INTRODUCTION

Viscosity is an important characteristic when using bitumen emulsion.
The viscosity of a bitumen emulsion must be adapted to suit its intended use: for example high viscosity is preferred for spraying on mountain roads but low viscosity for the impregnation of soils…
Various methods of altering the viscosity of bitumen emulsions are available:

Mechanical techniques

One of these consists of **varying the shear gradient** in the colloidal mill. This increases as the rotation speed is increased and the gap between the rotor and stator of the colloidal mill is reduced. However, a high shear gradient tends to reduce the median droplet size and the range of the droplet size distribution. This phenomenon, however, reaches a limit at a shear gradient of approximately 50,000 s^{-1} (1).

Another technique is to manufacture the emulsion in **a medium with a very high bitumen concentration** (80 to 90%), then to dilute it to the binder concentration required for the target application (the usual range is between 60 and 70%): this procedure encourages the formation of monodisperse particles (2).

However, **the characteristics of the droplet size distribution influences the viscosity of** the emulsion in the following manner: an emulsion with a smaller range of droplet sizes is more viscous as, with a constant volumetric bitumen concentration, the interactions between monodisperse spheres are more numerous than between polydisperse spheres. This effect becomes more marked the higher the binder concentration (3).
Likewise, **droplets with a smaller median size have** a larger specific surface area which is responsible for viscous reactions between the spheres.

Chemical techniques, mix design

The nature of the bitumen
Naphthenic bitumens, which are naturally acidic, produce more viscous emulsions than paraffinic bitumens.

The bitumen content
The effect of the nature of the bitumen on viscosity increases as the volume fraction which gives the maximized particle stacking within the emulsion Φ m is approached. Although the bitumen particles are deformable, particularly at high temperature, the interactions between the particles become large beyond a bitumen content of 70%, leading to a considerable increase in the viscosity of the emulsion.

The nature of the emulsifier
It has been shown that some emulsifiers, because of their ability also to produce water/oil emulsions, play a role in the inclusion of greater or lesser amounts of water in the bitumen droplets, which reduces the free water content of the emulsion (7). The **effective volume fraction is therefore higher** than would correspond to the bitumen fraction added initially.
The emulsifier content is generally adjusted on the basis of the required performance but an excessively low water content results in a course emulsion.

This study aims to determine the **respective roles of the droplet size distribution and the effective bitumen volume fraction** on the **viscosity of emulsions**, and to propose a rheological behaviour model.

1. EXPERIMENTAL SECTION

The experimental section is based on the characterization of several series of emulsions with different mix designs and variable percentages of paraffinic or naphthenic bitumen, manufactured with increasing rates of shear.

1.1- The materials

The following bitumens were selected for this study:

- 160/220 Nynas (Antwerp refinery): naphthenic
- 160/220 Esso (Port Jérôme refinery): paraffinic

Two types of emulsifier were also used:

- Polyamine: a “slow breaking” emulsifier
- Polyamido Imidazoline: a “fast breaking” emulsion

These were made cationically activated by hydrochloric acid.

1.2- Manufacture of the emulsions

Six series of emulsions were manufactured using an EMULBITUME laboratory colloidal mill:

- Series 1 (Esso , Polyamine), bitumen content: 65% to 71%
- Series 2 (Nynas , Polyamine), bitumen content: 65% to 71%
- Series 3 (Nynas , Imidazoline), bitumen content: 65% to 71%
- Series 4 (Esso, Imidazoline), bitumen content: 65% to 71%

- Series 5 (Nynas, Polyamine), bitumen content of 68%, a variable rate of shear: rotation speed 5000 to 9000 rpm.
- Series 6 (Nynas, Polyamine), bitumen content greater than 69%

The proportion of emulsifier was fixed at 5 g/l of emulsion and the proportion of acid was adjusted to obtain a pH of 2.5.

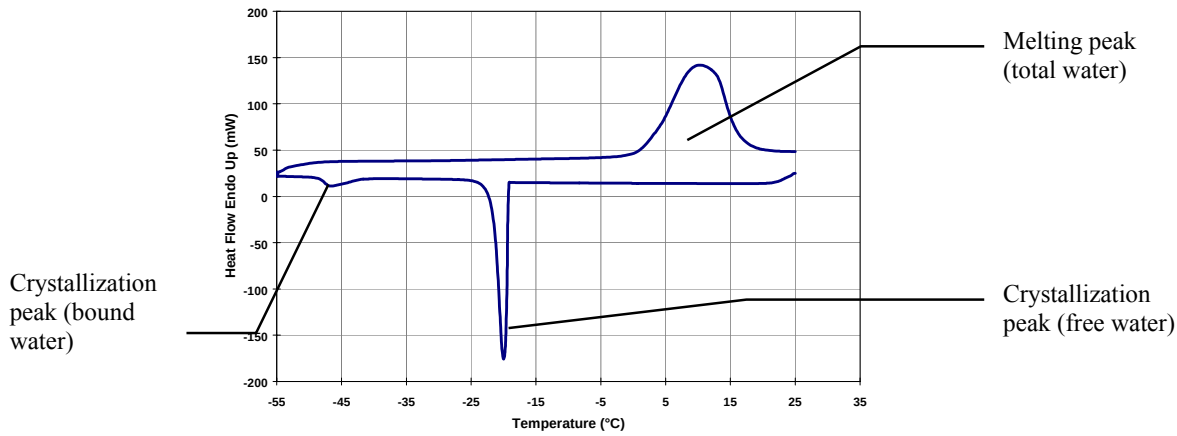
1.3- Characterization of the emulsions

- Bitumen content: measurement of the dry extract using an infrared balance, at 110°C → **Φ bit**
- Dynamic viscosity **η** at 25°C and 40°C in mPas (LVDV-E type BROOKFIELD viscometer, test conditions: S62 spindle – speed: 50 rpm)
- Laser granulometry (median diameter $\mathbf{D_{50}}$ in microns , standard deviation **σ** of the droplet size distribution, specific surface area **S**) - MASTERSIZER 2000 (MALVERN)
- Differential Scanning Calorimetry (DSC 204 - NETZSCH): The principle is to record the difference between the energy absorbed by the control crucible at different temperatures. Temperature scanning: slope falling from 25°C to -55°C followed by an inverse rising slope. Rate of heating and cooling:10 °C/min

A typical thermogravimetric curve is shown in Figure 1. A single melting peak is apparent.

2 exothermic crystallization peaks have been identified:
- 1 normal “free water” peak
- 1 peak or group of peaks in a temperature range of between -40°C to -50°C, corresponding to “bound water” which has very different characteristics from free water (5, 7).

Figure1: DSC thermogravimetric curve



The enthalpy of crystallization of the bound water ΔH_c has been taken as 219 J/g (6).
The mass of water involved in the observed thermal phenomenon has been calculated using the formula:

$E = \Delta H_c * m$

Where: E is the energy determined by integrating the peak
ΔH_c is the enthalpy of crystallization
m is the mass of bound water

The bound water fraction in relation to the emulsion, **Φ bound water,** is thus obtained directly. The effective volume fraction of the bitumen Φ**eff** is then calculated: **Φeff = Φ bit + Φ bound water**

2. RESULTS

2.1 The influence of the rotation speed of the colloidal mill on the droplet size distributions of bitumen emulsions

The results for **series 5** lead to the following plots of rotation speed versus median diameter (Figure 2) and versus standard deviation (Figure 3) .These trends confirm the previous findings with regard to mechanical action (1)

Figure 2: D_{50} versus rotation speed

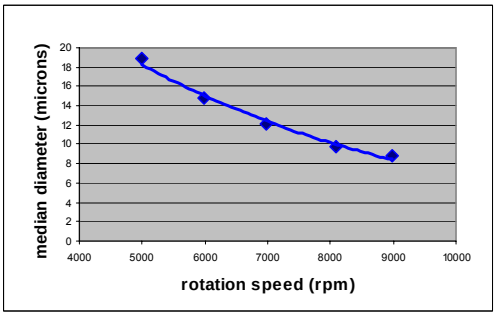
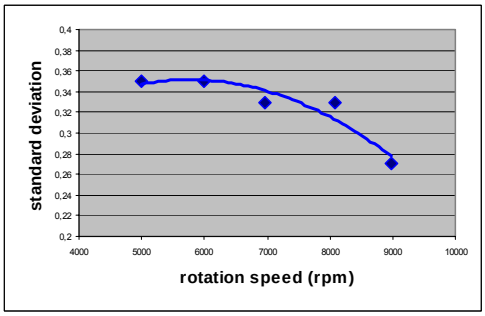


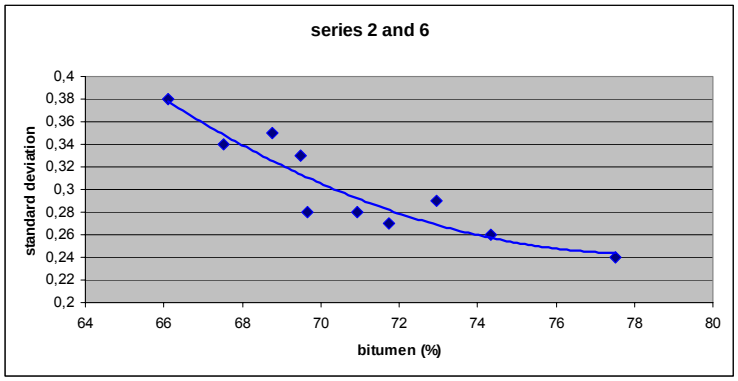
Figure 3: **σ** versus rotation speed



2.2 The influence of bitumen concentration on the droplet size distribution of bitumen emulsions

For a given mix design (**Series 2 and 6**) it has also been confirmed that manufacture with a higher concentration of the dispersed phase reduces the range of the droplet size distribution (Figure 4). The change in median droplet diameter is not significant.

Figure n°4: Standard deviation of the distribution versus % bitumen



2.3 Influence of the mix design (bitumen, emulsifier) on droplet size distribution and emulsion viscosity

Emulsions manufactured with Nynas naphthenic bitumen and imidazoline emulsifier have higher viscosity (Series 3). Their droplet size distribution is comparable with the other three Nynas series so this cannot explain the difference. However, their bound water content is higher, resulting in a higher effective volume fraction in the dispersed phase.

2.4 Impact on viscosity

For all the series considered together, the viscosity **η** has been plotted against the median diameter $\mathbf{D_{50}}$, the standard deviation **σ**, the bitumen content **Φ bit**, and the effective volume fraction in the dispersed phase **Φeff** (Figures 5 to 8 respectively).

Figure n°5

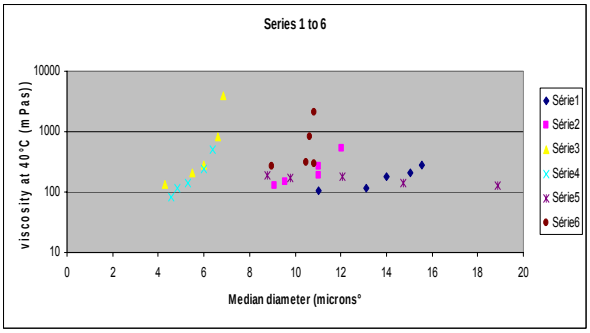


Figure n°6

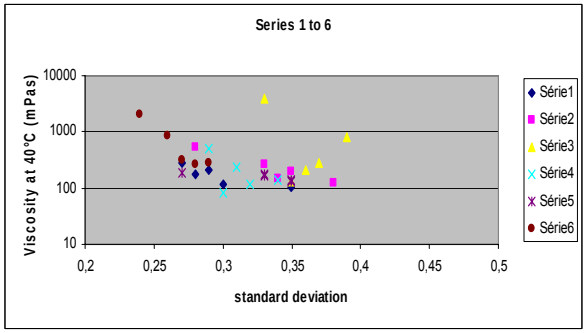


Figure n°7

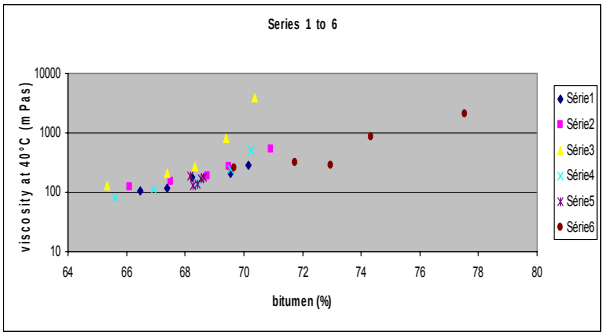
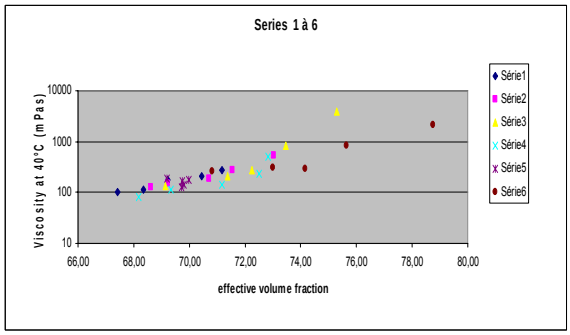


Figure n°8

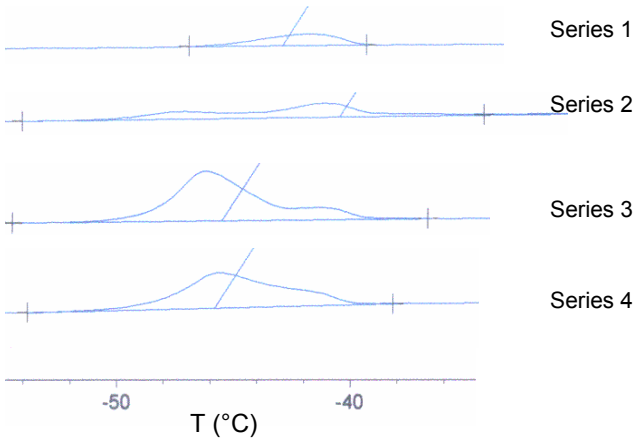


In spite of some divergences, the **effective volume fraction** provides a **better predictive trend for the viscosity of bitumen emulsion** than the other parameters.

3. DISCUSSION/ INTERPRETATION

3.1 Qualitative control of the inclusion of water

The thermogravimetric curves reveal differences depending on the type of emulsion. The emulsions in a given series all share the same profile:



On the basis of the usually accepted interpretations, namely that the phenomena observed during low temperature calorimetry are due to the crystallization of a fraction of the water in the emulsion, the existence of two peaks might correspond to the crystallizaton of **water that is either trapped between clusters of droplets or included inside the droplets**.

3.2 – Quantitative control of the inclusion of water

It has been shown that neither mechanical techniques (Figure 9), nor varying the concentration of bitumen during manufacture leads to a significant change in the percentage of bound water. However, **mix design** has a major influence as, in the mix designs we have studied, it can lead to a variation in the amount of bound water between 1% and 4% (Figure 10), increasing the volume fraction by the same amount.

Figure 9

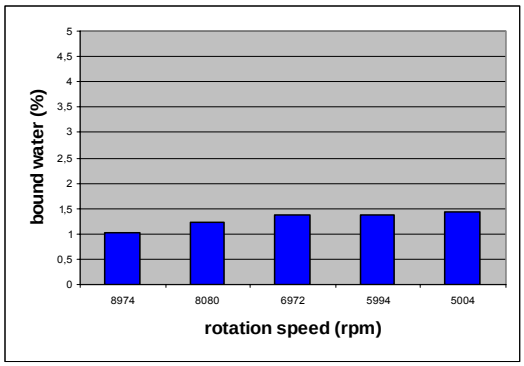
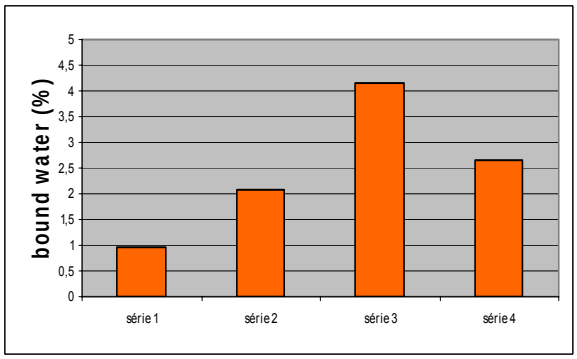


Figure 10



3.3 – Modelling viscosity

The change in viscosity between series 1 and 4 after correction of the volume of the dispersed phase was compared to the Krieger –Dougherty model (4):

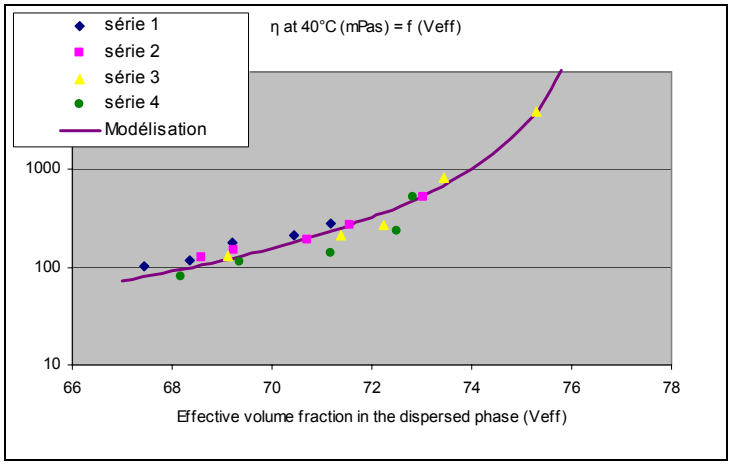
$$\eta = \eta_o [1 - \Phi/\Phi_m]^{-[\eta]\Phi m}$$

Where: η is the viscosity of the emulsion, η_o is the viscosity of the dispersing phase, Φ is the volume fraction taken up by the particles in the emulsion, and Φ_m is the limit value of the volume fraction taken up by the dispersed phase in the emulsion for which the viscosity tends towards infinity.

If η is taken as the viscosity at 40°C and Φ equal to Φ_{eff}, the result of modelling is given in Figure 11. The modelling curve has the following parameters:

η_o	1.1
Φ_m	76.7
$[\eta]\ \Phi_m$	1.04

Figure 11



CONCLUSION

It has been demonstrated that the inclusion of water or the trapping of water in the cluster of bitumen droplets leads to an increase in the effective volume fraction of the dispersed phase in a bitumen emulsion. Qualitatively and quantitatively, this phenomenon depends on the mix design of the emulsion, particularly the choice of the bitumen and the emulsion but is little affected by the concentration of bitumen during emulsion manufacture.

Control of this phenomenon is very important as it has a decisive impact on the rheological behaviour of bitumen emulsion. Droplet size distribution plays a secondary role.

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