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(54) Bitumen emulsions

(57) A bitumen emulsion comprising 40 to 80 wt. percent bitumen, 0.05 to 1.0 wt. percent emulsifier and 14 to 59.95 wt. percent water, the emulsion being substantially free of organic solvent, and containing emulsified bitumen droplets having a mean particle size of from 2 to 10 micrometers with a standard deviation of no more than 0.3. The emulsion is produced using a static mixing process. The emulsion can be used, for example, in road repair applications and has the advantage that the emulsion can be prepared and stored before use ('delayed-set') without the need to include organic solvent in the emulsion mix.

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BITUMEN EMULSIONS

This invention relates to bitumen emulsions, mixes of bitumen emulsions with aggregate material, and their use in road-making and similar operations.

Many road surfaces are constructed, maintained and repaired using mixes of aggregate material with bitumen binder. In the field of road repair this aggregate-bitumen mix is typically employed in one of the following forms:

(i) A hot mix of aggregate and heated bitumen. This method has the advantage that it sets rapidly after application to the road surface, but the disadvantage is that it must be mixed, transported to the roadside and used immediately to prevent premature setting on cooling. In addition the hot bitumen is a hazard to road workers, potentially causing burns and scalds.

(ii) A mix of aggregate and cut-back asphalt, i.e. bitumen diluted with an organic solvent such as kerosene or creosote to provide workability to the aggregate-bitumen mix. This has the advantage that it can be applied at ambient or near ambient temperatures and there can be some time delay, if desired, between preparing the mix and applying it to the surface. However it has the disadvantage that the bitumen takes longer to harden after application to the road surface, as the rate of hardening is dependent upon evaporation of the solvent, and, even so, some solvent remains in the bitumen causing the road surface to be slightly soft

and therefore have a tendency to deform under the weight of passing traffic. Furthermore the evaporation of the solvent into the atmosphere during hardening of the bitumen is an environmental pollutant and therefore undesirable.

(iii) A mix of aggregate and bitumen-in-water emulsion. This method has the advantage that it can be applied to the road surface at ambient temperature but the disadvantage that it must be applied immediately as the action of mixing the aggregate with the emulsion causes the emulsion to break, i.e. the bitumen and water phases separate, and the bitumen starts to harden. To increase the stability of the emulsion, and hence storage capability of the mix, increased amounts of emulsifier can be included in the emulsion, but this has the disadvantage that the emulsion can take a considerable time to break after application to the road, which delays the hardening of the bitumen and increases the time that the road has to be closed to traffic. Alternatively the storage life of the mix can be improved by adding organic solvent to the emulsion, but this has the disadvantage of a soft road surface and pollution as described under (ii) above for the cut-back asphalt mixes.

There is therefore a need for an aggregate-bitumen mix which combines the advantages of delayed-set properties before application to a surface, for example a road surface, together with rapid setting properties after it has been applied to the surface.

The present invention provides a bitumen emulsion comprising by weight based on the total weight of the emulsion:

a) 40 to 85 per cent bitumen;
b) 0.05 to 1.0 per cent emulsifier;
c) 14 to 59.95 per cent water,

the emulsion being substantially free of organic solvent, and containing emulsified bitumen droplets having a mean particle size of from 2 to 10 micrometres (μm) with a standard deviation of on more than 0.3.

We have found that by using bitumen droplets which have a particle size that is within a specific range and is substantially uniform, it is possible to form an emulsion which remains sufficiently stable when mixed with aggregate to act as a delayed-set emulsion without the need for an organic solvent and/or increased amounts of emulsifier, but which breaks sufficiently quickly after it has been applied to the road so there is as short a time as possible before the road can be opened to traffic. The absence or substantial absence of solvent provides an 'environmentally friendly' emulsion with little, if any, pollutants evaporating into the atmosphere when the emulsion breaks. The absence of solvent also has the advantage that, once the emulsion has broken, the road surface sets completely and is not subject to damaging deformation.

Preferably the bitumen droplets in the emulsion according to the invention have a mean particle size of from 3 to 9 um, more preferably from 5 to 8 μm. The standard deviation of this mean is preferably no more than 0.2, for example in the range from 0.1 to 0.2.

The bitumen employed in the emulsion may be any commercially available natural or petroleum-based bitumen (also known as asphalt) suitable for use in road construction, maintenance and repair. It may be a

straight-run bitumen or a blown or oxidised grade. The penetration (IP 49) may vary from 20 to 500 at 25°C, preferably 50 to 400, more preferably 100 to 250. Its Ring and Ball softening point (IP 58) is generally from 35 to 100°C, preferably 35 to 60°C. The amount of bitumen contained in the emulsion is from 40 to 85 weight percent, preferably 50 to 75 percent, more preferably 60 to 70 percent, based on the total weight of the emulsion.

The amount of emulsifier employed may range from 0.05 to 1.0 weight percent, but usually an amount from 0.1 to 0.5 wt.%, more preferably 0.2 to 0.4 wt.% is employed, i.e. a typical amount of emulsifier for a bitumen emulsion. The emulsifier may be cationic, anionic or non-ionic, or a mixture of cationic and non-ionic, or anionic and non-ionic emulsifiers, depending upon the chemical nature of the aggregate with which the emulsion is to be mixed, and upon the desired electrochemical properties of the emulsion.

Suitable cationic emulsifiers include hydrochlorides of fatty amines, fatty amido-amines, ethoxylated amines, imidoazalines, quartenary ammonium salts, and mixtures thereof. Preferably the cationic emulsifier is a diamine, for example tallow diamine hydrochloride, and more preferably is a mixture of a diamine with a quatenary ammonium salt. When a cationic emulsifier is employed, it is preferred to include an acid in the bitumen emulsion to counteract the alkalinity of the emulsifier. Generally acid is added to adjust the pH of the emulsion to approximately pH 3. Typically from 0.05 to 0.5, preferably from 0.1 to 0.3, weight percent acid based on the total weight of the emulsion is added. Suitable acids include inorganic acids, for example hydrochloric acid.

Suitable anionic emulsifiers include long chain carboxylic and sulphonic acids, their salts and mixtures thereof.

Suitable non-ionic emulsifers include ethoxylated compounds, for example ethoxylates of sorbitan esters, alcohols and alkyl phenols, and mixtures thereof.

A salt, for example a mineral salt such as calcium chloride, may be included in the emulsion according to the invention to balance the salinity, and also to modify the emulsion viscosity. If a salt is employed, typically the amount is from 0.05 to 0.5, preferably from 0.1 to 0.3 weight percent based on the total weight of the emulsion.

If desired, the bitumen may be modified by the incorporation into the bitumen of a polymeric additive, for example ethylene vinyl acetate or styrene-butadiene polymers, or mixtures thereof. These can be added in amounts up to about 25 weight percent based on the total weight of the emulsion. The polymers modify the bitumen to increase its resilience, which is beneficial, for example, when the bitumen is used for a road surface subject to heavy traffic.

The remainder of the bitumen emulsion according to the invention comprises water. This remainder may be from 14 to just under 60 weight percent, but is preferably 20 to 50 percent, more preferably 30 to 40 percent, based on the total weight of the emulsion. The emulsion is usually produced as an oil-in-water emulsion, i.e. the bitumen particles are surrounded by water molecules, although it may alternatively be produced as a water-in-oil emulsion.

The bitumen emulsion may be prepared by a static mixing process as disclosed in published European Patent Application 283246A, the disclosure of which is incorporated herein by reference. The process preferably comprised the following steps:

a) feeding the bitumen into a first static mixer at a temperature above 50°C;

b) introducing water under pressure into the first static mixer, the pressure being sufficient to prevent substantial vaporisation of the water, the weight ratio of water to bitumen in the first static mixer being between 3:1 and 35:1;

c) introducing the emulsifier into the first static mixer;

d) mixing the components in the first static mixer, and then passing the resultant mixture from the first static mixer into at least one other mixer in which the temperature is below the boiling point of water;

e) introducing water into the other mixer(s) in an amount such that the total amount of water present in the resulting emulsion is from 14 to 60% by weight based on the total weight of the emulsion; and

f) passing the mixture through the other mixer(s) and removing the resulting bitumen emulsion.

Preferably the said other mixer is also a static mixer.

To facilitate the introduction of the emulsifying agent into the first static mixer, the emulsifier, in part or in total, may be mixed with the water to be added to the first mixer to form an aqueous solution or "soap". If desired, the bitumen may be premixed with the water and/or the emulsifying agent prior to introduction into the first mixer.

The bitumen is preferably introduced into the first static mixer at a temperature of 100 to 200°C, more preferably 120 to 190°C, and at a pressure of 2 to 80 bars, more preferably 10 to 30 bars. The water or soap is preferably introduced into the same mixer at a temperature of 20 to 70°C, more preferably 30 to 50°C, and also at a pressure of 2 to 80 bars, more preferably 10 to 30 bars. The temperature in the first mixer is usually 70 to 250°C, more preferably 100 to 150°C. A high temperature facilitates the emulsification of the bitumen and water, and the relatively high pressure prevents the water from evaporating.

It is preferred to pass the resultant mixture from the first static mixer directly into the other mixer, which is also preferably a static mixer. The remainder of the water is introduced into this other mixer, preferably cold, for example 50 to 20°C, so that it cools the emulsion enabling the resultant emulsion to exit the other mixer below the boiling point of water. It is also advantageous to operate this other mixer at a reduced pressure relative to the first mixer so that the emulsion emerges from the other mixture at atmospheric pressure.

If other additives are to be included in the emulsion, they may be added at any stage during the process, although are preferably added to the first

static mixer to ensure thorough mixing, and conveniently are added at the same time as the emulsifier. If they are water soluble, as in an inorganic acid and/or a metal salt, they may be added to the water-emulsifier soap.

The process is preferably a two-mixer process, but more than two mixers may be used. These additional mixers may be static mixers or other types of mixers, such as a colloid mill. Examples of suitable static mixers are those known as Fulzer or Kenics mixers, which are well known to those skilled in the art of static mixing.

The bitumen emulsion may be used in the construction, maintenance and repair of road surfaces and in other applications where bitumen is required. However, the bitumen emulsion is especially beneficial for mixing with aggregate to be used for road repair, for example the filling in of cracks and pot-holes caused for example by the passage of heavy and/or frequent vehicles or frost damage, and trenches dug to bury pipelines or cable, for example, under the road. Road repair often requires the use of relatively small amounts of aggregate mix and the delayed-set property of the aggregate-emulsion mix of the invention enables one larger amount of mix to be prepared and stored, with small quantities being taken from the stored mix as and when needed.

In use the bitumen emulsion is mixed with aggregate, which may be of any type of aggregate suitable for the required application, provided the bitumen contains an emulsifier appropriate for the type

of aggregate selected, and is usually either siliceous or calcareous. The aggregate is mixed with the emulsion using conventional mixing techniques, typical proportions of aggregate to emulsion being from 6:1 to 30:1.

The emulsion-aggregate mix can be applied to the road using conventional techniques. It may be applied hot or cold, although for ease of handling it is applied at ambient temperatures, for example from 10 to 25°C. Once the emulsion-aggregate mix has been applied to the road the emulsion breaks and the bitumen hardens relatively rapidly and the road surface is ready for use. The actual time taken for the bitumen to harden depends upon a number of factors in addition to the characteristics of the bitumen emulsion including the speed and pressure of compaction of the bitumen-aggregate layer, for example by rolling; the porosity of the surface to which the emulsion-aggregate mix is being applied; the chemical and physical influence of the aggregate; and the weather conditions. Nevertheless the uniformity of the bitumen droplet size in the emulsion and the absence of organic solvent and excessive amounts of emulsifier significantly assist the breaking of the emulsion so that the hardening of the bitumen is generally faster than would be expected for conventional delayed-set mixes. The bitumen hardening time for a surface prepared from an emulsion-aggregate mix according to the invention may vary, for example, from about 10 minutes to a number of days, for example 5 days or more, but usually the surface can be used by traffic as soon as the mix has been compacted, especially in the case of road repair.

The invention shall now be illustrated by the following examples:

Example

A bitumen emulsion having the following composition and properties was prepared. The percentages of components are weight percents based on the total weight of the emulsion unless otherwise specified:

Bitumen:	Amount	64%
	Penetration 25°C/10 mm/5 sec	200
	Ring and Ball softening point	39°C
Emulsifier (tallow diamine hydrochloride)		0.6%
Hydrochloric acid		0.2%
Calcium chloride		0.2%
Water		35%

The emulsion was prepared using a two-stage static mixing process. The two static mixers employed were both Kenics mixers of the type described in Chemineers brochure 800E published by Chemineers Ltd., 1984. The bitumen and a soap solution comprising the emulsifier, hydrochloric acid, calcium chloride and one-third of the total amount of the water were injected into the first static mixer. The bitumen was injected under a pressure of 2800 kPa and was at a temperature of 125°C. The soap solution was injected under a pressure of 2800 kPa and was at a temperature of 50°C.

After passing through the first static mixer, the mixture was fed directly into the second static mixer into which the remainder of the water was injected at a

pressure of 400 kPa and a temperature of about 15°C. After passing through the second mixer the resulting emulsion exited at atmospheric pressure and a temperature of 80 to 90°C.

Using a Coulter particle size analyser the emulsion was found to contain bitumen droplets having a mean particle diameter of 5.5 μm and a standard deviation of 0.18.

An aggregate/bitumen emulsion mix was prepared by combining 93.8 wt.% limestone aggregate and 6.2 wt.% of the above bitumen emulsion. The size gradings of the aggregate conformed to British Standard 4987 (Table 5) for a 20 mm dense graded base coarse macadam and were as follows:

0-2 mm	30%
2-6 mm	15%
6-10 mm	10%
10-14 mm	15%
14-20 mm	30%

The aggregate and emulsion were mixed together at ambient temperature using a conventional mixer and mixing was continued until the emulsion had coated the aggregate particles.

The resulting mix was laid into damaged areas and pot-holes in a macadam simulated road surface. The mix was spread and approximately levelled by a hand-held leveller in the usual manner. It was then compacted into place by a small vibrating hard-steel roller machine.

The road, which had been closed to traffic during repair, was re-opened immediately after the mix had been compacted. During the following 4-6 hours after compaction the water separated and flowed from the emulsion and the repaired patches began to harden. The macadam reached its normal strength of 20 mm pen within about 4 days.

To test the ability of the aggregate/bitumen emulsion mix during storage a sample of the mix was placed in an open container and stored for one month at ambient temperature. After this time there was no sign of breaking of the emulsion and no apparent loss of workability of the mix.

CLAIMS

1. A bitumen emulsion comprising by weight based on the total weight of the emulsion:

(a) 40 to 85 per cent bitumen;
(b) 0.05 to 1.0 per cent emulsifier;
(c) 14 to 59.95 per cent water,

the emulsion being substantially free of organic solvent, and containing emulsified bitumen droplets having a mean particle size of from 2 to 10 micrometres with a standard deviation of no more than 0.3.

2. A bitumen emulsion according to claim 1 wherein the emulsified bitumen droplets have a mean particle diameter of from 3 to 9 micrometres.

3. A bitumen emulsion according to claim 1 or 2 wherein the standard deviation in the mean particle size of the emulsified bitumen droplets is no more than 0.2.

4. A bitumen emulsion according to any preceding claim wherein the emulsifier is a cationic emulsifier.

5. A bitumen emulsion according to any preceding claim which also comprises 0.05 to 0.5 weight percent acid, preferably an inorganic acid.

6. A bitumen emulsion according to any preceding claim which also comprises 0.05 to 0.5 weight percent of a salt, preferably calcium chloride.

7. Use of a bitumen emulsion according to any preceding claim in the preparation of a delayed-set bitumen emulsion-aggregate mix.

8. Use according to claim 7 in the repair of road or pavement surfaces.

9. A composition comprising a mixture of a bitumen emulsion according to any one of claims 1 to 6 and aggregate material.

10. A process for the preparation of a bitumen emulsion according to any of claims 1 to 6 which comprises:

(a) feeding the bitumen into a first static mixer at a temperature above 50°C;

(b) introducing water under pressure into the first static mixer, the pressure being sufficient to prevent substantial vaporisation of the water, the weight ratio of water to bitumen in the first static mixer being between 3:1 and 35:1;

(c) introducing the emulsifier into the first static mixer;

(d) mixing the components in the first static mixer, and then passing the resultant mixture from the first static mixer into at least one other mixer in which the temperature is below the boiling point of water;

(e) introducing water into the other mixer(s) in an amount such that the total amount of water present in the resulting emulsion is from 14 to 60% by weight based on the total weight of the emulsion; and

(f) passing the mixture through the other mixer(s) and removing the resulting bitumen emulsion.

Patents Act 1977
Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number 9109709.7

Relevant Technical fields

(i) UK Cl (Edition K) BIV

(ii) Int Cl (Edition 5) BOIF, C08L

Search Examiner

J H Warren

Databases (see over)

(i) UK Patent Office

(ii) ONLINE : WPI AND CLAIMS

Date of Search

20.6.91

Documents considered relevant following a search in respect of claims 1-9

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	EP 0283246 A2 (EXXON) (whole document)	1,10

SF2(p)

TPSAAO

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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