of this method for producing emulsions exhibiting a high degree of monodispersity, allows for designing the industrial facilities required for large-scale manufacturing of bitumen in water emulsions with a high degree of reproducibility in their properties.

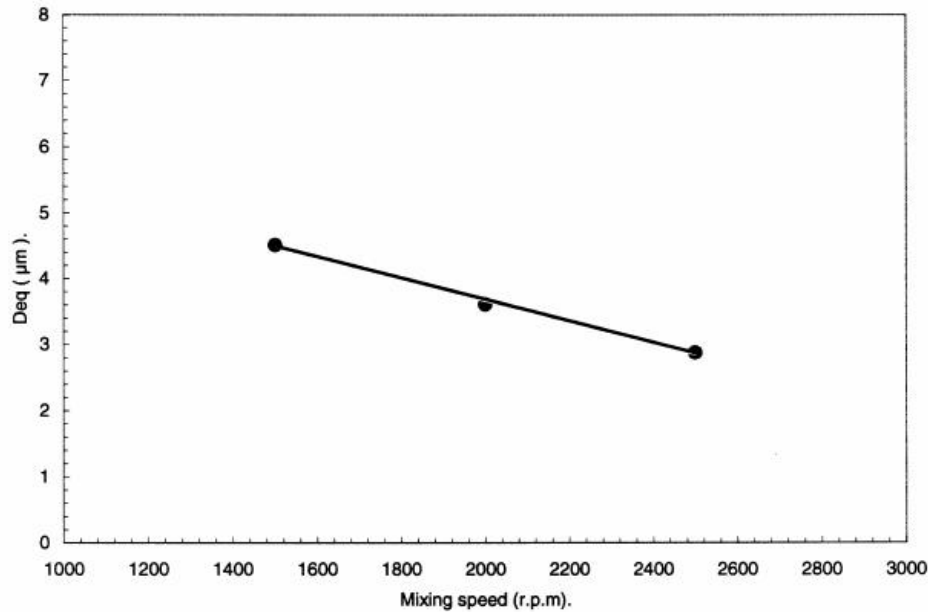
With this method it is possible to obtain the narrowest diameter size with just 6-7 minutes. The best mixing speed is 2500 rpm.

The way in which the mean droplet diameter changes with mixing time is illustrated for various mixing speeds in the following figure 29:



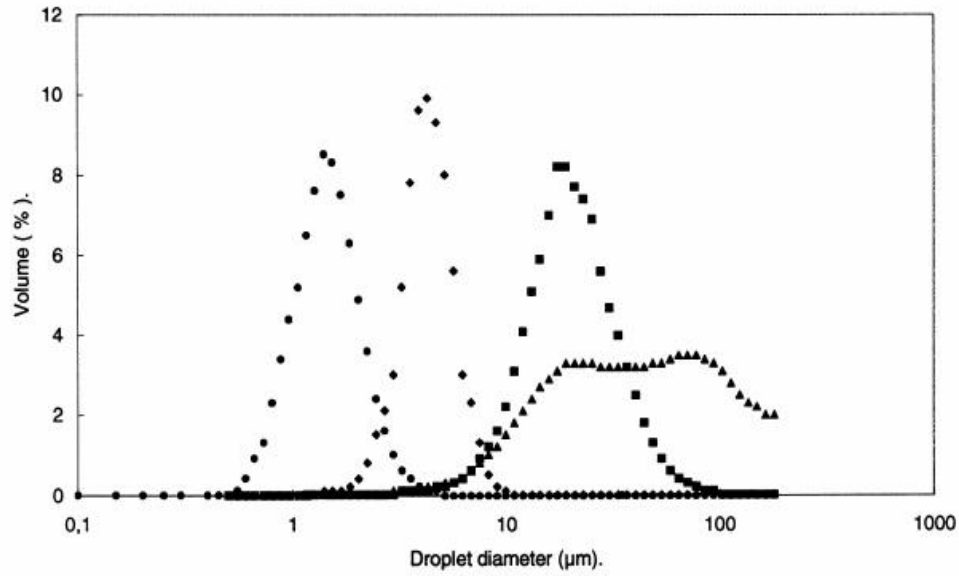
**Figure 29** : Droplet diameter distribution as a function of the mixing time at 2500 rpm and 65°C for bitumen-in-water emulsions having a bitumen volume fraction of 0.90: mixing times 6, 3 and 0.5 min, respectively, for curves from left to right.

As we could see in the following figure 30 it is clear that controlling the bitumen/water ratio we could control the mean droplet diameter obtained, but only when the applied mixing speed is above a certain critical value ( which is approximately 2500 rpm in this particular case):

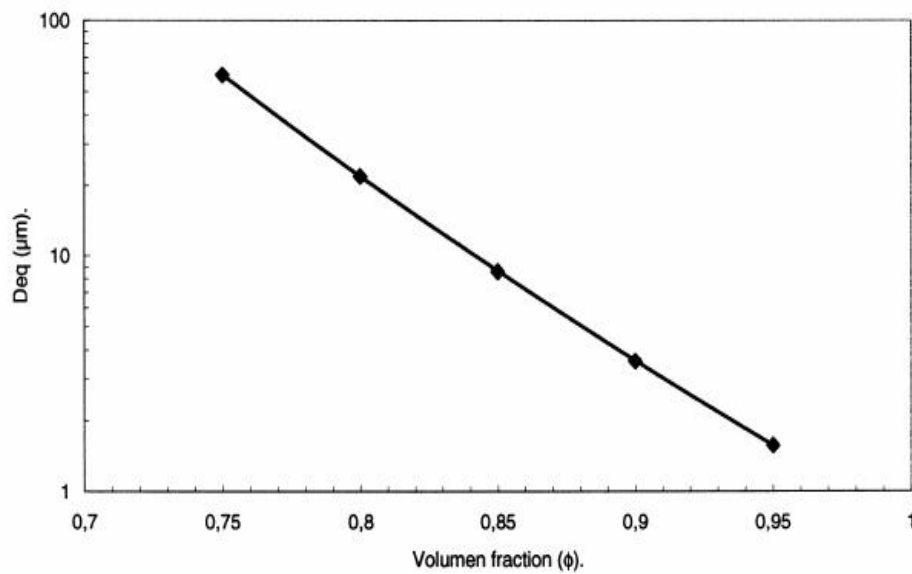


**Figure 30:** Equilibrium mean droplet diameter ( $D_{eq}$ ) as a function of the mixing speed for bitumen-in-water emulsions, having a bitumen volume fraction of 0.90.

The authors explained that in a series of experiment conducted at constant surfactant concentration ( 3000 ppm with respect to the bitumen), the bitumen volume fractions was decreased from a maximum 0.95 in order to assess the importance of the dispersed phase concentration on mixing efficiency. The resulting equilibrium droplet mean diameters and distributions for a 2500 rpm mixing speed are presented in figures 31 and 32 which exhibit two striking features. First, the decreasing quality of the distribution, and secondly, the increase of the mean droplet diameter as the bitumen volume fraction  $\phi$  decreases:

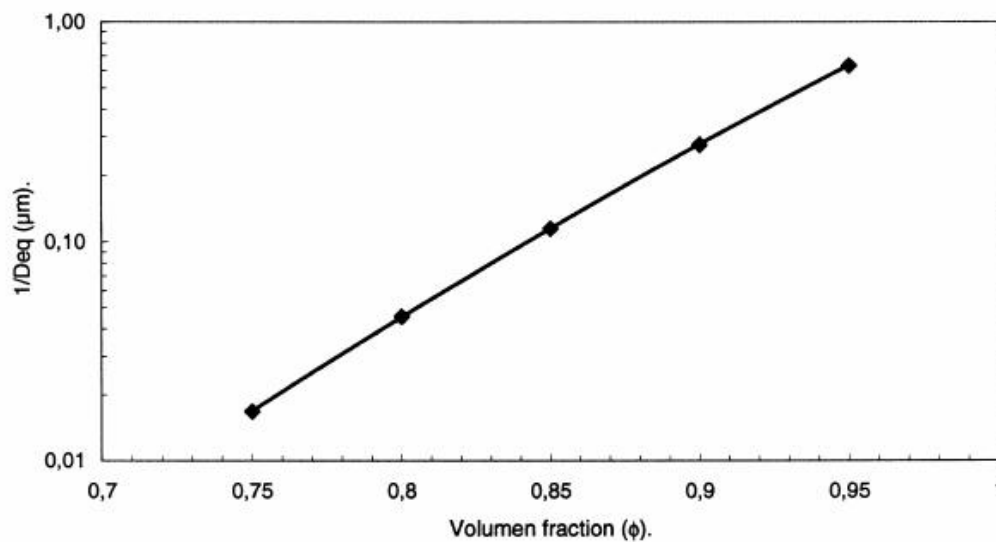


**Figure 31:** Droplet diameter distributions as a function of the bitumen volume fractions ( $\phi$ ) for emulsions prepared at 65°C mixing at 2500 rpm;  $\phi=0.95;0.90; 0.80, 0.75$  ( bimodal) from left to right, respectively.



**Figure 32:** Equilibrium mean droplet diameter ( $Deq$ ) as a function of the bitumen volume fraction ( $\phi$ ) for emulsions prepared al 65°C mixing at 2500 rpm.

The equilibrium droplet diameter ( $D_{eq}$ ) data are plotted in Figure 33 as  $1/D_{eq}$  versus the bitumen volume fraction ( $\phi$ ). In this format, the data reveal even more clearly the decreased efficiency of creating interfacial area as  $\phi$  decreases. The linear dependence of  $1/D_{eq}$  on  $\phi$  can be extrapolated to provide a critical oil phase volume, below which it can be suggested that emulsification by the HIPR method becomes highly unfavorable. This condition has been in fact identified in practice, in systems containing bitumen volume fractions lower than 0.75.

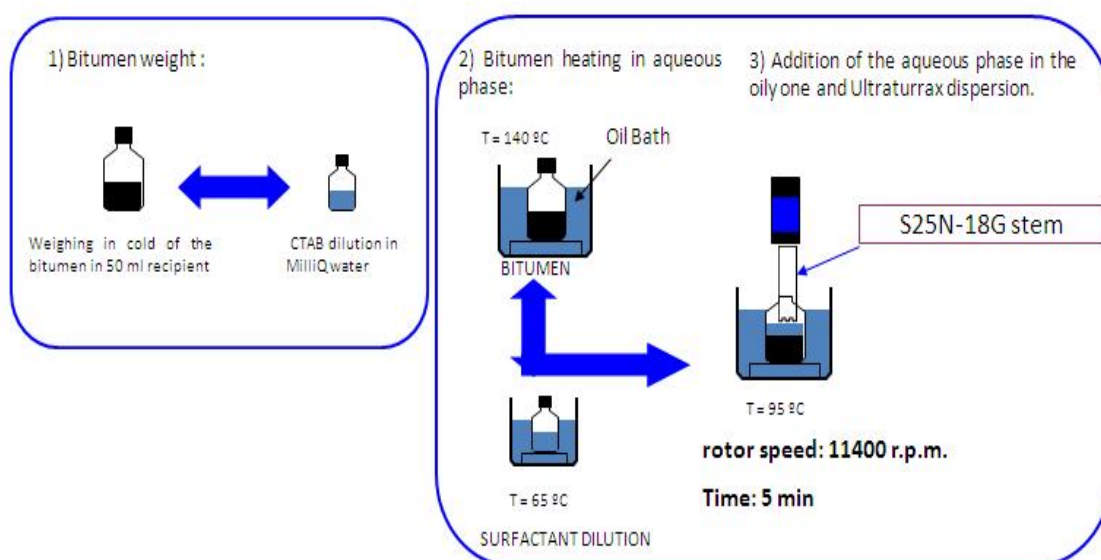


**Figure 33:** Inverse of the equilibrium mean droplet diameter ( $1/D_{eq}$ ) as a function of the bitumen volume fraction ( $\phi$ ) for emulsions prepared at 65°C; mixing at 2500 rpm.

It can be seen from the information contained in the previous figures, that the mean droplet diameter and the distribution change significantly, but uniformly with the mixing time and with the bitumen volume fraction. This suggests the creation of interfacial area occurs in a well controlled manner, which allow for the production of emulsions with any given mean droplet diameter and with a very narrow diameter and with a very narrow droplet size distribution.

Although the diameter size obtained with this method is better than the previous one, the narrowest diameter size distribuion obtained is around  $1.5\ \mu\text{m}$ . The authors don't pay any attention to the stability of this emulsions with is a very important parameter to be considered. The bitumen used in this paper is a bitumen from a very hight acid value so with a low penetration grade. It could be interesting to know if the method presented would work with a harder bitumen penetration grades.

In 2003, F. Leal Calderon et al. (13) presented another patent for a method for preparing concentrated bitumen emulsions and calibrated in a highly viscous phase. In the process they explained a method for the manufacture of a highly concentration stable emulsion, by emulsifying a first hydrophobic or hydrophilic phase having a viscosity between 1 and 5000 Pa.s with a second phase immiscible in the first phase, in the presence of at least one surfactant, by mixing together the first phase, second phase, and surfactant under a laminar shear regime:



**Figure 34:** Schematic representation of HIPR emulsion preparation in only one step.

The author stated that concentrated emulsions in highly viscous hydrophobic compound(s) are used in particular in their surfacing sector, such as, for example, in the road industry. They think that this is the reason why this emulsions represent an attractive alternative to the problem of spreading bitumen on road surfaces. In traditional techniques, the authors affirm, pure bitumen is used hot, which works out to be expensive and can be hazardous for the worksite personnel. When the bitumen is emulsified in water, the material obtained is entirely fluid at room temperature, thus allowing it to be used without difficulty. Under the effect of the evaporation and drainage of the water, a homogeneous bitumen fill is obtained after a few hours. Emulsions concentrated in highly viscous hydrophobic compounds are also used in the adhesives industry via bonding agents made with emulsion bases on colophony esters. For their part, emulsions concentrated in viscous hydrophilic compounds(s) are more particularly used in the pharmaceutical and food industries.

Calderon et al. affirm that the techniques available until the moment for preparing emulsions of this type in most cases require high temperatures, high pressures and/or high shear rates. Thus, if they consider the specific case of bitumen, the corresponding emulsions are currently prepared by hot injection. In general, the bitumen is heated to a temperature above 120°C and the continuous phase, generally water, is heated to about 60 °C. The mixture of the bitumen and the aqueous phase is injected into a turbo mixer with a very high stirring speed, of about 5000 rpm and under a pressure which can be up to 3 atmospheres. They say that after such a treatment, bitumen emulsions having a bitumen concentration not exceeding 70% by weight of bitumen, a large average droplet size (typically greater than 5 µm) and a polydispersity which is also large are generally obtained.

The authors though that this type of process have several drawbacks. In particular, conventional processes do not make it possible to prepare emulsions with a bitumen concentration of more than 70%. The emulsions available are not satisfactory in terms of monodispersity. The size of the bitumen droplets present in these emulsions is generally greater than 5 µm and very heterogeneous. The stability on storage and the breaking of this type of emulsions are found to be difficult to control and the surfacing resulting there forms are not sufficiently homogeneous.

Furthermore, the authors propose a process for preparing emulsions which are concentrated in a highly viscous phase such as bitumen and are also calibrated. In particular the invention is based on the demonstration that the direct mixing of a highly viscous phase, a phase which has a viscosity of between 1 and 5.000 Pa.s at the time

of emulsification, with a phase which is immiscible therewith, in the presence of a surfactant, leads, under low shear and in a very short space of time, to a viscoelastic paste which is advantageously found to have the specificities of an emulsion. With this method it is possible to obtain emulsions with a minimum average droplet diameter, of about 2 microns or even less for an optimum amount of this second phase. Emulsions obtained have a dispersed volume of 90% or more ( they are like a viscoelastic paste) and must be diluted with hot water ( 60°C) in the hours following its preparation, and preferably after dilution. Emulsions having, after dilution, a bitumen concentration of between 75% and 85% are found to be particularly stable for at least several months. That novel emulsification method maked possible to manufacture highly concentrated emulsions of “water in oil” or “oil in water” type by directly mixing together the two phases in a laminar shear regime. It thus differs clearly from conventional emulsification processes, such as the one manufactured by conventional method which operate in a turbulent regime. It also differs from the conventional techniques of emulsification in a laminar regime, such as Chirinos patent, which proceed by gradual incorporation of a first phase to be emulsified into a second phase and vicerversa.

The emulsion obtained by this method has an appearance of a viscoelastic paste. Advantageously, it is found to be redispersible despite a high concentration of one of its phases. It can thus be diluted so as to adapt the concentration of the final emulsion to the requirements of the application envisaged. Besides high concentration of one of its phases, the emulsion obtained by Calderon method has a very narrow particle size distribution and the average diameter of its droplets can be readily controlled by means of the shear rate or by means of the formulation parameters and more particularly the concentration of the second phase, also known as the diluents phase.

Calderon et alters demonstrates with different examples that the size of the droplets in the first phase decreases when the shear rate and/or the concentration of the surfactant increase. The inventors have thus demonstrated unexpectedly, that it is possible to adjust the size of the droplets in the first phase by controlling the amount of the second phase introduced to prepare the emulsion. The size of the droplets does not change monotonically with the amount of the second phase: the size first decreases and then increases when the amount of the second phase increases.



The examples and figures given below demonstrate the advantages presented in the Calderon method:

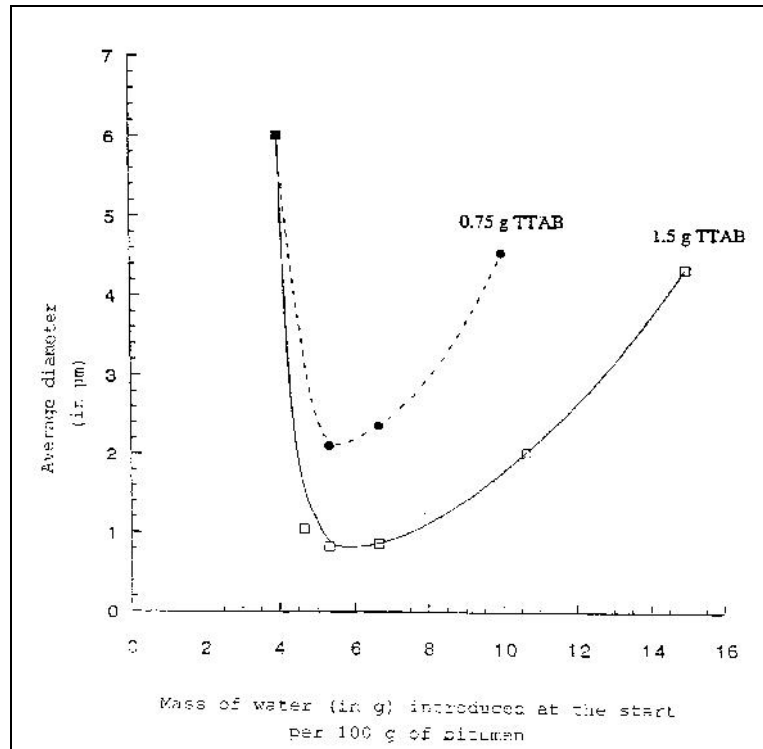
Example 1: Protocol for preparing an aqueous bitumen emulsion

100g of bitumen with a penetration index of 90/100 are heated to a temperature of about 100°C. An aqueous tetradecyltrimethylammonium bromide (TTAB) solution of variable concentration is prepared. The heated bitumen is poured onto the aqueous solution and the mixture is blended for a few seconds using a flexible grate, at 400 rpm ( $1000\text{s}^{-1}$ ) in a reactor 10 centimeters in diameter. The emulsion obtained almost instantaneously is characterized in terms of droplet diameter.

If we pay attention to the quantities used, the conditions and substances used we could conclude that it is a laboratory preparation. TTAB is a laboratory surfactant that will be very expensive to use in plant scale if we want to extrapolate this system to a manufacture system plant. They either not says at which surfactant concentration are working. So it seems, a priori impossible to prepare in an emulsion plant.

Example 2: Effect of the amount of water and of surfactant (TTAB) on the average diameter of the droplets in a bitumen emulsion at constant shear:

The protocol described in example 1 is repeated for two TTAB concentration, 0.75g and 1.5 g, and in the presence of an amount of water ranging between 4 and 14 for each of these concentrations. The emulsions obtained after each of the tests are characterized by the average diameter of their droplets. The results are given on the following graphic:

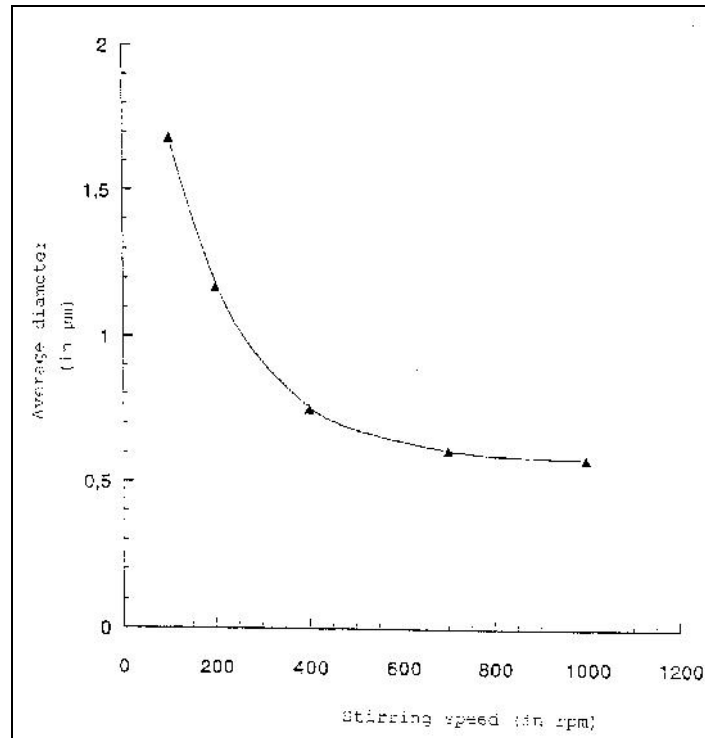


**Figure 35:** Average diameter size as a function of the amounts of water and surfactant concentration.

The finest emulsion obtained for a constant amount of water of about 5 grams per 100g of bitumen. The minimum droplet size thus obtained can also be reduced by increasing the amount of surfactant. Thus, for 1.5 grams of TTAB in 5.5 grams of water, the minimum diameter is reduced to 0.8 microns, as against 2 microns with 0.75 grams of TTAB. They don't say anything about the pH of water phase prepared and for the emulsions obtained.

Example 3: Effect of the shear rate on the average diameter of the droplets in the emulsified viscous phase

The protocol described in example 1 is repeated with 100g of bitumen, 1.5g of TTAB and 5.5g of water for variable stirring speeds. The emulsions obtained after each of the test are characterized by the average diameter of their droplets. The results are represented on the following graph:

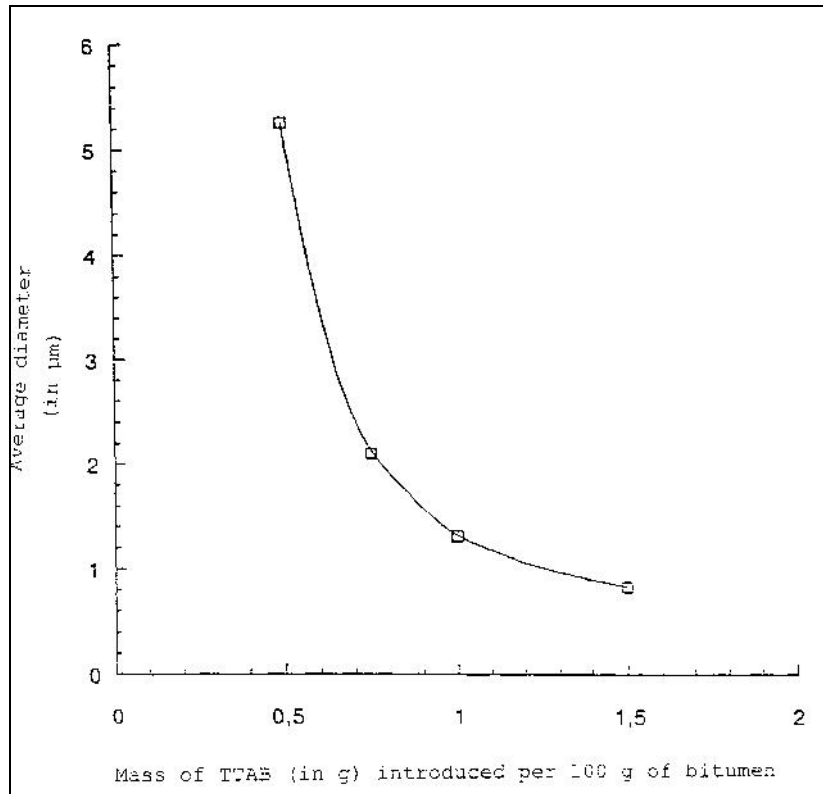


**Figure 36:** Average diameter size as a function of the shear rate applied during emulsificación.

We could observe that a high shear rate promotes the formation of droplets of markedly smaller average diameter. However the stirring speed should not exceed a threshold value of 1000 rpm (about  $2500\text{s}^{-1}$ ), above this value the excessively violent shear destroys the concentrated emulsion.

Example 4: Effect of the amount of cationic surfactant on the average diameter of the droplets of a bitumen emulsion with a constant volume of water and at constant shear

The protocol described in example 1 is repeated for different TTAB concentrations, in the presence of 5.5grams of water. The results obtained are representing on the following graphic:



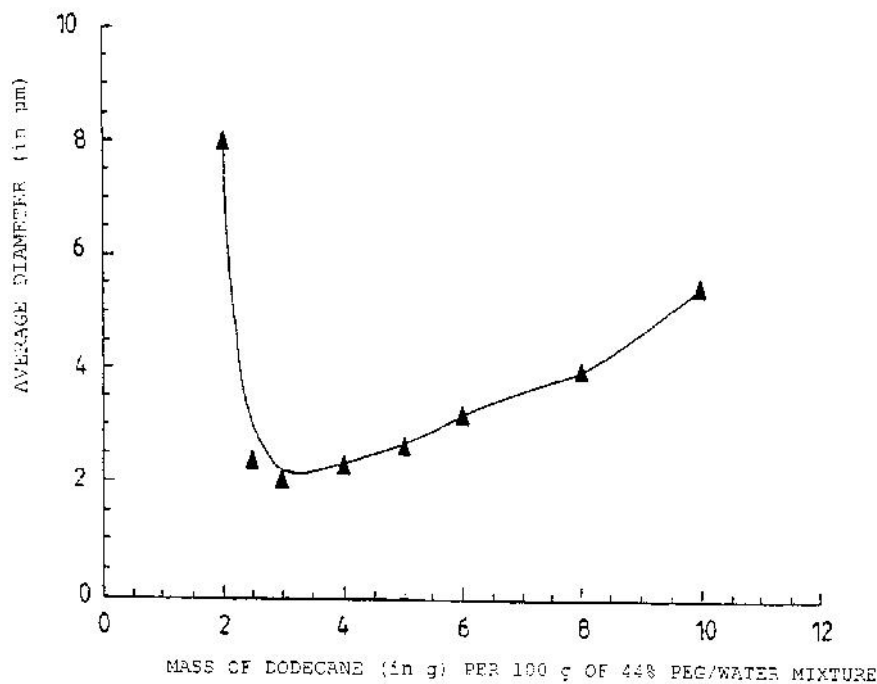
**Figure 37:** Average diameter size obtained for a stirring speed of about 400 rpm ( shear rate of about  $1000\text{s}^{-1}$  as a function of the amount of TTAB

It is noted that 1 gram of TTAB per 100 grams of bitumen is sufficient to achieve sizes of the order of one micron. A characterization of the yield for the processes as a function of the mass of TTAB introduced shows in fact that the maximum efficacy is virtually achieved for this maximum amount of TTAB. More specifically, this result is obtained by taking the yield as being the ratio of the mass of surfactants introduced. The mass of surfactants present at the interfaces is determinate simply by measuring the residual amount of surfactant present in the second phase after a controlled dilution.

This experience has been made at a stirring speed of 400 rpm. As we have explained in example 3, the best shear rate seems to be higher than 40 rpm, obtaining the best result in a value of 100 rpm. It could be interesting to repeat the example 4 at higher stirring speed.

Example 5: Assessment of the optimal amount of second phase relative to the average diameter of the droplets of an emulsion

In this example, the viscous hydrophilic phase to be dispersed in an aqueous mixture containing 44% polyethylene glycol PEG 35000, the surfactant used is Span 80 ( sorbitan monooleate sold by Sigma), present in a proportion of 1.5g per 100g of the phase to be dispersed, and the continuous phase is dodecane. Several mixtures of these compounds are prepared for different amount of dodecane at a shear of 400 rpm ( $1000\text{s}^{-1}$ ) in the reactor. The emulsions obtained almost instantaneously, are characterized by the average diameter of their droplets. The results are given on the following graphic:

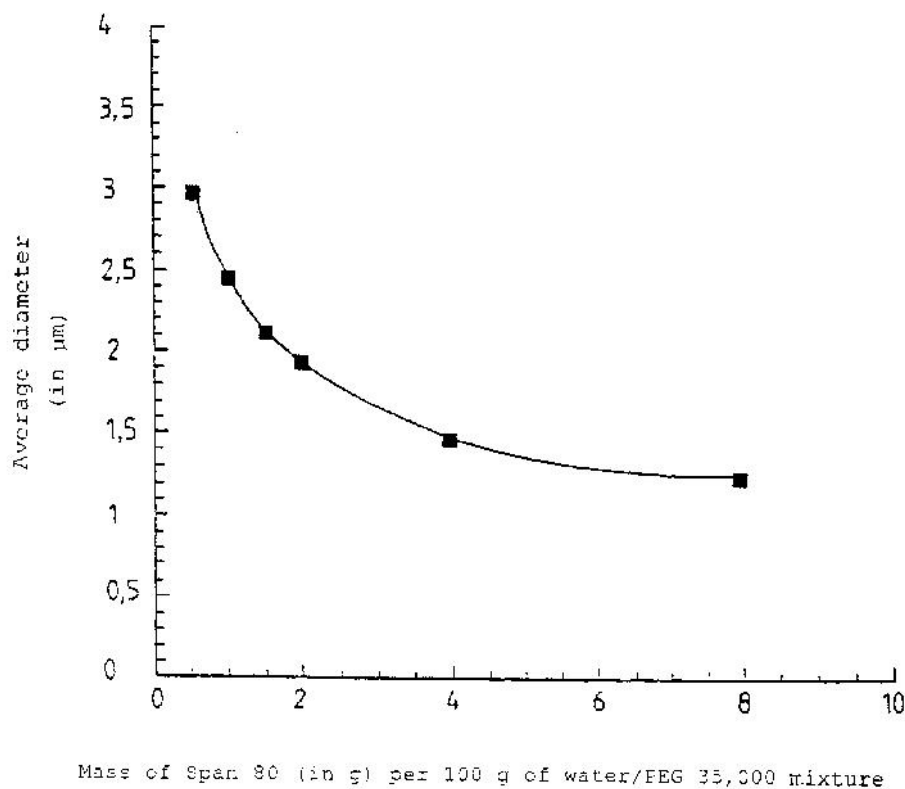


**Figure 38:** Average diameter size as a function of the amounts of oil, for an emulsification.

As we could see in the graphic the minimum diameter size obtained, of about 2 microns, is obtained for 3 g of dodecane. Nonetheless the optimal dodecane concentration is 2-4 grams, use higher concentration don't necessary mean smaller diameter size.

**Example 6: Effect of the amount of surfactant on the average diameter of the droplets of an emulsion at constant shear.**

The protocol described in example 5 is reproduced for several concentrations of Span 80 surfactant and 3 g of dodecane. The emulsions obtained after each of the test are characterized by the average diameter of their droplets. The results are represented on the following graphic:

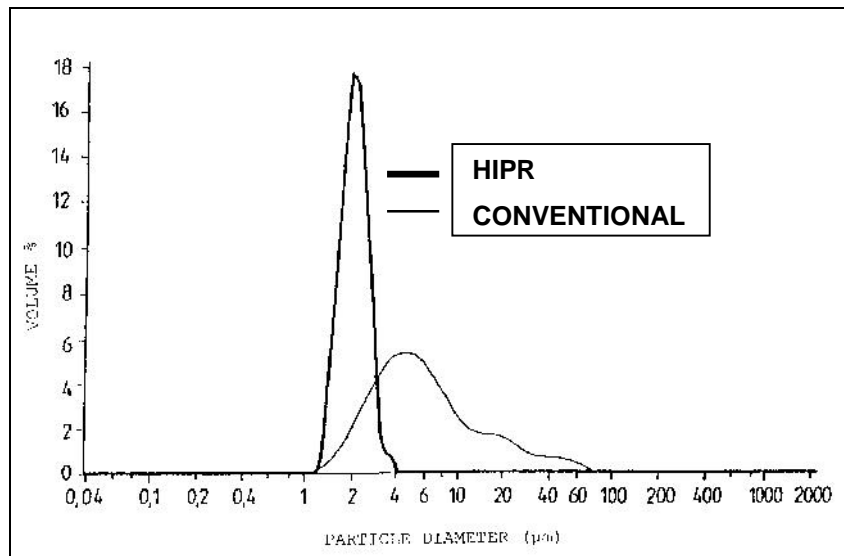


**Figure 39:** Average diameter size as a function of surfactant concentration at constant shear.

The finest emulsion is obtained for 4 g of Span 80.

Example 7: Comparison of a bitumen emulsion according to HIPR and of a conventional emulsion in terms of polydispersity and average droplet diameter

The industrial technique used consists in injecting, under pressure ( about 1.5 atmospheres) and 130°C, bitumen on the one hand and the aqueous soapy phase, on the other hand, between two coaxial rollers ( a rotor and a stator) spaced about 1 mm apart. The rotor rotates at a speed of about 5000 rpm. The emulsification takes place directly in the 1 mm gap, and does so in a turbulent regime. The fraction by volume of the phase to be dispersed cannot exceed 70% or else it will block the system. This assessment is carried out using an emulsion obtained in accordance with HIPR method, incorporating 0.75 grams of TTAB per 5.5 grams of water and 100 grams of bitumen and of a conventional industrial bitumen emulsion. This industrial emulsion contains 60 grams of bitumen, 0.5 grams of cationic surfactant and 39.5 grams of water. The granulometric distributions obtained by the two techniques are represented in the following graphic:



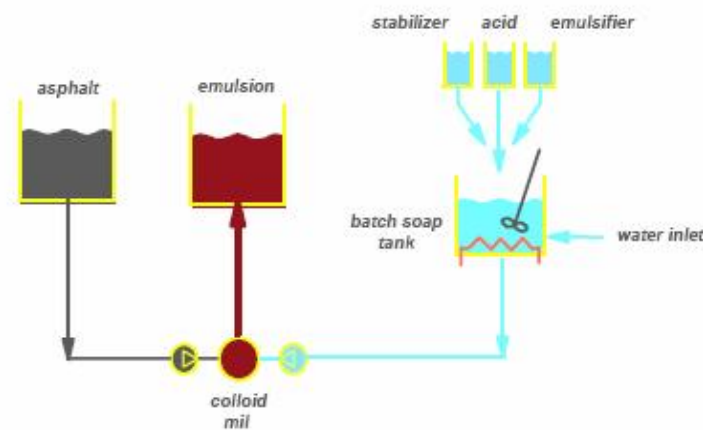
**Figure 40:** average diameter size using a conventional system front HIPR method.

For the emulsions according to HIPR method, an average size centered at about 2 microns is observed, with a polydispersity in the region of 30%. In turn the emulsion has a markedly larger average droplet diameter, i.e. 5 microns and a polydispersity not in accordance with the invention, i.e. markedly greater than 40%.

### 3. Summary

We could summarize the manufacture of bitumen emulsion and highly concentrated bitumen emulsion system in three different methods:

#### 3.1 Traditional method:



This method is known as "direct emulsification" due to the high shear and in general particle size is reduced by increasing the energy of agitation. Thus the corresponding emulsions are currently prepared by hot injection. (9)

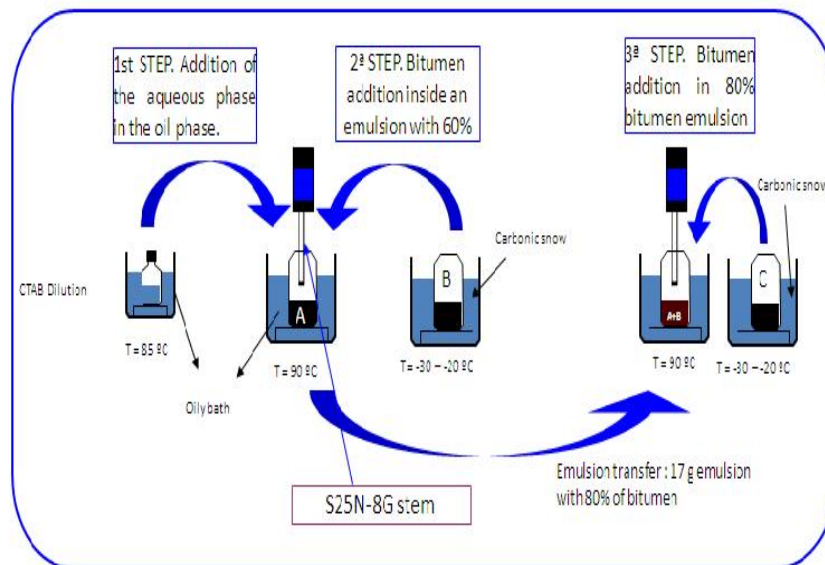
Generally, the bitumen is heated up to a temperature over 120 °C while the continuous phase, usually water, is also heated to approximately 60 °C. The mixture of bitumen and the aqueous phase are injected into a turbine under a very high rate of agitation, of the order of 5,000 revolutions per minute and under a pressure that can reach up to 3 atmospheres.

As a consequence of this type of treatment, bitumen emulsions generally have a concentration that does not exceed 70% in weight of bitumen, a significant average particle size (typically over 5 Pm) and also high polydispersivity. Emulsions obtained in this way, with a broad particle size distribution, and therefore with a high number of large sized drops ("distribution tail") have limited storage stability.



### 3.2. HIPR method by adding the oily phase in the aqueous phase:

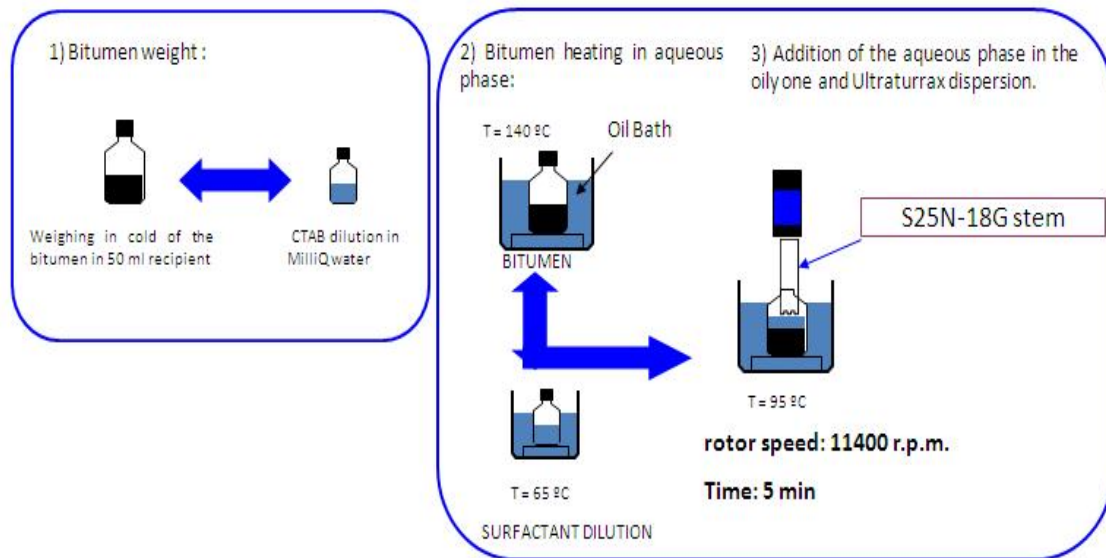
With this method it is possible to obtain highly concentrated bitumen emulsions. This method consist in adding the total oily phase in the aqueous phase and obtain a firstly emulsion. Once the emulsion is formed, we continue adding more oily phase, bitumen, in order to increase the final emulsion concentration.



With this method is possible to obtain highly concentrated bitumen emulsions, with a final concentration of 80% bitumen, but they have low storage stability.

### 3.3 HIPR by adding the aqueous phase in the oily phase:

This method consists in an inversion phase. We introduce all the aqueous phase in the oily phase in order to manufacture the concentrated emulsion and then if it is necessary we diluted the emulsion until the concentration desired.



With this method it is also possible to obtain a highly concentrated bitumen emulsions with a very narrow diameter size distribution and high storage stability.

### 3. Conclusions

Highly concentrated bitumen emulsions are still today not well understood.

There are very few papers related with this kind of emulsions. Most of the papers find it and used in this work are patents. There is still a lot of work to do in this aim.

The entire papers find are related to manufacture conditions such as effect of the rotor speed, effect of the temperature of the aqueous phase, the emulsion flow rate, the surfactant concentration, etc. on the main diameter particle size. We have not found any paper related with how the main component, the bitumen, could influence in the emulsion formulation, or which are the chemical bitumen characteristics which influence more at the manufacture moment. There are very few information about how bitumen precedence could influence in the final emulsion stability and performance. There are also very few papers related with the final properties of this highly concentrated bitumen emulsions, its performance, stability, viscosity, etc, so it could be a nice work to do in the future.

With conventional manufacture systems is not possible to manufacture emulsions with bitumen content higher than 70%. With these equipments, both the oil phase (bitumen) and the water phase are added at the same time (all at once) and are passed through a high-speed agitation chamber. This method is known as "direct emulsification" due to the high shear and in general particle size is reduced by increasing the energy of agitation. Thus the corresponding emulsions are currently prepared by hot injection. The bitumen is heated up to a temperature over 120 °C while the continuous phase, usually water, is also heated to approximately 60 °C. The mixture of bitumen and the aqueous phase are injected into a turbine under a very high rate of agitation, of the order of 5,000 revolutions per minute and under a pressure that can reach up to 3 atmospheres. As a consequence of this type of treatment, bitumen emulsions generally have a concentration that does not exceed 70% in weight of bitumen, a significant average particle size (typically over 5 Pm) and also high polydispersivity, so they have limited storage stability.

One of the best paper find it related with the conventional method manufacture system is the one presented by Gringras. In this paper the author says that the droplet size in bitumen emulsions produced in continuous mode (conventional method) by rotor-stator geometry are influenced by the process parameters. Experimental results indicate that the average droplet size decreases as the rotor speed increases or as the

emulsification temperature, the bitumen grade or the bitumen concentration decrease. The numerous models based on the balance of forces acting on the droplets in turbulent or laminar flow do not follow the experimental results presented before. It is possible to explain this discrepancy by the high decalescence rate and the complexity of the flow during the emulsification of high viscosity ratio in a rotor-stator machine. The choice of a rotor-stator mixer is generally based on the specific energy. This strategy for inline bitumen emulsification can lead to the production of emulsion out of the specifications required for the application. To avoid this situation, the residence time in the dispersing zone has to be considered as a design criteria especially when surfactants with long adsorption time are used.

The High Internal Phase Ratio (HIPR) method is the one used for the formation of highly concentrated bitumen emulsions. This method requires initial dispersion to be carried out at packing fractions greater than the critical. This facilitates the formation of highly concentrated emulsions with a very narrow droplet diameter distribution. According to this method it is possible to control with the formulation and the manufacture conditions the final morphology of the emulsion.

One of the foremost workers in the areas of HIPE's is K.J. Lissant of the Petrolite Corporation, St. Louis, Missouri, who has published numerous papers in this field and who held numerous patents related to HIPE technology. He has more than 25 patents related with this technology, but not in the field of bitumen emulsions.

M.L. Chirinos et al. (12) proposed a method to manufacture highly concentrated bitumen emulsions in 1995. It is a patent, and they propose HIPR method for the manufacture of bitumen in water emulsions. In this patent an HIPR bitumen emulsion in water is prepared by a method which comprises directly mixing 70% to 98% by volume of bitumen having a viscosity in the range 200 to 500,000 m Pa·s at the mixing temperature with 30 to 2% by volume of an aqueous solution of an emulsifying surfactant, percentages being expressed as percentages by volume of the total mixture. Mixing is effected under low shear conditions in the range 10 to 1.000 reciprocal seconds in such manner that an emulsion is formed comprising highly distorted bitumen droplets having mean droplet diameters in the range 2 to 50 micron separated by thin films of water.

In the different emulsions manufactured by Chirinos they get good results. It is a very good manufacture emulsion method, but in example 1 due to using a high

concentration of surfactant they don't reach a very narrow diameter size. They don't say anything about the stability, they mention that after 18 storage months there is no coalescence signal, but we did not know if they measure of if it is a visual observation. They neither say how they made the mean droplet size measure. Also, in example 2 Chirinos don't say what is the surfactant concentration used. There no mention to the stability, we suppose that they have made a visual evaluation and the values presented in the table 6 don't correspond to any laboratory test. Another question is what happens with harder bitumen, with a penetration grade lower than 65.

Another paper very interesting related with the formation of bitumen in water emulsions in the one by Gutierrez et al., 2002. This paper describes the most relevant issues associated with the development of a technology of the formation of highly concentrated bitumen in water emulsions. The authors have found that viscosity values for bitumen in water emulsions containing between 70 and 85% (v/v) of bitumen have been found to be several order of magnitude lower than the viscosity of the hydrocarbon itself. They give the information on the conditions required to produce emulsions with very narrow droplet diameter distribution is given. According to the authors the results indicate that the mean droplet diameter, the droplet diameter distribution and the bitumen volume fraction, significantly modify the rheological behavior. They measure the emulsion stability by following changes in the mean droplet diameter and in the rheological parameters with storage time.

Although the diameter size obtained with this method is better than the previous one, the narrowest diameter size distribution obtained is around 1.5  $\mu\text{m}$ . The authors don't pay any attention to the stability of this emulsions with is a very important parameter to be considered. The bitumen used in this paper is a bitumen from a very high acid value so with a low penetration grade. It could be interesting to know if the method presented would work with a harder bitumen penetration grades.

In 2003, F. Leal Calderon et al. (13) presented another patent for a method for preparing concentrated bitumen emulsions and calibrated in a highly viscous phase. In the process they explained a method for the manufacture of a highly concentration stable emulsion, by emulsifying a first hydrophobic or hydrophilic phase having a viscosity between 1 and 5000 Pa.s with a second phase immiscible in the first phase, in the presence of at least one surfactant, by mixing together the first phase, second phase, and surfactant under a laminar shear regime. It is the first paper presented

where the authors work in inversion phase adding the aqueous phase in the oily phase in only one step.

Although it is also a very good manufacture system the authors don't make any comment about the stability of this emulsion. Another parameter to be considered is the viscosity of this emulsions with is either commented on the paper.

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