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(54) BITUMINOUS EMULSIONS

(71) A P C—AZOTE ET PRODUITS CHIMIQUES S.A., a French Body Corporate, of 143 Route d'Espagne, 31053—Toulouse, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a method of making bituminous emulsions, and it is more particularly concerned with a method of making fast-breaking bituminous emulsions.

It is known that coatings for roads, parking areas, game areas, yards, industrial grounds and the like are usually formed from mixtures of mineral aggregates and bitumen, tar or any other suitable hydrocarbon binding agent. In the making of basic strata or of continuous layers of large surface area the mineral aggregates and the binding agent can be deposited simultaneously. According to a preferred technique, the mineral aggregates and the binding agent are mixed in advance in a mechanical mixer, a greater or less time before their application on the road or the like. The hydrocarbon binding agent must, in such cases, be fluid enough for it to be easily poured on to or spread over the aggregates. This fluidification is performed either by the hot coating technique or by the cut back technique or it may be done by the emulsion technique. In the latter case, the emulsions must necessarily be of the slow-breaking type in order to prevent an early breaking in the mixer.

However, for maintenance work on small surfaces or for the making of surface layers, the preferred technique comprises the spreading of a hydrocarbon binding agent, then a gravel and lastly a rolling operation. With the various binding agents which can be used, fast-breaking bituminous emulsions constitute the best choice. They allow working both in dry weather as under cold and damp conditions, they ensure a very good binding of the mineral aggregates and allow very rapid opening to traffic.

The emulsifying agents for the preparation of fast-breaking emulsions which are used at the present time are generally fatty amines, but these have the drawback of being pasty products, which are rather firm at normal room temperature. It is thus necessary to heat them when they are to be used in order to allow the formation of the emulsions. In industrial practice, it may even be required to heat the water and the hydrocarbon binding agent which is to be used for the preparation of the emulsion. This represents both a loss of time and a consumption of energy.

The products obtained by heating stoichiometric amounts of fatty acids and polyamines have also been suggested as emulsifying agents. However either the emulsions cannot be prepared with such reagents, or they break immediately. An attempt to add another component to such products has been tried but it is easy to see that such mixtures are complex and may be of a prohibitive cost.

The present invention sets out to obviate or at least reduce the above drawbacks. It allows the easy production of fast-breaking emulsions with an emulsifying agent which has the advantage of being liquid at normal room temperature.

The present invention provides a method of making fast-breaking bituminous emulsions by agitating an emulsifying agent at ambient temperature with an aqueous phase having an acidic pH value and bituminous hydrocarbon binding agent. The liquid emulsifying agent which is used is obtained by condensation at a temperature of from 160° to 180°C. of diethylenetriamine and a fatty acid with 12–18 carbon atoms having an iodine value at least equal to 25, and at least partial cyclisation of the condensation product at a temperature of from 190° to 240°C., the initial molar ratio between the diethylenetriamine and the fatty acid being at least equal to 5, the end product having a total amine value of at least 5·6 and optionally containing up to 10% of free diethylenetriamine. The amine value is a

measure of the basicity of an aminated compound.

Preferably each of the two above steps, i.e. the condensation step and the cyclisation step is carried out for at least 5 hours at the given temperature range. With shorter runs, the reaction may not be completed which may lead to compounds which do not have the required total amine value. During the second step the excess amine is removed by distillation.

Under these conditions, the reaction product comprises a mixture of single fatty chain components which may be cyclised or uncyclised, and of components with more than one fatty chain, which also may be cyclised or uncyclised. The components with a single fatty chain are of the aminoamide or imidazoline type and the components with more than one fatty chain are of the diamide or amidoimidazoline type.

We have found that in order to obtain a liquid agent having good characteristics as an emulsifying agent for the preparation of fast-breaking emulsions, the end product of the reaction must necessarily have a total amine value at least equal to 5·6, and preferably comprised between 5·8 and 6·0. When carrying out the invention, this result is obtained when the initial molar ratio between the diethylenetriamine and the fatty acid is at least equal to 5, and preferably between 5·5 and 7. It has indeed been found that when the initial molar ratio is lower than 5, the total amine value of the reaction product is lower than 5·6. This is probably due to the fact that the reaction between the polyamine and the fatty acid then leads to the formation of a high proportion (i.e. more than 30%) of products having more than one fatty chain, i.e. diamides and amidoimidazolines, which have a low total amine value of about 1·6. On the other hand, it has been found that there was no benefit to gain from increasing the initial molar ratio between the diethylenetriamine and the fatty acid beyond 7, since the total amine value of the reaction mixture is no longer modified.

The reaction mixture obtained can be distilled in order to separate the component having the desired total amine value, i.e. the almost pure imidazoline derived from the diethylenetriamine and the fatty acid.

It has been found, however, that it is not essential to proceed to such an operation and that the technical product of the above-described reaction gave very good results. This product is obtained by stopping the second step, during which the excess amine is removed from the reaction mixture, when the total amine value becomes less than 6·0. When this value is too low, for example lower than 5·6, it is sufficient to add the required amount of diethylenetriamine to set the total amine value to the required value.

The product thus obtained contains, in addition to the components with a single fatty chain mentioned above, an amount of free amine at most equal to 10% and preferably at most equal to 7%. The free amine is most generally diethylenetriamine. It is, however, also possible, if desired, to use triethylenetetramine or a mixture of these two amines to set the total amine value to the optimum value.

The fatty acids with 12–18 carbon atoms suitable for this reaction may be pure or of a technical quality, and may be used alone or in a mixture, which may include particularly acids of animal or vegetable origin, or the acids obtained by synthetic means. It has further been found that best results, in the application of these reagents, are obtained when using fatty acids or mixtures of fatty acids which are little saturated, i.e. which have an iodine value higher than 25. By way of example, we may mention the dodecoic, myristoleic, palmitoleic and/or oleic acids. The technical product formed primarily by a mixture of oleic and stearic acid, such as is derived from tallow for example and which has an iodine value of about 40, can be used with success. Preferably there is used a distilled oleic acid with an iodine value higher than 40.

The amine suitable for this reaction may also be the pure product or a product of technical quality.

The preparation of the bituminous emulsions may be done using known methods starting from usual hydrocarbon binding agents. One may use a bitumen of normal penetration index, such as 180/220 bitumen, or harder. The penetration index shows the resistance of a material to the penetration of a standardized cone. For the determination of this index, there is used a cone having a length of 50 mm and a vertex angle of 8·7–9·7 degrees. This cone is surmounted by a small weight and by a shaft which can slide freely in a guide tube provided with a stop-device. The movable part weighs 100 ± 0·05 g. The tip of the cone is brought into contact with the bitumen, the movable part is released for 5 seconds and then locked in its position and the penetration of the cone in the bitumen is noted. The penetration index is expressed in 1/10 mm. The bitumen concentration of emulsions of this type is generally approximately equal to 60%, though higher concentrations, for example 65% bitumen, can also be obtained.

It is sufficient to bring the water, hydrocarbon binding agent and the emulsifying agent into contact with each other, with agitation, in order to obtain the emulsion,

without any special precautions being necessary.

The aqueous phase, as in all cases where cationic emulsifying agents are used, has an acid pH value. The optimum values are in the range 3 to 3·5 and are easily determined by a man skilled in the art according to the characteristics of the bitumen. Acid pH values lower than 3 can be maintained; they allow a decrease in the amount of emulsifying agent which is necessary but they also decrease the adhesion power of the treated bitumen. Conversely, the establishment of pH values higher than 4 necessitates the use of greater amounts of emulsifying agent. These acid pH values can be obtained in a known way by the addition of an acid, such as acetic or hydrochloric acid, for example. The latter is preferably used, for reasons of price.

The quantities of emulsifying agent to be used are low. It has indeed been found that the quantities required are between 1·5 and 5 kg per metric ton, the optimum quantities being 2 to 3 kg per metric ton.

Example 1

This example illustrates the preparation of a liquid product to be used as emulsifying agent.

During a period of one hour 6·1 tons of diethylenetriamine were introduced into a cold reaction vessel after which 2·5 tons of oleic acid were added while under agitation. This mixture was heated for 6 hours at 170°C., after which the temperature was raised in one hour to 210°C. and kept for 6 hours at this value. There were recovered 2·7 tons of finished product having a total amine value of 5·82. The excess diethylenetriamine removed during the second step (5·25 tons) was used for another preparation.

Example 2

This example shows the breaking speed of an emulsion, depending on the nature of the mineral aggregate. The method used is related to the measurement of bitumen weight deposited on the aggregate under the following conditions: —

For this laboratory test 10 g of mineral aggregate of a particle size between 0·8 and 2 mm were weighed, washed and dried. They were placed in a beaker containing a glass rod. The whole was weighed (A) and placed for one hour in a cabinet saturated with water vapour, the beaker being covered with a moistened filter paper. There was poured into the beaker 10 g of an emulsion containing (C) g of bitumen and the whole was mixed with the rod. The whole was again left in the damp cabinet during one hour. The mineral aggregate was then washed with distilled water to separate the excess emulsion, the rinsing water passing over a 0·18 mm sieve to prevent any loss of aggregate. The washing was repeated until the water was clear. The beaker and the rod were then heated to 100°C. in a closed cabinet till the weight was constant, then cooled and weighed (B).

The breaking index according to this method is:

$$\frac{(B-A)100}{C}$$

The emulsion which was used, with 60% of normal road bitumen 180/220, had a pH of 3. The emulsifying agent, which comprised the reaction product of an oleic acid with an iodine value of 90 and diethylenetriamine, contained 5% of free diethylenetriamine and had a total amine value of 5·94.

With an alkaline aggregate, such as marble, the breaking index was 1·5; with an aggregate of mixed character, such as porphyry, the breaking index was 0·9.

Lower breaking indexes, for example 0·4 with porphyry and 0·8 with marble, have been measured with a usual aminated emulsifying agent. In addition, the preparation of bituminous emulsions with the latter type of reagent is bound to involve energy consumption: the water has to be heated to about 60°C., the emulsifying agent to about 80°C. and the bitumen to about 120°C.

With another known agent constituted by nitrogen heterocyclic compounds and having a total amine value of 4·98 and using for the penetration of the emulsion a bitumen of same penetration index (180/220) but of a different origin, the breaking indexes were 1·8 with porphyry and 1·4 with marble, as against 0·6 with porphyry and 0·2 with marble for the emulsifying agent of the present invention. The breaking indexes of the emulsions prepared with such agents having a low total amine value are higher but the stability of these emulsions is particularly bad, which makes it very difficult to use such a type of products.

Example 3

The breaking index with cement, which allows an evaluation of the capacity of the emulsion to coat fine aggregates, was measured using an emulsion prepared as above.

For this measurement, a sample of 100 g of emulsion was taken into which Portland cement was poured at 10 to 15 g/min, the introduction of the cement being carried out regularly. The emulsion was kept agitated with a small agitator. The breaking index with cement is the quantity of cement poured until breaking or agglomeration of the bitumen occurs.

When using as the emulsifying agent the product of the invention obtained from an oleic acid with an iodine value of 95 and diethylenetriamine, containing no free amine and having a total amine value of 5·72, the breaking index with cement was about 26%. By way of comparison, this index was 32% with a known aminated reagent; in this case, the breaking of the emulsion was less rapid than with the emulsifying agent of the invention.

Example 4

This example shows the storage characteristics of an emulsion containing 2 kg/metric ton of an emulsifying agent according to the invention, such as set out in Example 2.

For this laboratory test, a test-tube of 500 cc capacity with a length of 35 cm and a diameter of 5 cm was filled with the emulsion. This test-tube was left standing for 7 days in the dark at room temperature. After this time, the total sedimentation was measured, i.e. the difference in water amount between the higher and lower 50 cc. The composition of the emulsion in the lower part of the test-tube was also determined.

With this emulsion, the sedimentation after 7 days was 24%. In the lower 50 cc of the test-tube, the bitumen concentration was 68·3%, which corresponds in practice to an easy draining of the storage containers. It has also been noted that this value varied little with the pH of the emulsion. It varies, for example, from 66·8 to 70·2% when the pH varies from 2·5 to 3·5. On the contrary with the usual aminated reagents, the bitumen concentration varies from 64·5 to 74% in the same pH range; this latter value did not allow easy draining.

WHAT WE CLAIM IS: —

1. A process for the production of fast breaking bituminous emulsions, wherein a liquid emulsifying agent is used which has a total amine value of at least 5·6 and which is obtained by condensation at a temperature of from 160° to 180°C. of diethylenetriamine and a fatty acid having 12 to 18 carbon atoms and an iodine value at least equal to 25, and by at least partial cyclisation of the condensation product at a temperature of from 190° to 240°C., the initial molar ratio between the diethylenetriamine and the fatty acid being at least equal to 5, and in which process said emulsifying agent is agitated at ambient temperature with an aqueous phase having an acidic pH value and bituminous hydrocarbon binding agent.

2. A process according to Claim 1, wherein the product also contains up to 10% of free diethylenetriamine.

3. A process according to Claim 1 or 2, wherein the initial molar ratio between the diethylenetriamine and the fatty acid is between 5·5 and 7.

4. A process according to any of the preceding claims, wherein the condensation is carried out for 5 hours at 160° to 180°C. and the cyclisation is carried out for at least 5 hours at 190° to 240°C.

5. A process according to any of the preceding claims, wherein the cyclisation is stopped when the total amine value of the reaction product becomes lower than 6·0.

6. A process according to any of the preceding claims, wherein the total amine value of the reaction product is set by addition of diethylenetriamine.

7. A process according to Claim 6, wherein the diethylenetriamine is at least partially replaced by triethylenetetramine.

8. A process according to any of the preceding claims, wherein a fatty acid with 18 carbon atoms is used.

9. A process according to any of the preceding claims, wherein a fatty acid with 18 carbon atoms having an iodine value higher than 40 is used.

10. A process for the production of bituminous emulsions substantially as herein described.

11. A bituminous emulsion which has been prepared using a process as claimed in any of the preceding claims.

Agents for the Applicants:
STANLEY POPPLEWELL FRANCIS & ROSS,
Chartered Patent Agents,
1 Dyers Buildings,
Holborn,
London E.C.1N 2JT.

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