Asphalt emulsion formulation: state of the art of formulation, properties and results of HIPR emulsions

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Abstract

As a way to make pavements more economic, less polluting, and with lower energy consumption bitumen emulsions can be used. The formulation of bitumen emulsions is a complex task and they are usually produced using colloid mills. This method presents several limitations; the maximum bitumen concentration of the dispersed phase, 69%, being the most significant. The HIPR (High Internal Phase Ratio) method must be used for higher bitumen concentrations. With this second method, apart from it being possible to obtain concentrated emulsions, with a volume fraction higher than 70%, it is possible to control the distribution and average droplet diameter of the emulsion. This control is achieved by changing variables such as the volume fraction, the concentration and type of surfactant and the temperature of the dispersed phase, the type of bitumen used, and mechanical variables such as the rotational speed and time employed. The current study aims to review the state-of-the-art of the manufacture of bitumen in water emulsions, with a special emphasis on the concentrated bitumen emulsions manufactured following the HIPR method.

Keywords: bitumen emulsion; conventional method; HIPR method; formulation

1. Introduction

Dispersed systems consisting of two immiscible liquids are called emulsions. In emulsions one immiscible liquid is the continuous phase, which contains the other, or internal phase, dispersed as small droplets. Bitumen emulsions are a way to use bitumen at low temperatures. While pure bitumen is used for manufacturing hot mix asphalt mixtures at high temperatures, 140ºC-160ºC, emulsions are materials that can be pumped at room temperature [1].

Asphalt emulsion properties such as viscosity and stability depend on several variables: the properties of the continuous phase (salinity and pH), the water/oil ratio (WOR), the surfactant (molecular structure), the size of droplets (and their distribution), and the established procedure to prepare the emulsion such us rotational speed and mixing time [1,2].

Asphalt emulsions can be used for any traditional hot-asphalt and cutback applications but, the emulsion's viscosity is a particularly important parameter and must be set according to the pavement application [3]. For example, high viscosity is required when emulsion is spread over an undulating area, such as mountainous terrain. Furthermore, a very low viscosity is desirable for pavement priming [2]. Moreover, one of the main sources of pollution stemming from road construction is the manufacturing, spreading, and maintenance of asphalt mixes. A cleaner production of bituminous mixes requires lowering the manufacturing temperature of these mixes without worsening or reducing their level of mechanical performance. Half Warm Mix Asphalt (HWMA) are mixtures that are manufactured and spread at lower temperatures than Hot Mix Asphalt, about a 30-50ºC reduction in temperature [4]. There are different ways of manufacturing these types of mixtures that are still in development today. Even though these technologies are quite different, it seems that the use of bitumen emulsions in these mixes could be a good option [4,5]. But not all bitumen emulsions could be used in HWMA techniques; a highly concentrated bitumen emulsion is needed to obtain good results.

There are different procedures to prepare bitumen in water emulsions, but a colloid mill is the most widely used. In this case, emulsification generally takes place when the dispersed phase (bitumen) has a concentration between 60 wt.% and 70 wt.%. Therefore it is not possible to obtain concentrated emulsions [6]. To disperse two immiscible phases it is also possible to use the HIPR procedure (High Internal Phase Ratio) [7,8]. This procedure involves the direct blend of two phases, a highly viscous one, 1-5000 Pa·s, with a second immiscible in the first one; the presence of at least one surfactant is usually needed. With this system it is possible to obtain concentrated and highly concentrated bitumen emulsions, 70-95 wt.% [1].

Bituminous emulsions as a field has been subject to very little scientific study, much less concentrated or highly concentrated emulsions of bitumen in water, nor bimodal emulsions. The understanding of this type of chemical dispersion is still a pending issue. The aim of this review is to compile and assess the literature available up to now on this topic, which is quite widely spread over the literature and patents. The state-of-the-art of the manufacture of bitumen emulsions is presented chronologically, since its beginning with the HIPR method.

2. Asphalt emulsion manufacture

The manufacture of bituminous emulsions is not a simple task. Experts in the field, when formulating, must take into account a series of parameters related not only to the manufacturing process, but also to the final properties for which the emulsion has been designed. In the manufacture of a bituminous emulsion, parameters such as engine speed, temperature of raw materials, or pressure must be controlled. Additionally, it will be necessary to take account of the type of surfactant used and its concentration. Moreover, important parameters related to the final product such as storage stability, the breaking index of the emulsion, viscosity or the final drop size, should also be considered [1,9].

There are two different methods of manufacture of bituminous emulsions, the conventional method and the High Internal Phase Ratio (HIPR) method.

Currently the most widely used system for the manufacture of bitumen emulsions in water uses high energy systems through colloid mills (Figure 1) [10] Following these processes the emulsion is manufactured in turbulent regime, produced by a rotor-stator device working at very high rotation speeds of around 5000 rpm. The hot bitumen (at a temperature between 140-180ºC) together with the soapy phase (at about 40-60ºC) flow through the small opening (<1 mm) in the engine for a very short period. Using this system emulsions with a residual bitumen concentration of between 60-70%, and an average drop size of 5 to 50 μm, and wide granulometric distributions are obtained.

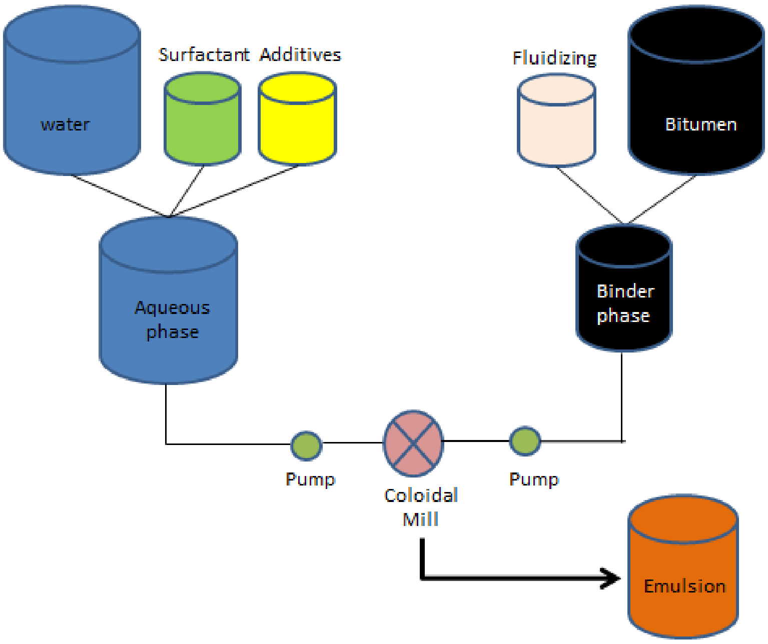


Figure 1. Manufacture process of an emulsion with colloid mills [adapted from 10].

For concentrations higher than 70% the colloid mill system is not effective as it leads to an increase in the production of large drops of emulsion and, consequently, the emulsions are not stable over time. The agitation process is not efficient at generating small droplets in an oily phase of high viscosity. The increase in the bitumen/water ratio increases the viscosity of the product to be emulsified, and reduces the effectiveness of shearing to break the drops [11].

The method known as **direct emulsification** takes place when the oil phase and the aqueous phase are added at the same time and go through a high speed stirrer. This manufacturing system has several drawbacks:

- It does not allow the manufacture of concentrated or highly concentrated emulsions of bitumen in water (higher than 70%).
- Satisfactory results cannot be achieved in terms of monodispersity.
- The average drop size of these emulsions is generally bigger than 5 µm and not homogeneous enough.
- The manufacturing system does not allow good control of storage stability, breaking rate, and viscosity of these emulsions.

When the materials to be emulsified are very viscous the system becomes inefficient, shear force destined to break the drops is lost, and larger drops are obtained, since part of the mechanical energy dissipates in the form of heat in the continuous phase.

The HIPR (High Internal Phase Ratio) method (Figure 2) also disperses two immiscible phases. It uses phase inversion that takes into account the physicochemical nature of each component and the proportions of each used during manufacturing. That is to say, by varying the formulation and the composition of the manufacturing variables the type of emulsion obtained as well as its properties can be controlled.

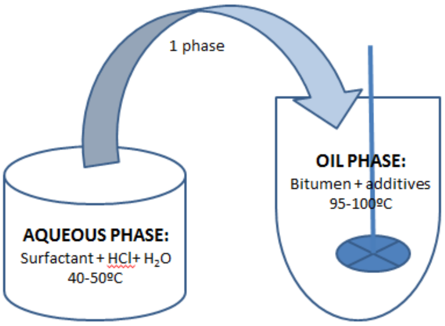


Figure 2. HIPR manufacture method [1].

This method consists of the direct mixing of a very viscous phase, 1-5000 Pa·s at 100 °C, with a second phase, immiscible in the first, and at least one surfactant. A viscoelastic paste is obtained with low shear, in a laminar regime, and in a very short time. This paste can be subsequently diluted to the required dispersed phase concentration. With this system it is possible to obtain concentrated and highly concentrated emulsions, 70-95wt.%, stable in storage, with narrow granulometric distribution and small drop size (around 1 μm). The drop size of the emulsions made with this method can be easily controlled by means of the shear rate, formulation parameters, or by the diluent phase concentration used at the time of manufacture [6-8].

In general terms, the reverse phase formulation process is a process by which an emulsion changes its morphology from water in oil (W/O) to oil in water (O/W) or vice versa. According to Calderon et al. [11], the process of forming a reverse phase emulsion is not instantaneous. Four distinct zones of kinetic behaviour can be clearly differentiated (Figure 3). Zone I, which takes place in the first seconds of the manufacturing process, is characterized by a strong increase in viscosity as a result of the homogenization of the dispersion. Zone II takes place between the first few seconds and 1 minute after starting the process and it is characterized by keeping a constant viscosity. It corresponds to the formation of the inverse emulsion of W/O as a result of the difference in the oil-water ratio. Zone III, between minute 1 and minute 2.5, shows again a steep increase in viscosity that can be attributed to the formation of multiple emulsions O/W/O, where the incorporation of the bitumen drops into the drops of water leads to an increase in the apparent volume of the dispersed phase. The system changes from being O/W/O to O/W following the Bancroft rule, which establishes that the formation of an oil-in-water or water-in-oil emulsion does not depend on the relative percentages of oil or water but on which of the phases of the emulsion has more affinity for the emulsifier. It is considered that at the end of Zone III the phase inversion process has concluded. And finally, Zone IV, from minute 3on, where the viscosity increases slightly until it remains constant; this is associated with the gradual reduction of the average drop size under continuous mechanical agitation.

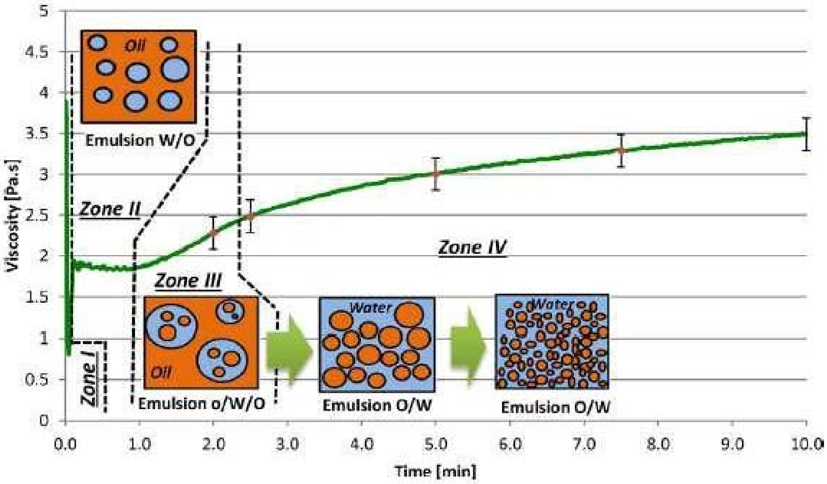


Figure 3. Description of the evolution morphology in the kinetics of an emulsion formulation [11].

3. Conventional, concentrated and bimodal bitumen emulsions

The most widely used method to prepare bitumen in water emulsions in an industrial process uses colloid mills for its manufacture. This method uses temperatures between 140-170ºC, pressures around 1-3 atm, and/or a high rotational speed, 5.000-10.000 rpm. Therefore, emulsions are manufactured in a turbulent flow. As desired, emulsification takes place at concentrations of the dispersed phase (bitumen) between 60 wt.% -70 wt.%, or what is the same, at a volume bitumen fraction of 0.6-0.7. Higher concentrations are not recommended since very large drops are obtained and emulsions will not have the required storage stability. Moreover, by the traditional method it is very difficult to obtain small droplet size, and therefore storage stability. The breaking rate and viscosity of these emulsions are difficult to control by modifying the manufacturing system [1,6].

Emulsions with fractions of dispersed phase volumes higher than 0.74, which corresponds to the maximum packing of monodisperse spheres, are called concentrated or highly concentrated emulsions [2]. Therefore a thin film of continuous phase will separate the scattered droplets where they touch each other (Figure 4). Moreover, attractive Van der Waals forces will generate a pressure of disunion [3] inside the interfacial film. Therefore, the interfacial liquid film becomes thinner due to the change in pressure with time and may eventually break, destabilising the emulsion. Thus, the stability of an emulsion depends on the stability of the interfacial liquid film, which in turn depends on the pressure of disunion [3]. The disbonding pressure is a force per unit area, which opposes the drainage of the continuous phase contained in the interfacial liquid film [12].

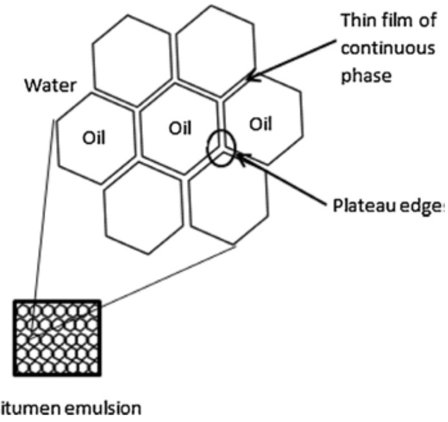


Figure 4. Polyhedric structure of a concentrated emulsion [12].

The stability of the system will be preserved by a monolayer of surfactant adsorbed on the surface of the dispersed droplets in the emulsion, which is responsible for conferring an adequate magnitude to the disunion pressure. As mentioned above, in emulsions it is essential to control stability control [13] and the rheological properties during the formation process and later during storage and transport [3]. It is possible to control the properties of these systems through a careful control of the nature and magnitude of the interaction forces between drops. The main forces that act within the interfacial liquid film, contributing significantly with the pressure of disunion, are the London, Van der Waals and electrostatic repulsion forces [5,6].

Concentrated and highly concentrated emulsions are characterized by having high viscosity [2]. As the concentration of residual bitumen increases, the final viscosity of the emulsion increases exponentially. In addition, they are emulsions with a small size and small granulometric distribution, a factor that enhances the high viscosity of this type of binder.

To use emulsions as binders in asphalt mixtures, high concentrations of residual bitumen are needed, or what is the same, a low content in water since this can hinder the compaction of the mixture and consequently obtain unacceptable final mechanical results. Therefore, the formulation of concentrated emulsions needs to be developed to obtain low viscosity, with different rheological behaviour from conventional emulsions. This may be achieved with bimodal emulsions.

Bimodal emulsions are characterized by having two granulometric distributions, with different and controlled drop sizes, forming a characteristic bimodal distribution [14,15]. A first small drop size, $d(0.5)_s$, of around 1 µm, and a second large one, $d(0.5)_l$, of around 5 µm. The optimal distribution between the two emulsions is a ratio of 1/2, twice as much of the emulsion with the large size than that with the small size (Figure 5).

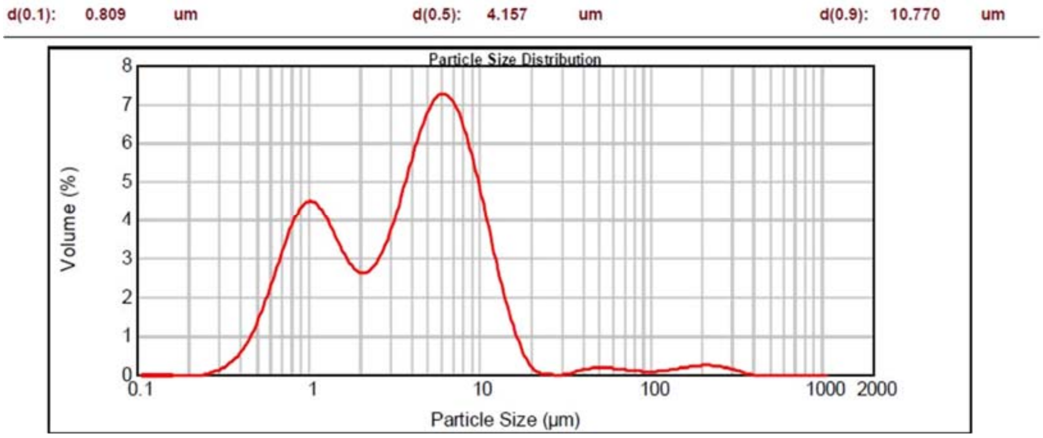
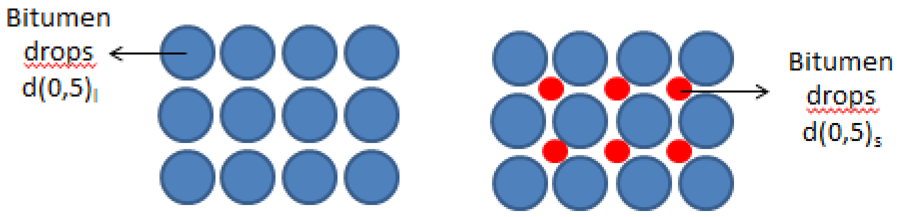


Figure 5. Example of mean particle size distribution of a bimodal emulsion.

In the bimodal emulsions the decrease in viscosity that can be observed compared to their equivalent monomodal emulsions can be attributed to the packing of the drops in the emulsions (Figure 6). This happens because in bimodal emulsions the small drops try to replace the holes of the cubic matrix generated by the distribution of the large drops [3,16].



Emulsión (A) Emulsión (B)

Figure 6. Scheme of a monodal and a bimodal emulsion. Adapted from [15].

4. State-of-the-art

The first document related to the manufacture of bitumen in water emulsions dates from 1949 and is the one from Wastts et at. [16]. The authors illustrate a method of making improved smaller average particle size asphalt emulsions for their use in waterproofing and sizing paper and paperboard. However, these emulsions have one very undesirable feature; the bituminous residues obtained on the paper are readily water re-emulsifiable or water leachable. Just one year later, in 1950, Fenelon et al. [17] patented another method for preparing improved smaller particle size emulsions, also focused on waterproofing. This patent employs wood rosin and petroleum resin to prepare what is called either a fine solution or a dispersion containing no particles larger than 0.1 micron. But, when the percentage of petroleum resins exceeds 50% and the free rosin becomes less than 10%, the emulsions are cloudy dispersions having observable particles of a size bigger than 0.1 micron. Furthermore these emulsions lose their ability to size paper when they are stored for any appreciable time. Another disadvantage of these emulsions is that they require the use of a setting aid, such as papermaker alum, to cause the asphalt to become firmly attached to the cellulosic fibres [18].

It seemed necessary to develop a bitumen emulsion manufacture that provided new and improved bitumen in water emulsions of small average particle size which did not cream or precipitate and could be resistant to metal container storage conditions. In 1962, Eugene et al. [18] patented an invention related to new and useful bitumen in water emulsions and to the process of preparing those improved emulsions. This patent was still not focused on asphalt pavement.

In 1971 Dybalski et al. [19] patented a bituminous dispersion containing a bituminous phase (from 20 to 90 wt.%) that could provide unusually good adhesion with the addition of certain aryl-substituted aliphatic nitrogen compounds. These compounds are long-chain monoaralkyl or diaralkyl amines, aralkyl diamines, and their oil-soluble salts. This invention relates to improvements in bituminous dispersions, generally known under the name of cationic bituminous emulsions, of both the oil-in-water and water in-oil types. More particularly, it relates to improved bituminous dispersions characterized by an unusually good adhesion to siliceous and calcareous aggregate surfaces. So, this patent can be considered the first patent related to the manufacture of bitumen in water emulsions. In 1989, Marchal et al. [20] introduced the use of colloidal mills in the manufacture of bitumen emulsions. This fact allowed improved emulsion properties such us a relatively low average particle size, continuous and speedy preparation by a process comprising of feeding emulsion components into the first of at least two static mixers, arranged in series. The final emulsion product is obtained from the outlet of the second mixer.

Despite the process patented by Marchal et al. [20] emulsion manufacture was still a difficult task, and the emulsions obtained frequently had low stability. In 2003, Samanos [21] improved the previous method with the first patent focused only on the production of bitumen emulsions to be used in construction and maintenance of roads surfaces. He stated that emulsions of bituminous binders are conventionally prepared by mixing a disperse phase and a dispersing phase in a suitable mixer. The dispersed phase can consist either of pure bitumen or of bitumen mixed with a fluidizing agent and/or an elastomer. Using this method, the authors were able to manufacture emulsions containing 50-70wt.% bituminous binder. The process of the invention allows better control of the rate of breaking almost independently of the viscosity and the particle size distribution of the emulsion.

A lot of the studies developed later on are based on the manufacturing process developed by Samanos et al. [21-25]. In addition, they begin to study the influence of the parameters related to the manufacturing system using a colloid mill, such as the influence of the temperature of the aqueous and oily phase, the shear rate, the dispersed phase content, the concentration of surfactant used, the penetration of bitumen, and the flow velocity, in the obtaining of the final average drop size of the emulsion.

To comply with the limitations of manufacturing with the method based on the use of colloid mills, the method known as High Internal Phase Ratio (HIPR) can be used, since it allows highly concentrated emulsions of bitumen in water to be obtained. This requires an initial dispersion superior to the critical packing of monodisperse spheres. This method facilitates the formation of highly concentrated emulsions with a small droplet size distribution. In addition, it allows the drop size obtained to be controlled by controlling the physico-chemical parameters related to the formulation.

Lissant et al. [23] can be considered the father of concentrated emulsions of bitumen in water since he published for the first time in 1974 a method of manufacturing a concentrated emulsion. However, most of his studies are related to petroleum, oils, cleaning products, cosmetics, etc. and not to bitumen emulsions in water.

In 1982, Aronson et al. [24] published a patent related to the HIPR method where the different parameters related to the manufacturing system of the emulsions or their raw materials such as surfactants, aqueous phase, different additives, foaming agents, etc. are described. It is focused on improving the stability of emulsions and in this work different tests related to storage stability under accelerated temperature and aging conditions, and in freezing conditions are performed. It is excellent work to understand the influence of raw materials or the manufacturing system of emulsions made with the reverse methodology, however, the approach is very general and does not include the manufacture of bitumen emulsions in water

Chirinos et al. [25] were the first authors to publish a patent related to the manufacture of highly concentrated emulsions of bitumen in water using the HIPR method in 1997. The authors proposed the manufacture of the emulsion with a method that involves the direct mixing of 70 to 98% of bitumen volume having a viscosity in the range of 200 to 500 000 mPa·s, to an aqueous phase containing between

0.1-5% surfactant. The mixing takes place at a low agitation in a range between 10-1 000 rpm and in two phases. Therefore highly concentrated emulsions are formed having a mean droplet size between 2-50 µm separated by a very thin film of water. Depending on the final concentration of bitumen in the emulsion, the authors proposed three manufacturing methods: in a single phase, in two phases, or in three phases for highly concentrated emulsions. If carried out in a single step, the entire oil is introduced into the aqueous phase, while if it is carried out in several phases, first an emulsion is made with a high bitumen content and then it is completed adding more bitumen to the emulsion until achieving the desired final concentration. In this study the authors presented numerous examples of manufacturing emulsions using the HIPR method. It should be highlighted that it is a good method to manufacture concentrated and highly concentrated emulsions of bitumen in water, although the average drop sizes achieved by the authors were between 5-15 µm, and the stability of the proposed emulsions was either not contemplated or was a completely qualitative assessment. Moreover, the concentration of surfactants used in manufacturing is not very clear, and the study uses only a single type of bitumen, 65 dmm penetration grade bitumen. It would be interesting to study how the proposed method behaves for harder bitumen.

Gutierrez et al. [9] in 2002 studied the effect of different manufacturing parameters such as the mixing time, the initial fraction of volume used in manufacturing and the agitation speed in the final droplet size of emulsions manufactured following the HIPR method. The authors stated that emulsions containing between 70-85 vol.% of bitumen have a viscosity several orders of magnitude below that of the parent hydrocarbon itself. Therefore, the authors thought that these emulsions had a big potential in processes of production, transportation, storage or commercialization of very heavy hydrocarbons. The emulsions were formulated with an initial bitumen fraction of 0.90 and once formed they were diluted in fractions between 0.60 and 0.85. As surfactants, non-ionic and natural products were used at a concentration of 3000 ppm. The mixture of aqueous and oily phase was mixed for several minutes by means of a Rushton-type stirrer. The emulsions were stored at 25-45 °C. With these manufacturing conditions, they obtained emulsions with a very small average droplet size and a closed granulometric distribution.

One of the first effects studied by Gutierrez et al. [9] is the effect of mixing time on the final drop size. The study demonstrates that the average drop size varies depending not only on the duration of agitation but also on the speed. As the time increases, the average drop size decreases, reaching a maximum time above which the average size no longer improves and remains stable. When the stirring speed increases the average drop size decreases, but when the stirring time increases, the values obtained are more similar, being almost equal for emulsions formulated at 8 minutes and 2000 or 2500 rpm. Another parameter studied by the authors is the bitumen/water fraction. The final drop size of the emulsion can be controlled by varying the proportion bitumen /aqueous phase used during manufacturing, providing the mixing speed exceeds a certain critical value of approximately 2500 rpm. According to the authors, it can be concluded that the average droplet size is influenced by the fraction of the initial volume of bitumen to be emulsified, with 0.95 being the most favourable and 0.75 the most unfavourable, and being difficult to emulsify with a fraction below 0.75 of initial volume.

From the information extracted from this study by Gutierrez et al. [9] the average drop size of the bituminous emulsion varies significantly and uniformly depending on the mixing time, the speed, and the initial volume fraction used. These results suggest that the creation of the interfacial phase occurs in a controlled manner, which allows the production of emulsions with a desired small size and a narrow granulometric distribution. Although the results in terms of average drop size obtained by these authors are better than those of Chirinos et al. [25], the authors do not mention the stability of the emulsions, which is a very important parameter to consider. In addition, the bitumens used in this study are soft penetration bitumens, around 150 dmm. It would be necessary to observe these results with harder bitumens, type 15/25. Nor do they refer to the problems of viscosity that can be found in emulsions with so small average size, about 1.5 μm, and 80% residual bitumen. These emulsions will be very difficult to pump and transport due to their high viscosity.

To study the storage stability of this type of emulsion, Calderon et al. [6], in 2003 presented a patent explaining how they prepared highly concentrated emulsions of bitumen in water taking into consideration the storage stability. According to the authors, the method presented allowed the manufacture of concentrated or highly concentrated emulsions of bitumen in water or water-in-oil directly by mixing in a single phase and working in a laminar regime. These authors stated that the particle size obtained by this method was narrower than that obtained by conventional methods. This fact is controlled by the manufacturing system. Moreover, they studied the effect of the amount of water mixed surfactant and the shear rate in the final average diameter of the droplet to be able to correlate it with storage stability. They concluded that these types of emulsions were much more stable than emulsions manufactured with a colloid mill system.

The average droplet size was extensively studied by Gringas et al. [22] in 2005. The procedure parameters used to manufacture the emulsion in this paper are summarized in Table 1.

Table 1. Summary of the process and formulation developed by Gringas et al. [22].

Process parameters	**Unit**	**Range**
Rotor speed	s^{-1}	52-87
Emulsion mass flow rate	kg/h	90-400
Bitumen temperature	ºC	70-140
Aqueous phase temperature	ºC	30-90
Bitumen content	wt.%	55-75
Bitumen grade	1/10 mm	10/20; 160/220

The main conclusions from the study carried out by Gringas et al. [22] are that the average droplet size of an emulsion obtained by a conventional method based on a turbulent regime and using a continuous rotor/stator model is influenced, and to some extend limited, by the parameters related to the manufacturing system. Specifically, the authors claim that the average droplet size increases when: the mill speed decreases, the emulsification temperature increases, or the concentration of surfactant decreases. With this manufacturing system it is difficult to control the flow rate at which the emulsion must be made and emulsification problems are registered when the viscosity of the bitumen increases and the concentration of residual bitumen exceeds 69%.

Regarding the application of this type of emulsion, Lesueur et al. [25] presented in 2008 the results obtained in an emulsion using the HIPR method for the manufacture of cold mixtures for the first time. It shows a significant improvement of the use of nanoemulsions manufactured with the HIPR method, compared to conventional emulsions. The HIPR method makes it possible to manufacture emulsions with a controlled drop size and a very narrow granulometric distribution, which translates into a high specific surface area. These emulsions are of great interest for techniques such as cold recycling because they have high conserved resistance strength as well as a high module in the short term modulus due to the high specific surface of these emulsions.

If the average drop size needs to be reduced even more, homogenizers should be used in the manufacture of the emulsions. Paez et al. [27] in 2010 filed a patent that describes a process that is carried out to prepare emulsions of bitumen in water with a final average size of drop of 1 μm using the method of inversion of phases for its manufacture, combining low agitation static agitators and high speed homogenizers . The authors also mentioned the application of this type of emulsions in the construction of pavements. The authors obtained emulsions with a droplet size lower than 1 μm, using soft penetration bitumen (150/220 and 80/100).

If we want to know if an emulsion is direct or inverse we should refer to the paper by Arenas-Calderon et al. [11]. This work studies the different phases through which an inverse emulsion passes until it becomes a direct emulsion. Different emulsions were produced from which samples were taken at different times, and were then subjected to observation under a microscope. To observe whether emulsions are direct or inverse, the authors submitted the emulsions to aqueous and oily visualization mediums. The micrographs show that in the first 5 seconds of emulsion formation, most emulsions were inverse, since their droplets were distributed in the oily medium, while after 1 minute the emulsions were direct and no droplets could be seen in the oily medium.

As far as bimodal emulsions are concerned, there is very little literature. In 1994 Rivas et al. [14] patented the required methodology to develop the formulation of bimodal emulsions. The authors stated that in order to formulate bimodal emulsions it is necessary to start with monomodal emulsions of controlled size. For the manufacture they used the HIPR method because it is a method where the average drop size is controlled more easily. The authors also studied the viscosity of the emulsions, obtaining as a result that the bimodal emulsion had lower viscosity than their monomodal counterparts and that it is also stable in storage. According to the authors, the average size desired for the large monomodal size emulsion is 15 to 30 µm, while for the small size it is 5 µm. In addition, the ratio between the large and small size emulsions must be equal to or higher than 5, and preferably higher than or equal to 10 [15].

A summary of the presented state-of-the-art can be found in Table 2.

Table 1. Chronological State-of-the-art of manufacture, properties and results of HIPR bitumen in water emulsions

Reference	**Conditions**	**Results**	**Drawbacks**
Lissant [23]	HIPR technology	---	Not related to bituminous emulsions with water
Aronson [24]	Description of the parameters related to the manufacture of emulsions: temperature, oils, aqueous phase, additives, etc.	Improvement in the stability of emulsions	Not related to bituminous emulsions with water
Rivas et al. [14]	Bitumen from Cerro Negro Ratio bitumen/water phase: 90/10; 85/15 Bitumen concentration=70-85% $d(0.5)_l$: 15-30 µm $d(0.5)_s$: 5 µm Ratio large/small - 1/5 (better 1/10)	Bimodal emulsions with a lower viscosity than the corresponding monomodal emulsion	Harder bitumen, with lower penetration Stability over time
Chirinos et al. [7]	Bitumen viscosity: 200-500 Pa.s Ratio bitumen/water phase: 70/30-98/2 Shear speed: 100-1.000 s^{-1} Manufacturing method in two phases	High Polidispersity d(0.5) = 2 - 50µm Bitumen concentration = 70 - 98% Good storage stability Possibility to emulsify hard penetration grade bitumen	Method used to test stability Viscosity of emulsion obtained Penetration grade bitumen used Surfactant concentration used
Gutierrez et al. [9]	Bitumen used: "Cerro Negro" Bitumen concentration = 0.40 – 0.85 % T= 60ºC Surfactant concentration: 3000 ppm	The volume fraction of bitumen, the mean droplet diameter and the droplet diameter distribution strongly affect the rheological	No stability studied Only soft penetration grade bitumen are used in the study

		behavior of monomodal bitumen in-water emulsions At low bitumen concentration emulsions behave as Newtonian liquids, for bitumen concentration higher than 70%, emulsions behave as non-Newtonian fluids	
Calderon et al. [6]	Bitumen viscosity: 1-5.000 Pa.s Manufacturing method in one phase Surfactant concentration: 0.5 – 5% Laminar regime, Re<1000 Shear speed: 250-2.500 s^{-1} Patm	Bitumen concentration ≥ 75% d(0.5) increases when shear speed increases, the quantity of oily phase d(0.5) obtained <2µm. Polydispersity < 40% Laminar regime	Stability and viscosity of the emulsion obtained are not mentioned Penetration grade bitumen used is not expressed, nor the manufacturing time of the emulsion
Gringas et al. [22]	Shear speed: 52-87 s^{-1} Flow rate: 190-400 kg/h T: 70-140ºC Penetration grade bitumen: 10/20; 160/220	Bitumen concentration: 55-75% d(0.5) increases as soon as colloidal mill speed decreases, emulsification temperature increases, and surfactant concentration decreases.	HIPR method is not used Mean droplet size is not possible to control with this method Hard bitumen penetration grade are difficult to emulsify
Lessueur et al. [26]	Bitumen 70/100 Manufacturing method in one phase HIPR Viscosity bitumen > 1 Pa·s	Good cohesion High resistance to storage High degree of coverage	Only applied to cold recycling It is necessary to evaluate the behaviour of this type of

			emulsions in the rest of the mixtures
Paez et al. [28]	Manufacture method in inversion phase Mix of static agitators of high shear with low shear ones Use of homogenizers Penetration grade bitumen used: 150/220; 80/100	Submicron emulsions obtained d(0.5)< 1µm	Manufacturing difficulty Low performance low repetitiveness
Calderon et al. [11]	Bitumen used: 70/100 Ratio bitumen/water phase: 90/10 Shear speed: 300rpm t=2 min	Phases related to the step from direct to invers emulsion Microscopic observation of the different phases Invers emulsion step to direct emulsion in less than 1 minute	Studies of hard penetration grade bitumen are desired

5. Conclusions

Summarising, emulsion manufacturing techniques can be grouped into two large groups. Emulsions manufactured by the conventional method and emulsions manufactured by the method known as *High Internal Phase Ratio* (HIPR). The conventional method is also known as the *direct emulsification method*. Emulsions made with the conventional method have a residual bitumen concentration that cannot exceed 70wt.% bitumen, have an average droplet size of around 5 μm and a high polydispersity. On the other hand, with the HIPR method it is possible to obtain concentrated and highly concentrated emulsions of bitumen in water, with an average droplet size of 1 μm, stable in storage.

For the manufacture of emulsions following the HIPR method two manufacturing systems can be differentiated: a single phase, where the entire oil phase is introduced into the aqueous phase, or in two phases, where a quantity of controlled bitumen is partially introduced into the manufacture, followed by the entire soapy phase. Once the emulsion is formed, the concentration of residual bitumen is increased by the addition of the soapy phase slowly.

Acknowledgements

The authors would like to thank the Catalan Government for the quality accreditation given to their research group GREiA and DIOPMA (2017 SGR 1537 and 2017 SGR 118, respectively). GREA is certified agent TECNIO in the category of technology developers from the Government of Catalonia. Dr. Camila Barreneche would like to thank ACCIO for her Grant TecnioSpring Plus TECSPR17-1-0071. Núria Querol would like to specially thank Sorigue Company for giving her the opportunity to develop this research in the company.

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