

EMULSIFICATION OF HIGH SOFTENING POINT HYDROCARBONS

EMULSIFICATION D'HYDROCARBURES A HAUT POINT DE RAMOLLISSEMENT

Auteur(s) Author(s)	Nom(s) Name(s)	Prénom(s) First name(s)	Affiliation
1	JAMES	Alan	Akzo Nobel
2	LOGARAJ	Sundaram	Akzo Nobel
3			
4			
5			

Adresse postale : Akzo Nobel Surface Chemistry LLC, 7101 Adams St, Willowbrook, IL 60527, U.S.A.

Mailing address :

RESUME

L'émulsification d'hydrocarbures à haut point de ramollissement, par exemple asphaltènes dérivés de solvants desasphaltants de fractions de brut, a été étudiée.

Les facteurs critiques d'une bonne émulsification étaient : la viscosité de l'hydrocarbure à la température d'émulsification (i.e. température après mélange des phases), devaient être inférieure à environ 20.000 mPa.s.; une procédure correcte de démarrage du moulin colloïdal, avant stabilisation des températures et des pressions, pour éviter que la viscosité de la phase hydrocarbonée ne dépasse les limites supérieures pendant le démarrage ; des modifications sur le moulin colloïdal nécessaires pour supporter les températures et les pressions ; La chimie des émulsifiants en rapport avec les températures élevées d'émulsification.

Les températures minimales d'émulsification variaient entre 110 et 165°C pour les matériaux ci-dessus, qui ont des points de ramollissements entre 80 et 120°C.

ABSTRACT

The emulsification of high softening point hydrocarbons including asphaltenes derived from solvent de-asphalting of crude oil fractions has been studied.

Critical factors for successful emulsification were: the viscosity of the hydrocarbon at the emulsification temperature, (i.e. temperature *after* mixing the phases), should be below approximately 20,000 mPa.s; the correct start-up procedure for the colloid mill, before temperatures and pressures had stabilized, to avoid that the viscosity of the hydrocarbon phase exceeded the above limits during the start-up phase; some modifications to the colloid mill and proper selection of the emulsifiers to ensure stability at the temperatures involved.

The minimum emulsification temperatures ranged from 110-165C for the materials studied, which had softening points in the range 80-120C.

Mots clés maximum 5 : asphaltènes, bitumes, bitumes- polymères, émulsification à haute température.

Key words maximum 5 : asphaltenes, bitumens, polymer-modified, High temperature emulsification.

EMULSIFICATION OF HIGH SOFTENING POINT HYDROCARBONS

1. Introduction

Conventional bitumen emulsions used in road maintenance are prepared from relatively soft bitumens, typically with softening points in the range 30-70C. Some special emulsions used for industrial applications may have softening points up to 80C. There are uses for bitumens with higher softening points, for example in higher performance paving materials, in roofing, and in industrial coatings and so a potential demand for emulsions of these materials exists. The work reported here was mainly directed at emulsification of asphaltenes, which are obtained from the solvent deasphalting processes such as the ROSE process. The softening points of the resulting asphaltene depend on the type of solvent used and range from about 70C to about 300C. The asphaltenes studied here had softening points in the range 80-120C. The projected use for the emulsions was as fuel – the asphaltenes have a fuel value around 17000 BTU/LB, which is better than coal and petroleum coke.

Emulsification of conventional bitumens is performed in a colloid mill. Hot bitumen and warm water phase, which contains the emulsifier, are delivered separately in the right proportions to the mill where the bitumen emulsion is formed. The temperatures of the bitumen and water phase are chosen to give an exit temperature generally below 100C (for unpressurized mills) or up to 120C or so for pressurized equipment.

In order to emulsify higher softening point materials using conventional colloid mill technology, a method for predicting the right emulsification conditions from the properties of the starting materials is essential, because if emulsification fails to occur, or is incomplete, the unemulsified or broken material will lead to a difficult clean-up job, or even damage the equipment. The work reported here was directed to a practical method of predicting the right emulsion temperatures from the viscosity of the bitumen, and checking the emulsifier for chemical stability at the temperatures of emulsification. Some handling and combustion data on the produced emulsions are presented elsewhere (1, 2).

2. Parameters Affecting Emulsification

The major challenge for the work was to produce emulsions of the high softening point materials which had small particle size and had good stability and handling characteristics. Pumping tests showed that stability was improved when the emulsions had small median particle sizes and oversize particles were absent.

The general parameters affecting emulsification of normal bitumens in colloid mills have been well studied. Shear rate, temperature, emulsifier choice and concentration, are known influences on droplet size (3 – 5). Particle size distributions of bitumen emulsions stabilized with suitable emulsifiers, are consistent with a “permanent break-up” model of emulsification in a colloid mill – droplets are formed by sequential break-up with re-coalescence not being important. (6). Only in the formation of high bitumen content (>68%) emulsions is there evidence for some coalescence (7).

2.1 Emulsification Temperature

The temperature of the emulsion when it exits from the mill can be calculated from the temperature of the water phase and the temperature of the bitumen phase:

$$T_w = T_e + (T_e - T_b) * (C_{pb} / C_{pw}) * (b / w) \quad (\text{Equation 1})$$

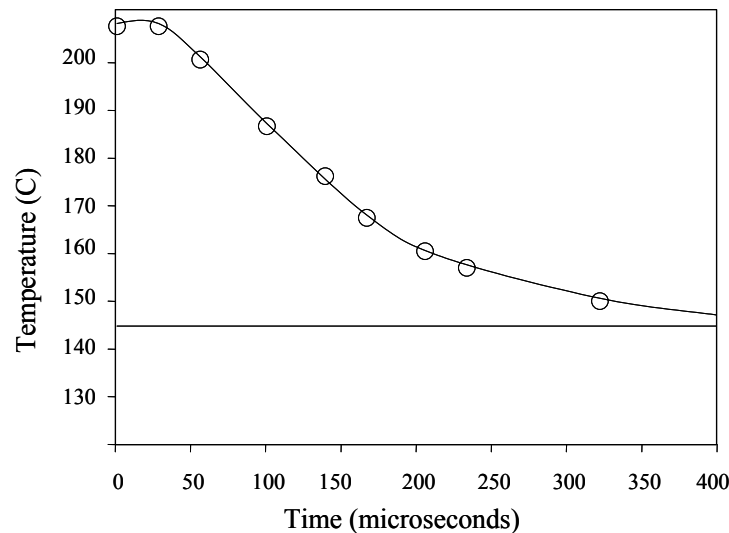
T_e = Temperature of emulsion °C
 C_{pb} = Heat capacity of bitumen
 C_{pw} = Heat capacity of water-phase
 w = % water-phase
 T_w = Temperature of water-phase °C

T_b = Temperature of bitumen °C
 $C_{pb} = 1.90 \text{ kJ/°C/kg}$
 $C_{pw} = 4.18 \text{ kJ/°C/kg}$
 $b = \% \text{ asphalt-phase}$

The bitumen phase must be at a minimum temperature so it is liquid enough to pump into the colloid mill. In the equipment used in the pilot study, the asphalt could be delivered to the mill at the right flow rate if it had a viscosity below about 2000 mPa.s.

It was quickly apparent that temperature was the critical parameter when emulsifying the high softening point materials. The starting temperatures of the two phases does not have a marked effect on the particle size of the emulsion. It is the temperature after mixing of the water and bitumen that determines the particle size (5). This suggests rapid equilibration of the temperatures of the water and bitumen phase. Calculations based on a nominal 20 micron sphere of bitumen suggests temperature equilibration should occur in less than 300 microseconds, less than 0.5% of the residence time in the shear zone of the colloid mill (Figure 1).

Figure 1: Calculated Temperature at the center of a 20 micron bitumen droplet after mixing with water phase. Bitumen temperature 225C, water 80C, emulsification temperature 145C.



Emulsification depends on the break-up of the bitumen into droplets, a process which in part is dependent on the viscosity of the bitumen. Since the temperature of the bitumen rapidly reaches that of the emulsion, then it is the viscosity of the bitumen at this temperature which determines the possibility of emulsification.

A study with conventional bitumens indicated that for the emulsion mill used in this study (a modified Akzo Nobel SEP0.3) the bitumen should have a maximum viscosity of 20,000-30,000 mPa.s at the emulsification temperature (i.e. the temperature after mixing the water and bitumen phases). This has been born out on studies of a range of high softening point materials and for the mill studied was only slightly affected by rotational speed and emulsifier concentration. The viscosity of bitumen decreases with temperature. The maximum viscosity of 20-30,000 mPa.s corresponds to a minimum emulsification temperature. (Figures 2 and 3). Data was obtained with a Brookfield DV II+ coaxial cylinder viscosity.

The rotation speed of the mill used was kept in the range 9000-12000 rpm. Within this range the rate did not have a significant effect on the minimum emulsification temperature, although higher speeds did give smaller median particle sizes. What was found was a rather sharp transition temperature between good and poor emulsions and more or less catastrophic blockage of the equipment when the minimum emulsification temperature was not reached. Datalogging of pressures, flows and temperatures showed that even transient blockages led to rapid changes in flows which resulted in wide fluctuations in temperatures and pressures which quickly exacerbated the initial problem. This is because any disturbance in the flows will affect the temperatures after mixing (Equation 1). Accurate flow control is essential in the high temperature, high pressure system, and the pilot plant had flowmeters with feedback to the pumps on both the water and bitumen phase lines. But the system could not respond to the rapid changes of flows caused by transient blockages. Control problems are less on larger plants, but good temperature and flow control are still essential.

Once the minimum emulsification temperature and the minimum pumping temperatures are determined from viscosity measurements on the bitumen (as illustrated in Figure 2 and 3), the temperatures of the water phase and bitumen can be chosen so as to generate this temperature after mixing in the desired proportions, using Equation 1. In practice the temperature of the high softening point bitumens had to be much higher than the pumping temperature in order to generate the right emulsification temperature after mixing since the water temperature in the pilot plant was limited to 100C maximum. Without a pressurized water phase system, the softening points of the materials requiring emulsification are effectively limited to about 130C.

Figure 2: Determination of Emulsification Conditions from Bitumen Viscosity. (Asphaltene, Softening Point 117 C)

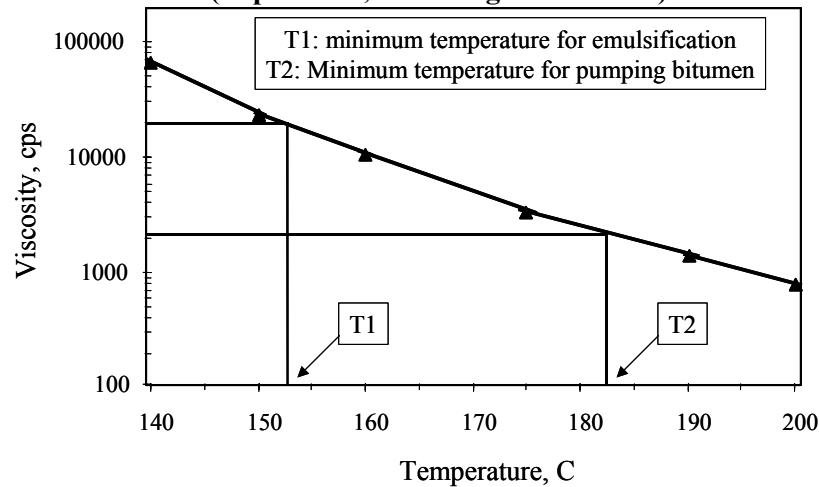
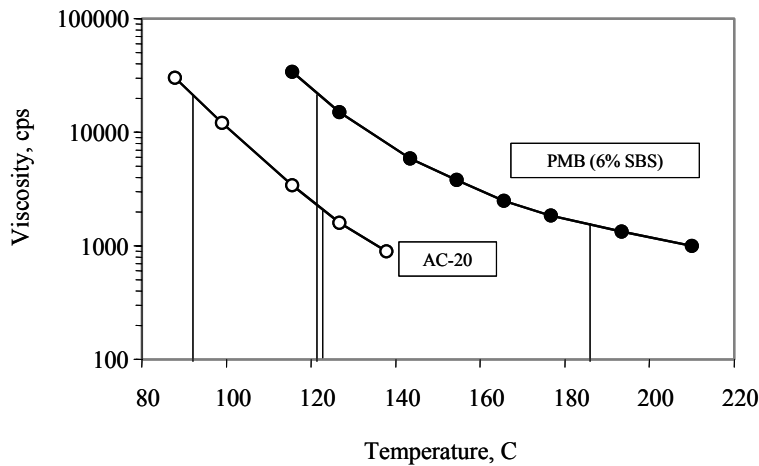


Figure 3: Similar Data for AC-20 (soft bitumen) and Polymer Modified Bitumen

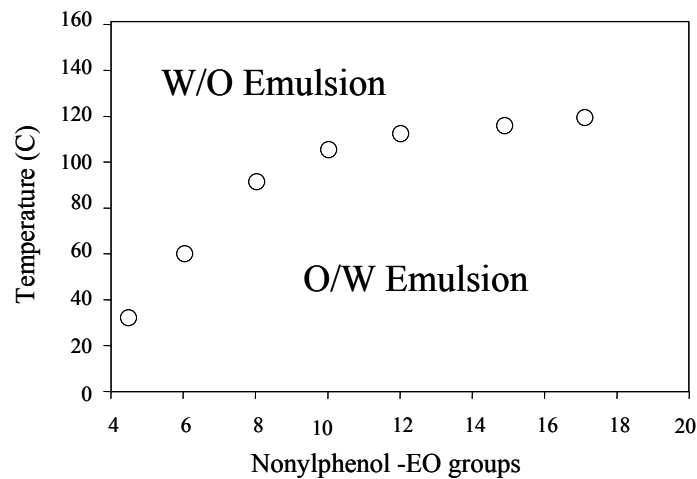


For the materials studied, emulsification temperatures ranged from 115-150C (Table 1). This required a heat exchanger on the outlet of the mill to cool the emulsion to below 100C, and a backpressure of up to 10 bar over gauge to prevent boiling of the emulsion.

2.3 Emulsifier Chemistry

At high emulsification temperatures some emulsifiers may no longer be effective. Nonionic emulsifiers based on ethoxylated alcohols exhibit cloud point behavior (Figure 4). Essentially at high temperatures they tend to form water in oil emulsions. These types of emulsifiers are limited to emulsification temperatures below approximately 110C.

Figure 4: Effect of temperature on the phase inversion temperature of emulsions made with nonionic emulsifiers and paraffin (From ref. 9)



Another concern was that emulsifiers could be chemically unstable at the emulsification temperature. Although in the pilot emulsion plant the exposure to high temperatures was very short (i.e. between the mill and the heat exchanger), in some designs of combined emulsification and power generation plant, intermediate cooling of the emulsion before combustion might be avoided and then the chemical stability of the emulsifier becomes more of an issue. Also in the case of a shutdown emulsion could be exposed to high temperatures for an extended period.

In order to check the stability of emulsion formulations at high temperature, samples of emulsion were placed in sealed pressure tubes in an oil bath at different temperatures. After heating the tubes were cooled, and the contents examined for particle size. Emulsions prepared from the tallowdiamine emulsifier used for conventional bitumen emulsions showed much better thermal stability than quaternary amines. Emulsions prepared with tallowdiamine survived 2 minutes at more than 220 C, whereas an emulsion prepared with tallowquaternary showed significant breaking after 2 minutes at 140C. It is not clear whether this reflects chemical instability or changes in the surface activity of the products.

3. The Start-up Problem

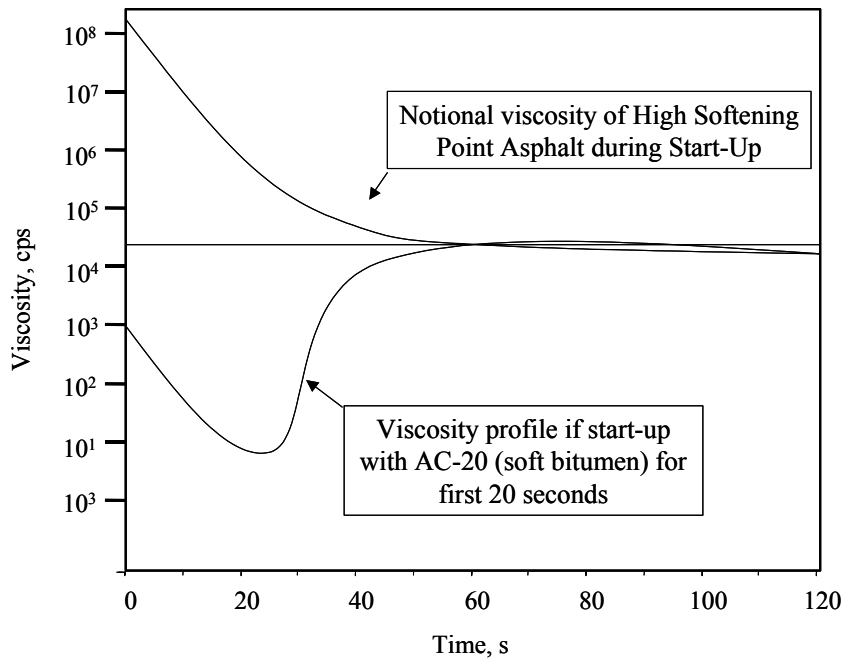
The start up of emulsification involves first passing water phase through the mill, then introducing the bitumen. This means that at the start up, the temperature approximates that of the water phase, and only reaches the design temperatures as the bitumen content reaches the design (Equation 1). In the pilot mill, temperature probes indicated it took 90 seconds to reach the design temperatures (slightly longer than the 10–20 seconds or so required to achieve the correct mixture in the milhead), although temperatures were within 10C of the design within 40 seconds. This presents a problem since until the design temperature is reached, the bitumen viscosity will be too high to enable good emulsification. The result is that there is a risk that the mill will be overloaded during start up, or that some “trash” will be produced during start up which could cause blockages in the heat exchanger and other down stream equipment. During proving trials, a pressurized collection vessel was used to collect this “trash” before allowing emulsion to pass through the heat exchanger (1).

In order to prevent this problem it is necessary to reduce the viscosity of the bitumen during the start up phase. This can be achieved by either starting up on regular bitumen, then switching to the high softening point material once temperatures and pressures have stabilized, or introducing flux or solvent into the high softening point bitumen during the start up, and stopping the flow of flux once the temperatures and pressures have stabilized (Figure 5). Without start-up with the softer bitumen, the viscosity of the bitumen phase would exceed the 20,000 cP maximum for easy emulsification. A typical schematic of the emulsion plant is shown in Figure 6. Experience on full-scale emulsion plant has indicated that the period of

adjustment is very short (a few seconds) and the level of soft bitumen or flux (solvent) introduced into the emulsion is insignificant.

Figure 5: Calculated bitumen viscosity changes in the pilot mill during the start-up of a 67% asphaltene emulsion.

Bitumen temperature 225C, water temperature 80C, emulsion temperature 145C.



During shut down of the plant, the soft bitumen or solvent is again introduced into the mill, so that the section of piping between the injection point and the mill is full of softer material, ready for the next start-up.

Table 1. Representative Emulsification Conditions

Bitumen	Softening Point C	Temperature C			Residue %	Primary Emulsifier	Median particle Size (µm)
		soap	bitumen	emulsion			
Asphaltene	118	92	224	162	69.4	0.4 % TDA ¹	1.7
Asphaltene	104	96	216	160	69.7	0.3% TDA	2.6
Gilsonite	121	97	227	156	65.2	0.35% TDA	10.0
Asphaltene	96	88	215	149	67.0	0.8% TQA ²	2.5
PMB(6%SBS)		83	190	130	64.1	0.3% TDA	3.8

1) Tallowalkyldiamine 2) Tallowalkyltrimethylammonium chloride

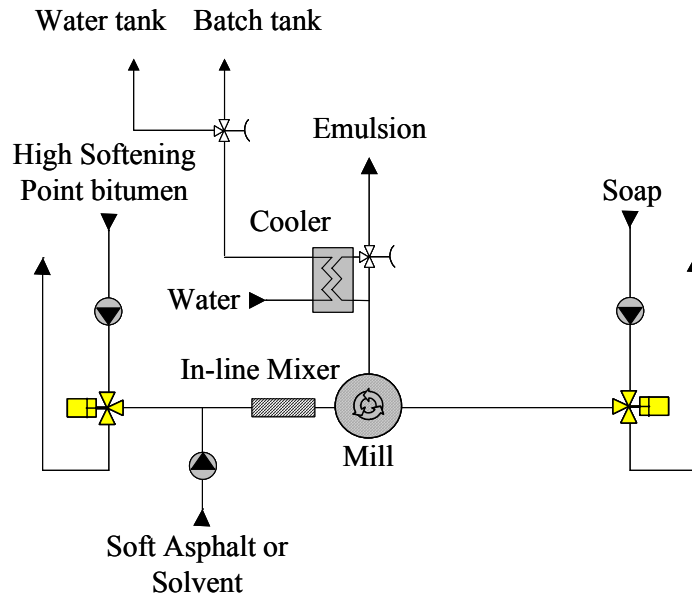
There is also a short period of adjustment in the backpressure of the system, which takes a few moments to stabilize after start up. Pressure changes could be minimized by a novel “reverse pumping” system (2)

4. Conclusions

Once the method for the determination of the right emulsification temperature were worked out and the start-up problem was solved, it was found to be fairly straight forward to extend conventional colloid mill technologies to the higher temperatures required to emulsify high softening point bitumens (Table 1). Many of the emulsifiers effective in regular bitumen emulsions are effective also at higher temperatures.



Figure 5: Schematic of Emulsion plant (Batch)



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