MODIFIED BITUMENS DERIVED FROM PARTICLE STABILIZED EMULSIONS

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ABSTRACT

Bentonite modified bituminous binders show higher stiffness and improved ageing properties but the process of forming the nanocomposite with hot bitumen presents practical problems. Clay stabilised and clay modified bitumen emulsions provide an alternative route to similar composites with the advantages that the emulsions can be used in low energy roadbuilding and maintenance processes. In this study, bitumen emulsions were produced containing clays, the emulsion residues were recovered by evaporation and the properties measured.

Bitumen can be emulsified with clay without any chemical emulsifier, but the addition of surfactants to the bitumen gave emulsions with smaller particle size, in the range 5-20 micron. The particle size of the bitumen droplets was reduced as the concentration of the clay or the surfactant increased, and was also dependent on the pH of the mineral dispersion. Fatty amine surfactants gave minimum particle size with alkaline dispersions, fatty acid surfactants with acid dispersions. The clay stabilised emulsions needed high levels of clay, greater than 5% basis residue, to achieve stable emulsions. To explore the effects of lower levels of clay, clay was post-added to chemically stabilised emulsions or co-milled together with organic emulsifiers through a colloid mill.

Compared to the original bitumen, dramatic physical property changes were observed for clay modified residues. Performance grading and classical consistency tests on the residues (without RTFOT) showed a significant increase in top PG temperature and softening point but with minor effect on low temperature properties. Co-milling of the clay gave a higher degree modification than post-addition.

Keywords: bitumen, emulsion, clay, nanocomposite

1. INTRODUCTION

The environmental impact of road construction and repair depends greatly on the durability of the materials used and the quantities of materials used and transported. Longer lasting structures, thinner structural layers (of equal bearing capacity) and rapid, low temperature preventive maintenance techniques add up to green road building technology. Bitumens can be modified with nano-sized organically modified bentonite clays ("organoclays"). These nanoclay modified bituminous binders have shown higher stiffness and improved ageing properties compared to unmodified binders (1,2,3), holding out the promise of a reduction in materials usage and better durability, but the process of forming the nanocomposite with hot bitumen and organoclays presents practical problems. The high viscosity of the bitumen can impede delamination of the clays used, the thermal stability of the organic treatments on the clays limits mixing and storage temperatures, and the modified binders themselves have high viscosity which can make handling difficult.

Instead of dispersing organoclay into hot bitumen, both clay and bitumen can be dispersed in water in emulsion form. Evaporation of the emulsion potentially provides an alternative route to similar clay-modified binders. Emulsions can be used in cold-in-place techniques which are particularly environmentally favourable because they avoid transport and heating of the aggregate. The stiffer residues obtained from the clay-modified emulsions hold out the possibility of thinner structural layers. The principle of using clay in emulsion in the preparation of nanocomposites has already been demonstrated for polymer latex (4). While the majority of bitumen emulsions used today in paving operations are chemically stabilized (i.e. their stability is derived from organic surface active agents), bitumen emulsions prepared with bentonite clays are not novel and some of the earliest patents regarding bitumen emulsions dating from before 1920 involve the use of clays (5, 6). Today, clay-containing emulsions find use in protective coatings, roofing and sealers for driveways and car parks. With the proper modification of clay slurry pH, bitumen can be emulsified without the need for surface active agents, or with the addition of surfactants only into the bitumen phase, which eliminates the risk of run-off of potentially hazardous emulsifiers in cold-mix processes which is a concern when using chemically-stabilized emulsions (7).

In earlier work (8, 9), clay-stabilised bitumen emulsions were prepared using bentonite clays, with and without the addition of surface-active agents to the bitumen phase. But low levels of clay are not alone able to emulsify bitumen , and in this work, to provide residues with lower clay contents for rheological studies, surfactants were included in the recipes. We make a distinction between the clay-stabilised emulsions of the first process and the clay-modified emulsions of the latter process. The use of lower levels of clay together with surfactants or emulsion in this way is also already known in non-paving applications of bitumen emulsions as well as for polymer-clay nanocomposites.(10, 11). The emulsion residues were recovered by low temperature evaporation and the properties determined by traditional methods (penetration, softening point) as well as PG (Performance Grade) grading**.**

2. PREPARATION OF CLAY-STABILISED and CLAY-MODIFIED EMULSIONS

2.1 Preparation of clay- stabilised emulsions
In clay-stabilised emulsions the emulsion is stabilised primarily by clay particles. An oil-soluble surfactant, if present, is added to the bitumen phase. Hot bitumen (optionally with added surfactant) (140°C for PG64-22 and PG 58-28 bitumens used in this study) was added to hot clay slurry (50°C) of 2-10% solids content, with high speed agitation. In the work reported here, the agitation was provided by a high speed mixer (Silverson or Cowles disperser). The emulsions formed had residues of 30-35% by weight.

2.2 Clay modified emulsions
With levels of clay less than about 5% basis the residue, no emulsions were formed by direct emulsification as described in 2.1. To obtain residue samples with lower levels of modification, either surfactant emulsifiers were mixed with the clay dispersion before emulsification through the colloid mill, or portions of clay slurry were mixed with chemically-stabilised slow-setting bitumen emulsion. The clay-modified, chemically stabilised emulsions had residues of 50-60% and surfactant contents of approximately 2% basis emulsion.

3. GENERAL FEATURES OF THE EMULSIONS

3.1 Clay-stabilised emulsions
The effect of the manufacturing conditions on the particle size of the emulsions was determined. The Figures 1-3 show median particle sizes of the resulting emulsions as determined by Beckman Coulter LS230 light scattering equipment. The results show that clay-stabilised emulsions prepared in the absence of added surfactant or with the addition of tall oil (mixed fatty acids) to the bitumen phase, the smallest particle size is obtained between pH 3 and pH 5 (Figure 1) and no emulsion was formed when the emulsion pH exceeded 7. When tallow diamine is added to the bitumen the optimum emulsion pH becomes 8-10, no emulsion was formed at low emulsion pH. The basic nature of the amine meant that there was significant difference in the pH of the clay slurry before emulsification and the

final emulsion pH. The higher the level of surfactant, and/or the higher the level of clay, then the smaller the particle size obtained for the clay-stabilised emulsions (Figures 2 and 3). It was not possible to make good quality clay-stabilised emulsion below a dosage of approximately 5% clay basis residue. Manufacture of clay-stabilised emulsion through the colloid mill gave smaller particle size than those made with high speed disperser, (datapoint under the right arrow on the Figure 2). The clay-stabilised emulsions made with bentonite were generally highly viscous (5000-50000 mPa.s) with strong shear thinning behaviour and the viscosity was pH dependent (8). As has been noted before (8), the particles in the clay stabilised emulsion had ovoid shape quite unlike the spherical particles found in chemically stabilised emulsions.

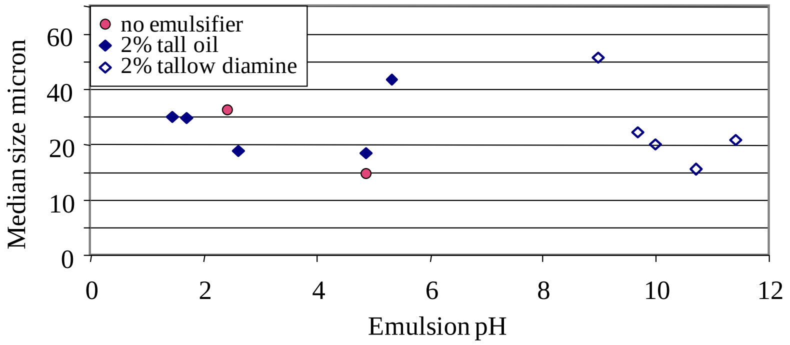

Figure 1: Effect of pH on the particle size of bentonite-stabilised emulsions. Approx 13% clay solids basis residue. Additive concentration basis PG 64-22 bitumen.

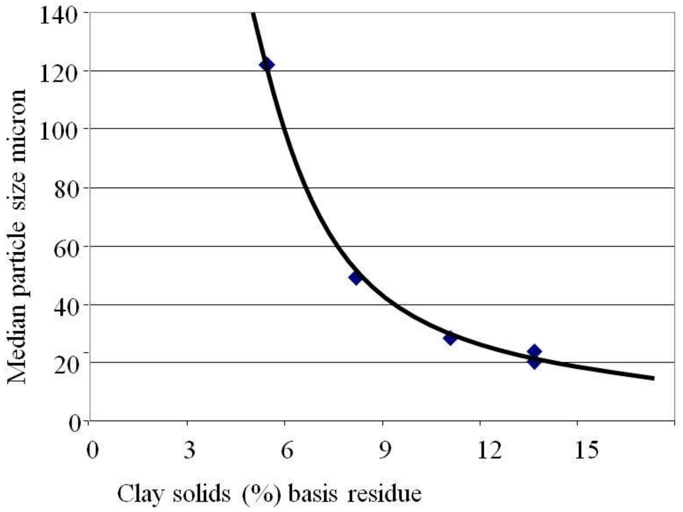

Figure 2: Effect of bentonite content on the particle size of clay-stabilised emulsions prepared with PG64-22 bitumen which contained 2% tallowdiamine. The emulsions were prepared with a high speed mixer.

3.2 Clay-modified emulsions

The chemically stabilized emulsions modified will low levels of clay had median particle sizes in the range 2-7.5micron and low viscosities similar to unmodified emulsions.

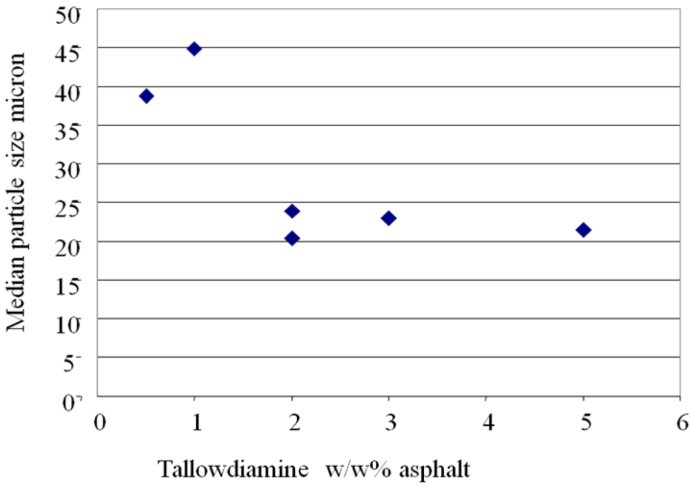

Figure 3: Effect of additive content on the particle size of clay-stabilised emulsion. Bentonite content approximately 13% basis residue. Emulsion pH 9.3-10.4. Emulsions were prepared from PG64-22 bitumen using a high speed mixer.

4. RESIDUE PROPERTIES

The emulsions were placed on a silicone mat and allowed to evaporate at room temperature then in an oven at 60°C according to ASTM D7497.

Figures 4 and 5 show the effect of bentonite clay on the penetration and softening point of the residue of clay-stabilised and clay-modified emulsions derived PG 58-28 bitumen. The values at zero clay represent the residue from unmodified emulsion. Some variability in the penetrations between the residues from similar emulsions was seen.

Figure 6 shows the effect of clay on the top and bottom PG grades of the emulsion residues. The residues with high levels of clay modification were not free flowing and were moulded by hand into the bending beam. The samples containing high levels of clay showed some variability in the PG top grade measured. Otherwise the PG grading was done as normal except that the RTFOT step (designed to mimic the hot mix process) was omitted. The residue from the unmodified emulsion based on nominally PG58-22 bitumen actually graded as PG64-28.

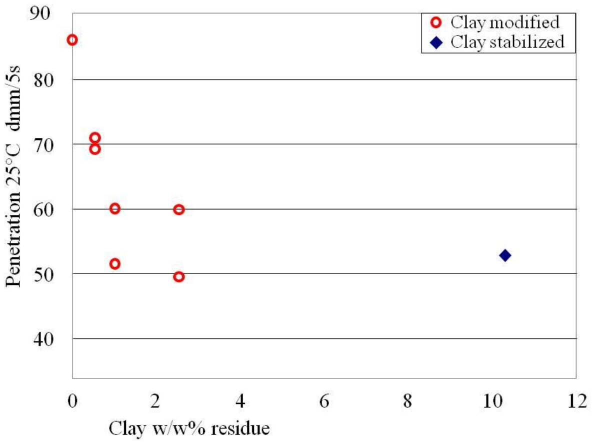

Figure 4: Penetration of emulsion residues from clay stabilised and clay modified emulsions. Emulsions were prepared from PG58-28 bitumen.

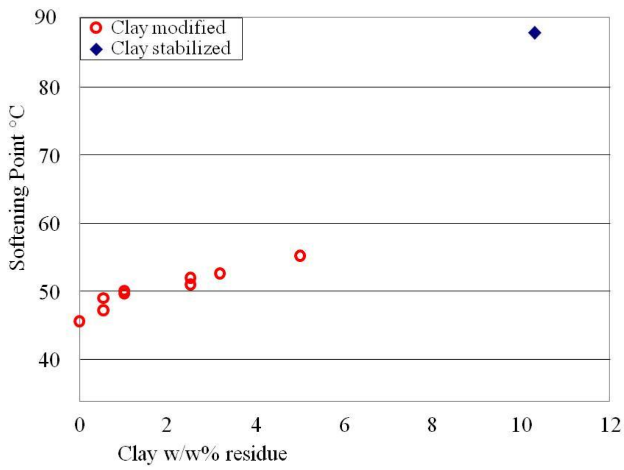

Figure 5: Softening point of emulsion residues from clay stabilised and clay modified emulsions. Emulsions were prepared from PG58-28 bitumen.

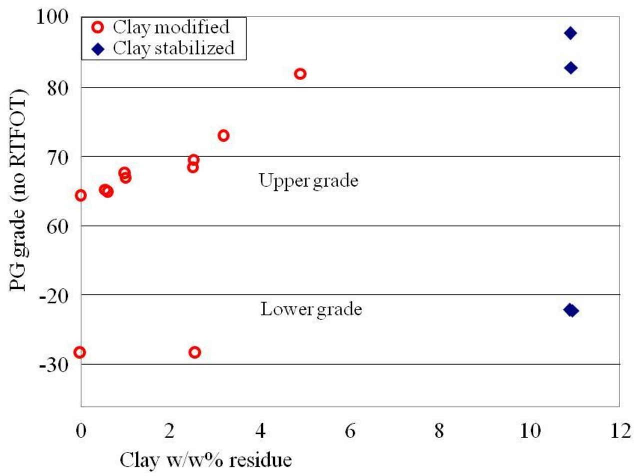

Figure 6: Effect of bentonite clay on original binder top grade and low temperature grade by BBR.

5. DISCUSSION

Bitumen emulsions containing clays can be prepared by directly mixing clay slurry and hot bitumen as we described in more detail earlier (8). But the technique is limited to high degrees of modification (greater than about 5% clay basis residue). In this work stable emulsions with lower levels of clay modification were achieved by combining chemical emulsifiers with the clay. High levels of clays lead to significantly increases in the viscosity of the emulsion, but low levels (<2.5% clay basis residue) have only small effects and these modified emulsions show behaviour similar to chemically stabilised ones. All the residues from emulsion containing clay show very marked changes in penetration, softening point and PG grading, which was dependent on the actual clay content of the residue. The changes in softening point and penetration are similar to those observed with bitumen modified in the hot process with organobentonite (1). Bearing in mind the higher density of the clay compared to bitumen, the additions are small in volume terms and the degree of modification suggests more than a simple filler effect. Emulsion residues are not at the moment specified by Performance Grade but in these tests it was clear that the lower PG temperature of the residues, when determined without the RTFOT, was not adversely affected by low levels of clay while there was a significant increase in the upper PG temperature.

The nature of the process means that it would be rather easy to also incorporate other emulsified or dispersed organic modifiers such as polymer latex and, as shown in earlier work, alternative mineral particles could also be used.

6. CONCLUSION

Bentonite clay can be used to stabilise bitumen emulsions, without the need for conventional organic “chemical” surfactants , using a high speed disperser but quite large quantities of clay are required. Low levels of bentonite clay can be easily incorporated into bitumen emulsions if chemical emulsifiers are included in the recipe. The residues from the emulsions have significantly higher softening points, lower penetrations and higher PG top grade, while the lower PG is not much affected.

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