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# Toward a new experimental method for measuring coalescence in bitumen emulsions: A study of two bitumen droplets

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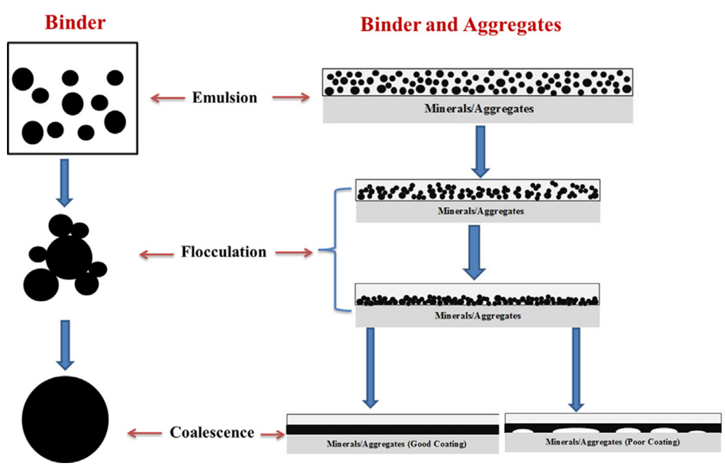
## HIGHLIGHTS

- A new experimental method to study coalescence of two bitumen droplets is presented.
- The developed test procedure is a novel state of art, quite simple and repeatable.
- It is possible to study the coalescence process in bitumen emulsions on a large scale.
- This method will serve its widespread applicability in cold mix asphalt technology.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Cold mix asphalt (CMA) emulsion technology could become an attractive alternative for the road industry due to low startup and equipment installation costs, diminished energy consumption and reduced environmental impact. The performance of cold asphalt mixtures produced from emulsions is strongly influenced by a good control of the breaking and coalescence process. The wetting of bitumen on the surface of the aggregates is hereby of major importance for the performance of the asphalt. Premature coalescence of the bitumen emulsions away from the surface, could lead to poor adhesion and decreased mechanical strength of the asphalt. Today, the breaking and coalescence mechanisms of bitumen emulsions are still not fully understood due to their complexities and the lack of fundamental experimental methods and existing models. However, in the past years efforts have been made in defining relationships for understanding the bitumen emulsions. In this paper, a new experimental method is presented to study coalescence of bitumen by using shape relaxation of bitumen droplets in an emulsion environment. The coalescence of spherical droplets of different bitumen have been correlated with neck growth, densification and surface area change during the coalescence process. The test protocol was designed in a controlled climate chamber, to study the coalescence process with varying environmental conditions. The kinetics of the relaxation process was influenced by the temperature as well as other parameters.

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The research showed that the developed test procedure is repeatable and able to study the coalescence process on a larger scale. However, the relationship between the measured parametric relationships at the larger scale and the bitumen emulsion scale still needs further investigation.


## 1. Introduction

Bitumen is a highly viscous semi-solid at room temperature [1] and is commonly mixed with stone materials for production of asphalt concrete. For a good coating of the stone materials, the viscosity of the bitumen needs to be reduced to enhance its wettability. There are several options to reduce its viscosity to optimum levels, such as heating, dissolving in solvents (cut-back bitumen), foaming the bitumen, or making oil/water type bitumen emulsions. For several reasons, such as its ability to reduce the overall energy usage, cold asphalt mixtures using emulsion technology is an attractive method. Bitumen emulsions are produced by applying high shear force and chemical treatment while warm bitumen and water phase containing emulsifying agents are mixed by the application of mechanical energy to disperse the bitumen into small droplets.

Though the main focus of this paper is bitumen emulsions for the application in asphalt pavements, much can be learned from other emulsion applications. Emulsions, in general, are among the most important colloids in everyday life and have a variety of usage in different fields, such as the paint industry, the food industry, lubrication products, the cosmetic industry and the road construction industry. The application of bitumen emulsions for pavements can be various: e.g. spray applications like surface dressings or chip seals, fog seals, tack and prime coats or mixed with stone material as in slurries or micro surfacing and cold mix paving. Regardless of its application, there are two main parameters controlling the bitumen emulsions: (1) its stability (storage and chemical stability) and (2) its breaking or phase separation upon mixing with aggregates or existing asphalt concrete layers [2]. This paper is focusing on an experimental method towards studying breaking of bitumen emulsions and understanding coalescence mechanism during the phase separation from bitumen emulsions.

For the study of coalescence and flocculation, light scattering or light reflectance and light transmission methods [3–9] have been described in the literature for investigation of crude oil emulsions. These methods include a strong light source and a very sensitive detector to measure light scattered and transmitted. However, the use of conventional light scattering experiments is quite challenging for experiments on dark color crude oil emulsions with multiple scattering events. Nevertheless, some researchers have still tried to apply these techniques on bitumen emulsions and Miller [10] described how to obtain effective scattering parameters from light transmission experiments using a semi-empirical theory for its interpretation. However, much effort is still required to achieve a good resolution at micro scale in real bitumen emulsion environment.

Micromechanical methods like the 'micropipette technique' or the 'vesicle deformation test' were reported in the literature [11–13] for studying the shape relaxation of two droplets. These tests are based on a simple pressurization of the material into spherical shapes. For the coalescence experiments, two distinct pipettes that are coupled with the two different independent micromanipulators are usually brought into contact and pressed against each other to introduce the contact. These types of test methods have shown some promising results, though so far they have been found to be too unpredictable in terms of repeatability to have control over the procedure and, given the large number of variables involved, complex to interpret. These methods do not represent a real bitumen emulsion on a larger scale and drops are forced to coalesce. Moreover, they do not elaborate on the effects of other physio-chemical parameters (e.g. temperature, surfactants, pH and additives) on breaking and coalescence behavior of bitumen emulsions.

Hence, a reliable and repeatable test procedure for studying the coalescence process in bitumen emulsions under varying conditions is still needed to bring cold asphalt technology to its full market advantage.

### 1.1. *Breaking & coalescence*

Emulsions can be broken down through various processes such as sedimentation, creaming, Ostwald ripening, flocculation, coalescence or phase inversion. In this study, the main focus is towards flocculation and coalescence as breakdown processes. Flocculation is a reversible process whereby droplets stick together as agglomerates of droplets, without losing their individual integrity. Coalescence is the breaking process of emulsions in which droplets merge together into bigger ones. Bitumen emulsions start breaking or rupturing when in contact with aggregates, as the porous surface of aggregates extracts water away from the emulsion. Furthermore, hydrolysis reactions (releasing of ionic species) take place at the surface of the aggregate minerals. After this, a phase separation by flocculation and coalescence should quickly occur leading to a push out of water from the emulsion as illustrated in Fig. 1a. Two drops of certain radius '$R$' approach each other with negligible initial velocities, touch and form a tiny contact bridge due to Van der Waals interactions. This bridge contact length '$r_b$' quickly expands under the influence of interfacial stress as illustrated in Fig. 1a and finally merges into a larger drop and, as a result, increases the bitumen phase density by minimizing the surface area.

Coalescence is seen as the last step in the breaking process of bitumen emulsions. A continuous film of bituminous binder is developed during coagulation that covers the aggregates followed by curing or setting of the binder, which eventually determines the mechanical strength of the cold asphalt mixture. Good adhesion can be achieved in the case of complete wetting of aggregates by the bitumen and poor adhesion will be achieved if there is a premature coalescence away from the surface or if water is still present at the interface as presented in Fig. 1b.

Studies of coalescing fluid bodies can be traced back to the 19th century by the work of Reynolds and Lord Rayleigh [14,15]. The hydrodynamics of droplet coalescence can be explained in the context of diffusion or capillary forces [16], viscous forces [17–20], inertial forces [21,22] and interfacial forces [22,23]. Especially, droplet coalescence has been studied extensively for systems dealing with microfluidics [24–27] to develop improved coatings in various fields. However, there is still no fundamental test method available today that enables a detailed investigation of the coalescence process for bitumen emulsions. The general practice that has so far been adopted within Europe and the USA for emulsion breaking include the Filler breaking test (EN Standard [28–30]), Resonance Frequency test or Tuning Fork Method (developed in France), Evaporation-Filtration test where coalesced binder